NONLINEAR SPECTROSCOPIC PHENOMENA IN MOLECULAR GASES AND THEIR INFLUENCE ON LASER BEAM PROPAGATION IN THE ATMOSPHERE

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Some results of investigation of such nonlinear low–threshold spectroscopic phenomena in atmospheric gases as saturation, "clearing upB in the absorption line wing, effect of the intense laser radiation on vibration relaxation, and Raman scattering stimulated by bifrequency radiation are treated in the paper. Consideration and practical use of the phenomena in the problems of intense optical radiation transfer and remote sensing of gaseous and aerosol composition of the atmosphere are also discussed.

INTRODUCTION

Intense laser radiation, propagating through molecular gaseous medium or the atmosphere, can significantly change the optical characteristics of the medium (the absorption coefficient and the refractive index, for example) within the propagation channel. This change in its turn determines a variation of power, spectral, and spatial characteristics of laser beams in the process of their thermal blooming. Even comparatively weak nonlinearities of the optical characteristics of the molecular atmosphere can affect the parameters of the intense laser radiation at long distances. The nonlinear phenomena and their consequences are more pronounced under resonance conditions when the optical radiation frequency is close to one of a number of resonance frequencies of molecules in the gaseous medium.

In the present paper, some results of investigations of nonlinear spectroscopic effects in atmospheric gases and their consideration and practical application to problems of intense optical radiation transfer and remote sensing of gaseous and aerosol composition of the atmosphere are discussed. The best–understood nonlinear effects accompanying an interaction of intense continuous or pulsed radiation with molecular gases are the spectroscopic saturation effect[1] and the dynamic Stark effect[2] on vibrational-rotational (VR) transitions, stimulated and spontaneous Raman scattering,[3] effect of radiation field on intermolecular interaction potential and relaxation,[4,5] optical breakdown in a gas,[6] and a variety of others.[7] This paper deals only with the phenomena, for which the threshold intensity under realistic atmospheric conditions is much lower than that of the air optical breakdown. Among them are the spectroscopic saturation effect, "clearing up" in the absorption line wing, variation of vibrational relaxation time with the increase of optical radiation intensity exciting the vibrational transitions in molecules, and Raman scattering stimulated by bifrequency radiation on rotational and vibrational-rotational transitions.

1. RESONANCE ABSORPTION SATURATION ON VIBRATIONAL–ROTATIONAL TRANSITIONS IN ATMOSPHERIC MOLECULES

The spectroscopic saturation effect causes the decrease of the resonance absorption coefficient and consequently of the refractive index in the anomalous dispersion region with the increase of laser radiation intensity. The threshold intensity I_{sat} of the effect is determined by the characteristics of resonance transition, namely, by absorption cross section σ and relaxation times τ_R (rotational) and τ_V (vibrational) of the excited vibrational-rotational state.

As the condition $\tau_R \ll \tau < \tau_V$ is fulfilled (τ is the duration of the laser monopulse interacting with the vibrational-rotational transition typical of the conditions of the ground atmosphere[7]), the dependence of the absorption coefficient $\varkappa$ on the intensity I for a rectangular laser pulse (I = const for $0 \le t \le \tau$; $I = 0$ for $t > \tau$) has the form[8]

$$\varkappa(I) = \varkappa_0 \left\{ \frac{2\sigma I - \delta_2}{\delta_1 - \delta_2} e^{-\delta_1 t} + \frac{\delta_1 - 2\sigma I}{\delta_1 - \delta_2} e^{-\delta_2 t} \right\}, \qquad (1)$$

where

$$\delta_{1,2} = \frac{1}{2}\left(2\sigma I + \frac{1}{\tau_R}\right) \pm \left\{ \frac{1}{4}\left(2\sigma I + \frac{1}{\tau_R}\right)^2 - \frac{2\, q\sigma I}{\tau_R} \right\}^{1/2}. \qquad (2)$$

Here, σ is the cross section of resonance absorption, in cm^2; I is the radiation intensity, in photons/cm^2; q is a fraction of molecules on rotational sublevels interacting with radiation (for absorption VR transitions $\Delta J = 1$, so q may be thought of as approximately equal for lower and upper vibrational states in the molecules with the vibrational constant B_0 much less than the energy of the

thermal photon, i.e., molecules of CO_2, SO_2, NO_2, etc.). The values of the parameters σ and τ_R under standard atmospheric conditions vary within the limits $10^{-17} \geq \sigma \geq 10^{-23}$ cm^2 and $\tau_R \sim (3–10)\cdot 10^{-10}$ s·atm (Ref. 7). The parameter q specifies the ratio of population of a level with the given rotational quantum number to the number of molecules in the given vibrational state ($q < 1$). The saturation parameter I_{sat} (or E_{sat}) characterizing the radiation pulse intensity (or power), at which the absorption coefficient is halved, also varies over wide limits from several hundreds of kW/cm^2 to several hundreds of MW/cm^2 depending on the intensity of the resonance absorption line.

The experimental data on the absorption saturation on vibrational-rotational transitions of the main atmospheric molecular gases were obtained in the series of works[7,9–11] by optoacoustic laser spectroscopy method allowing the determination of the saturation intensity I_{sat} (Ref. 10) in the process of quasistationary interaction between the radiation and absorbing gas or of the saturation energy E_{sat} (Ref. 9) in the case of short-pulse absorption for $\tau \leq \tau_V$. The saturation on vibrational-rotational transitions in CO_2 and H_2O was measured by the optoacoustic method[11,12] using a pulsed CO_2 laser and a ruby laser; the measurement results are presented in Table I.

The saturation effect in atmospheric CO_2 absorption lines should be taken into account when solving the problems on propagation of the pulsed CO_2-laser radiation with intensity ≥ 1 MW/cm^2, particularly for the beams with the inhomogeneous intensity distribution over the beam cross section.

2. EFFECT OF INTENSE RADIATION ON INTERMOLECULAR INTERACTION POTENTIAL AND VIBRATIONAL RELAXATION IN A GAS

The findings characterizing the action of intense laser radiation on intermolecular interaction potential (it determines the absorption in far wings of spectral lines) and vibrational relaxation in gases were described in Refs 4, 5, and 13. It was shown in Ref. 4 that in the high–power field of CO_2–laser radiation the classical potential of the H_2O molecule interaction with the collision partner is

$$V(R) \simeq V_0(R)\,(1 - bI), \qquad (3)$$

where R is the distance between the interacting molecules; I is the radiation intensity; the parameter b specifies the threshold intensity at which the decrease of $V(R)$ and the corresponding decrease of the absorption coefficient in the line wing $\varkappa_k(I)$ start as well as the decrease of the probability of the vibrational-translational relaxation w_{VT} determined by $V(R)$ (Refs. 4, 13, and 14).

This situation is opposite to the case of resonance absorption of intense radiation on vibrational-rotational transitions, when the absorption coefficient $\varkappa$ decreases with the I increase due to saturation and w_{VT} increases because of gas heating and incorporation of additional relaxation channels to the population of upper vibrational-rotational state, which significantly exceeds the equilibrium.[3]

The experimental results illustrating the form of the dependence of vibrational–translational relaxation time τ_{VT} as a function of CO_2–laser radiation intensity for CO_2 (resonance excitation) and H_2O (nonresonance excitation) molecules in the far line wing are depicted in Fig. 1.

The ratio $\tau_{VT}(I)/\tau_{VT}^0$ is lowered in the case of resonance excitation of vibrational-rotational transition in the CO_2 molecule by CO_2–laser radiation with $I \gtrsim 0.4$ MW/cm^2, where τ_{VT}^0 is the VT relaxation time in a weak light field, i.e., the intensity amplification for resonance CO_2 excitation leads to the accelerated relaxation, which agrees with the conclusions of Ref. 3.

For the H_2O molecule excited by the same radiation far from resonance, the behavior of the ratio $\tau_{VT}(I)/\tau_{VT}^0$ is opposite in character. It first grows and τ_{VT} grows too, because the intermolecular interaction potential, determining the efficiency of the molecular collision, is lowered.[4] It should be pointed out that the characteristic intensity for which the deviation of $\tau_{VT}(I)/\tau_{VT}^0$ from unity becomes noticeable correspond to the saturation intensity ($I_{sat} \sim 0.25 - 0.35$ MW/cm^2) for absorption by CO_2 (Ref. 11) or to the threshold intensity of the clearing-up phenomenon in the H_2O line wing ($I_k \sim 2–3$ MW/cm^2) (Ref. 4).

TABLE I. Absorption coefficient in line centers of CO_2 *and* H_2O *in atmospheric air vs. laser radiation intensity.*

Laser, wavelength, μm pulse duration, ns	I, MW/cm^2	Gas	P_g, Torr	$\varkappa(I)/\varkappa_0$
Ruby 0.69, 50	5 ± 0.5	H_2O–air	P_{tot} = 750	1.0 ± 0.1
	35 ± 3.5		P_{H_2O} = 10	0.8 ± 0.1
	5 ± 0.5	H_2O–air	P_{tot} = 270	1.0 ± 0.1
	35 ± 3.5		P_{H_2O} = 3.0	0.6 ± 0.1
CO_2 10.6 (P20) 300	0.15 ± 0.02	CO_2–air	P_{tot} = 98	1.0 ± 0.05
	1.80 ± 0.15		P_{CO_2} = 3.0	0.4 ± 0.05

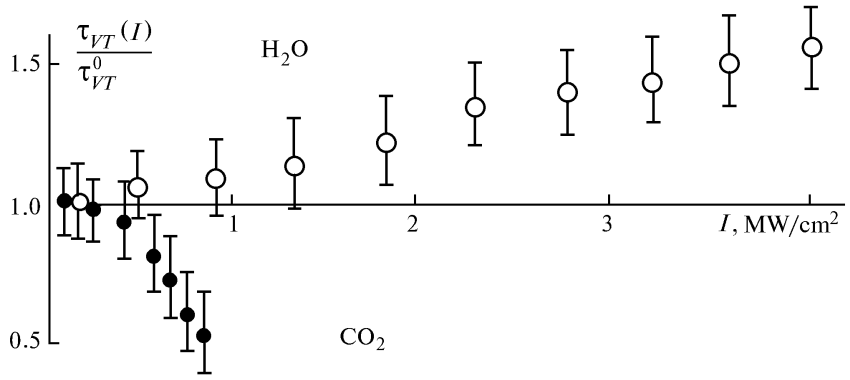

FIG. 1. Time of vibrational-translational relaxation in H_2O *and* CO_2 *vs. the intensity of exciting* CO_2*–laser radiation.*

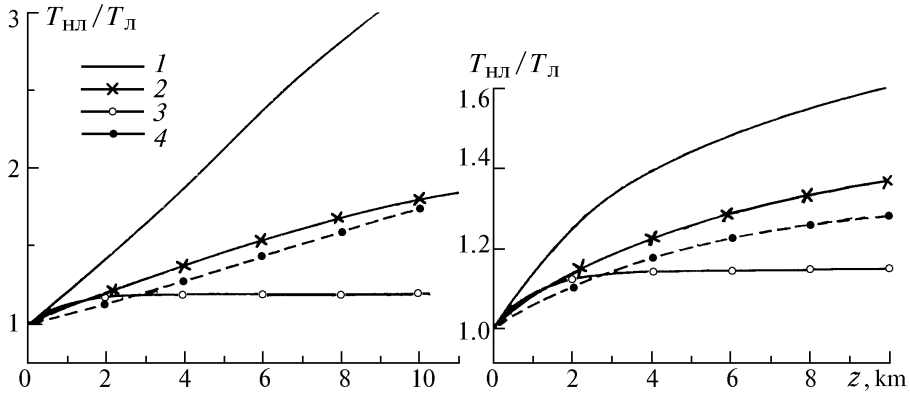

FIG. 2. Ratio of atmospheric nonlinear transmittance, T_{nl}*, of pulsed* CO_2*-laser radiation to the linear one,* T_l*, at a wavelength of* 10.6 μm *for* $I_0 = 4.0$ MW/cm^2 and $\tau = 5 \cdot 10^{-8}$ s: *horizontal homogeneous (a) and vertical (b) paths. 1 and 4) transmittance along the beam axis (divergence length is 50 km), 3) transmittance along the beam axis (divergence length is* 1 km), *2) transmittance along the beam edge (*$r = a_0$*, divergence length is* 50 km*), 1 and 3) model of the atmosphere (mid–latitudes in summer), 4) model of the atmosphere (mid–latitudes in winter).*

The two types of the τ_{VT} dependence on I in the atmospheric channel of intense CO_2–laser beam propagation, caused by the radiation absorption by two main gaseous constituents of the atmosphere, may result in complex kinetics of thermal emission and nonlinear refraction along the propagation path. The beam thermal blooming under these conditions has not yet been treated.

The pulsed CO_2–laser energy transfer through the atmosphere was considered in Ref. 1 accounting for the nonlinear dependence of the CO_2 resonance absorption coefficient and the H_2O continual absorption. It was shown there that the ratio of the intense CO_2–laser radiation transmittance to that of weak one reached 1.2–3 on the path 10 km long depending on the path type, beam angular divergence, and initial intensity of the beam (Fig. 2).

3. BIFREQUENCY EXCITATION OF RS SPECTRA IN MOLECULAR GASES

The Raman scattering (RS) phenomenon can be considered as inelastic interaction between a photon with energy $h\nu_0$ and a molecule, resulting in emission of a photon with lesser energy $h\nu_s$ (Stokes component) or with greater one $h\nu_{as}$ (anti–Stokes component). The molecule itself is brought into a state with greater or lesser energy. The RS can take place on rotational, vibrational-rotational, and electronic vibrational-rotational transitions.

If the intensity of the laser radiation, interacting with a medium, is sufficiently high, then the intensity of the scattered Stokes wave will correspondingly increase. It results in interaction between pump and Stokes waves through the molecular oscillations of frequency $\Omega = \nu_0 - \nu_s$ (ν_0 is the frequency of the

incident laser radiation). So the intense beams of scattered radiation are formed. Such a phenomenon is known as stimulated Raman scattering (SRS). Whereas the intensity of spontaneous Raman scattering line is several orders of magnitude less than the intensity of the laser radiation exciting the medium, the intensities of Stokes and anti–Stokes beams in the SRS process are comparable with the pump wave intensity. Although the intensities of stimulated Stokes and anti–Stokes waves are high, the SRS spectroscopy is little used in atmospheric optics because of high SRS thresholds in atmospheric gases at standard temperatures and pressures.

An additional possibility for excitation of active RS transitions arises when using pulsed bifrequency radiation. Upon exposure of the molecular gas to radiation beams of two collinear and synchronized lasers with the emission frequencies ν_1 and ν_2 ($\nu_1 - \nu_2 \simeq \Omega$; $\nu_2 \simeq \nu_s$) and tunable difference frequency it is possible to study the RS line shape with high spectral resolution limited only by a sum of widths of the laser radiation lines ($\sim 10^{-2}$–10^{-3} cm^{-1}) (Ref. 16).

The RS spectra in molecular gases as well as the absorption rotational and vibrational-rotational spectra can be studied by the photoacoustic method.[16,17] The number of molecules excited in unit volume by the pulsed radiation of frequencies ν_1 and ν_2 is estimated as

$$N_2 = \Delta I_2 \, A_2 \, T / h \, \nu_2, \qquad (4)$$

where

$$\Delta I_2 = I_2(z) - I_2(0) = I_2(0) \, (e^{-g_s z} - 1). \qquad (5)$$

Here, g_s is the gain of the Stokes beam (of frequency ν_2), A_2 is the cross sectional area of the Stokes beam, and T is the time of interaction between pumping and Stokes beams.

Using the standard photoacoustic detection instrumentation, the SR spectra were obtained[17] in pure CO_2 at a pressure of about $6.6 \cdot 10^3$ Pa ($\approx$ 50 Torr) excited by the second harmonics of a YAG–laser ($I_1 \le 2 \cdot 10^7$ W/cm^2) and a dye laser (Stokes wave, $I_2 \approx 8 \cdot 10^6$ W/cm^2) with pulse durations of 10 ns.

The selective excitation of rotational and vibrational-rotational active RS transitions allows one to study the processes of their relaxation in the same manner as it was realized in Refs. 18 and 19 where the radiationless relaxation of atmospheric molecules was studied by the photoacoustic method.

The estimates by Eqs. (4) and (5) together with the above–mentioned results show that the level of the intensities I_1 and I_2, at which the SRS phenomenon is observable, is accessible by many pulsed short–wave lasers and is 2–3 orders of magnitude lower than the level of threshold intensity of the air optical breakdown in the short-wave range. According to Ref. 6, the air breakdown in the laser radiation field at a wavelength of 1.06 μm takes place when the intensity $\ge 10^9$ W/cm^2.

4. APPLICATION OF NONLINEAR SPECTROSCOPIC EFFECTS TO SOUNDING OF THE ATMOSPHERIC GAS COMPOSITION

The method of differential absorption and scattering[20] is a principal method for sounding of gas composition of the atmosphere. Its idea is in comparison of the intensities of laser radiation transmitted through the atmosphere (or backscattered) at two frequencies ν_1 and ν_2 alternatively. One frequency is absorbed within the sounded gas line and the other falls on the line wing, where the resonance absorption is negligible in comparison with the background one. This method can be realized using the lasers with continual or discrete frequency tuning, all other parameters of the pulse being stable.

If a single-frequency nontunable laser is applied to measure a certain gas concentration, then the saturation phenomena may be used providing the gas absorption line coincides with the laser frequency. In this case, it would suffice to vary the radiation intensity rather than the frequency.[21]

The total absorption coefficient of air (or of gaseous mixture) $k(\nu)$ is a sum of resonance absorptance $\varkappa(\nu)$ of the examined gas and nonselective absorptance α due to absorption in wings of lines and bands of other gases, aerosol absorption, scattering, and so on:

$$k(\nu) = \varkappa(\nu) + \alpha \, .$$

If we pass from small values of the sounding radiation intensity $I \ll I_{sat}$ (I_{sat} is the saturation intensity) to $I \sim I_{sat}$, we can separate the contributions of $\varkappa$, changing with the I increase due to the saturation effect, and α, independent of I when $I \le I_{sat}$. So, it is possible to determine the concentration of the absorbing gas from the known value of $\varkappa$ using the relation $\varkappa = n\sigma(\nu)$, where $\sigma(\nu)$ is the absorption cross section at frequency ν and n is the number density of molecules, in cm^{-3}.

For a homogeneous horizontal path of length l and a beam with small angular divergence, the radiation intensity in the initial and end points of the path and the coefficients $\varkappa$ and α are connected via the relationship[21]

$$\ln\left(\frac{I_l}{I_0}\right) + \frac{\varkappa}{\alpha} \ln \frac{\alpha + \varkappa + \alpha(I_0/I_{sat}) \, (I_l/I_0)}{\alpha + \varkappa + \alpha(I_0/I_{sat})} = l(\alpha + \varkappa). \qquad (6)$$

There are three unknowns in Eq. (6): α, $\varkappa$, and I_{sat}. Triple variation of the radiation intensity in the initial point of the path ($I_{01} \ll I_{sat}$; I_{02}, $I_{03} \simeq I_{sat}$) allows us to determine all unknowns from Eq. (6).

As a rule, the value of I_{sat} is known (or can be calculated from the available characteristics of the resonance transition in the absorbing molecule[7,8]). So, only two variations of the intensity are sufficient to determine α and $\varkappa$.

The maximum sounding range in the method of differential absorption and scattering depends on the absorptance of the sounded gas. If the wavelength of the laser coincides with strong absorption line (this is typical of such gases as NO_2, CH_4, and molecules of organic compounds), the maximum sounding range will be insufficient because of fast attenuation of the radiation energy on the sounding path.

The effect of active SRS by N_2 (or O_2) molecules, being the main atmospheric gas, can be used for energy transfer from the beam of frequency ν_2 into the sounding beam of frequency ν_1 during their collinear propagation along the sounding path. This potentiality was estimated numerically in Ref. 22.

The propagation of two collinear synchronized beams of pulsed radiation with frequencies ν_1 and ν_2 (ν_1 coincides with the absorption line frequency and ν_2 satisfies the condition $\nu_2 - \nu_1 \simeq \Omega$, where Ω is the frequency of rotational or vibrational RS in nitrogen, and falls in the dip between the absorption lines) is described by the set of equations[23]

$$\frac{\partial E_1}{\partial \tau} + i \frac{\Delta_\perp}{2 k_1 \operatorname{Re} \alpha_1} E_1 = \left(\mu |E_2|^2 - \frac{\alpha_1}{2 \operatorname{Re} \alpha_1} \right) E_1, \quad (7a)$$

$$\frac{\partial E_2}{\partial \tau} + i \frac{\Delta_\perp}{2 k_2 \operatorname{Re} \alpha_2} E_2 = - \left(\mu \delta |E_1|^2 + \frac{\gamma}{2} \right) E_2, \quad (7b)$$

where E_1 and E_2 are the strengths of the radiation field at frequencies ν_1 and ν_2, $\gamma = \frac{\alpha_2}{\operatorname{Re} \alpha_1}$, α_1 and α_2 are the complex absorption coefficients at ν_1 and ν_2, τ is the optical thickness of the medium at ν_1, $k_{1,2} = \nu_{1,2}/2\pi c$, c is the velocity of light, and

$$\delta = \frac{\nu_2}{\nu_1} \frac{|E_{10}|^2}{|E_{20}|^2}, \quad \mu = \frac{g}{\operatorname{Re} \alpha_1} |E_{10}|^2. \quad (8)$$

Here, g is the wave gain at frequency ν_1 due to the energy transfer from the wave of frequency ν_2 during the SRS process, E_{10} and E_{20} are the field amplitudes upon entering the medium.

Usually under atmospheric conditions $g < \operatorname{Re} \alpha_1$ for $I_1 \sim 10^6 - 10^8$ W/cm^2 (Ref. 24). In this case, the solution for axially symmetrical beams may be represented in the form

$$E_1(\tau) = E_{1L}(\tau) \left\{ 1 + \frac{\mu}{\operatorname{Re} \gamma} (1 - e^{-\operatorname{Re} \gamma \tau}) + \frac{\mu^2}{2 \operatorname{Re} \gamma} (1 - e^{-\operatorname{Re} \gamma \tau})^2 + \ldots \right\}, \quad (9a)$$

$$E_2(\tau) = E_{2L}(\tau) \{ 1 - \mu \delta (1 - e^{-\tau}) + \ldots \}, \quad (9b)$$

where E_{1L} and E_{2L} describe the amplitude variations of of both beams in linear medium.

To transfer the energy from the beam of frequency ν_2 to the sounding one, the use of SRS at rotational transitions in N_2 or O_2 is preferable. Therewith, the frequencies ν_1 and ν_2 are close and the condition of synchronism is fulfilled at long distances.[25]

The required frequency detuning $\Omega = \nu_2 - \nu_1 \simeq \simeq (5–10)\,c$ (c is the absorption linewidth of the sounded gas) is easily accessible. Taken as the criterion of the sounding range increase is the ratio of the path length at which the intensity of the beam with frequency ν_1 decreases to the predetermined level, when the energy is transferred from the second beam, to the path length at which the first beam undergoes the same attenuation without energy transfer.

Figure 3 shows the estimates of the optical thickness increase that can be obtained due to interaction between two waves during the SRS process for indicated values of the parameter μ, characterizing the ratio of ν_1 wave gain due to SRS to the absorption coefficient on the sounding path.

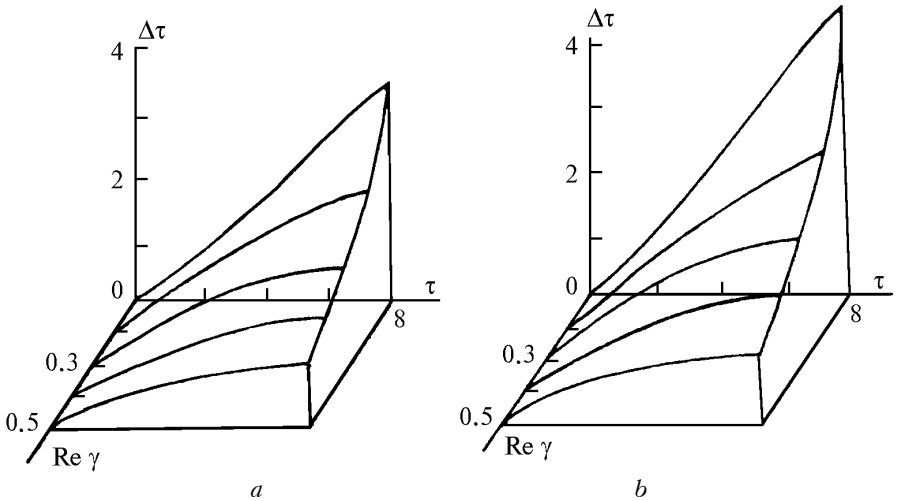

FIG. 3. Increase of the maximum sounding range in case of sensing of the resonantly absorbing gas vs. the energy transfer into the sounding laser beam for $\mu = 0.2$ *(a)* and 0.4 *(b).*

The parameter $\mu \simeq 0.1-0.3$ can be obtained by pulsed lasing in visible and IR ranges with intensities from 1 to $5 \cdot 10^2$ MW/cm^2 being not exotic.

CONCLUSION

The above–described nonlinear spectroscopic phenomena such as saturation on rotational–vibrational transitions of the atmospheric molecules, clearing up in the far wings of spectral lines, change of the vibrational relaxation rate in the field of intense radiation, and Raman scattering on rotational and vibrational–rotational transitions stimulated by bifrequency radiation are characterized by the threshold intensities lower than the threshold intensity of the air breakdown. The power of the up-to-date pulsed lasers used for detection of atmospheric gas composition is sufficient even for nonfocused beams. The available experimental data and theoretical estimates demonstrate that these phenomena can be applied to widen the capabilities of the existing methods for sounding of gas composition of the atmosphere. Variation of the vibrational relaxation rate, as the type of interaction between radiation and gaseous medium changes from resonance to nonresonance one, should be taken into account when analyzing the high–power IR laser radiation propagation through the atmosphere.

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