LASER PHOTO—ACOUSTIC SPECTROSCOPY OF THE ATMOSPHERE

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An overview of the program of the laser photo—acoustic spectroscopy development at the Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Sciences from 1974 to 1994 is presented. Physical basis of the method and specifications of the photo—acoustic spectrometers with pulsed and cw lasers of IR and visible spectral ranges are shown. The main results of fundamental investigations of absorption spectra fine structure and parameters of individual spectral lines of atmospheric molecular gases, nonlinear spectroscopic effects in gases, and measurements of time of vibrational relaxation of high vibrational states in H_2O molecule are described. The prospects of development of photo—acoustic spectroscopy instrumentation and its applications to atmospheric study are discussed.

INTRODUCTION

An active use of lasers in investigations of physico—chemical properties of the atmosphere, local and remote gas—analysis, and remote sensing stimulates development of highly sensitive methods of absorptional laser spectroscopy.

Three methods of high resolution laser spectroscopy complemented each other develop at the Institute of Atmospheric Optics of Siberian Branch of the Russian Academy of Sciences (IAO SB RAS): laser spectrophotometry with use of multipass gas cells, intracavity laser spectroscopy, and laser photo—acoustic (PA) spectroscopy based on cw and pulsed lasers use.[1]

The PA method is of considerable current use in study of absorptional and Raman spectra, measurement of relaxation constants and chemical reactions rates as well as in local gas—analysis of multicomponent media.[1–5] The use of PA method in combination with frequency tunable lasers offered considerable scope for creating multifunctional laser spectrometers characterized by high sensitivity and identity of the measuring procedure in different spectral ranges. An application of PA methods with laser excitation to study the absorptional spectra of atmospheric and foreign gases manifests the following benefits:

— high spectral resolution determined by linewidth of laser radiation;

— high absorptional sensitivity up to 10^{-9} cm^{-1} at small volume (about 10 cm^3) of the gas under study;

— amplitude linearity of the recorded PA signal at the absorption coefficient variations in limits of five orders;

— possibility to obtain high energy density or laser radiation (LR) power at short length of PA cell due to its focusing;

— simplicity of PA registration channel inclusion into spectrometers of different types.

The history of the PA methods development at the IAO SB RAS started in 1969. When executing the corresponding scientific program, new fundamental results of utmost significance were obtained for physics of optical radiation interaction with molecules, spectroscopy of molecules and intermolecular interactions, and optics of molecular atmosphere. The key results are:

— detection of the spectroscopic saturation effect at rotational—vibrational transitions in H_2O and CO_2 molecules[6–8];

— experimental study of H_2O absorptional line shape transformation in strong field of resonant optical radiation of linear and circular polarization[9,10];

— detection and interpretation of "lightening" effect in far wing of H_2O spectral line under intense nonresonant laser radiation (LR)[11,12];

— investigation of fine structure of air, H_2O, and NO_2 absorption spectra with $7 \cdot 10^{-4}$ cm^{-1} resolution within 587—597 nm region[13];

— implementation of new techniques for measuring vibrational relaxation time of rapidly relaxing transitions in molecules[14,15];

— elaboration of dual—channel PA spectrometers and investigation of H_2O spectral lines broadening and shift by atomic and molecular gases as well as air pressure in the visible region[16,19];

— achievement of unique sensitivity of cw dye laser PA spectrometer with intracavity location of PA cell[20];

— development of instrumentation to study dynamics of gas exchange of plants, exposed to environmental stresses, by means of PA methods[21];

— elaboration of instrumentation, measuring techniques, and software for laser and nonlaser PA gas analysis.[22,23]

An overview of fundamental results obtained by spectroscopists of the IAO SB RAS from 1974 to 1994 by means of cw and pulsed laser PA spectrometers in the visible and IR regions is presented in the article. Physical basis of the PA method and characteristics of a series of PA spectrometers devised and employed at the IAO as well as results of investigation of absorption spectra fine structure and individual spectral lines parameters, nonlinear spectroscopic phenomena arising at resonant and nonresonant interaction between LR and molecular gases, methods of measuring times of vibrational relaxation of H_2O high vibrational states are considered here subsequently. In conclusion, the problems of the PA spectroscopy instrumentation development and applications to the atmosphere investigation are illuminated.

1. PHYSICAL BASIS OF THE PA SPECTROSCOPY METHOD

The photo–acoustic effect, i.e., generation of acoustic waves in a matter due to optical radiation absorption was discovered in 1881 by Bell, Tyndall, and Roentgen. The PA method based on use of this effect refers to the calorimetric ones. When radiation passes through a cell filled with an absorbing gas, the latter is heated. The heat released in the closed volume of the cell causes generation of pressure pulse. The amplitude and shape of the pulse are detected by a sensitive microphone. An electric signal from the microphone is amplified and then measured by some standard methods for measuring pulsed or periodic electric signals.

In the case when optical radiation is resonant to vibrational–rotational transition in the molecular gas under study, the process of conversion of the optical radiation energy to electric signal passes the following stages: excitation of molecules − rigid relaxation of the excited molecules − gas heating − pressure pulse generation − forced vibration of the microphone membrane − electric signal generation. In the case of radiation of moderate intensity,[3] i.e., the gas absorption coefficient $k(\nu)$ is independent of the radiation intensity I, the pressure pulse amplitude $p(t)$ and the amplitude of the detected electric pulse $U(t)$ linearly connected with each other are described by the expression

$$p(t) \approx U(t) \approx k(\nu)W, \qquad (1)$$

where W is the laser (optical) pulse energy at the PA cell input.

Expression (1) describes a medium of low absorbability, i.e., its optical depth $k(\nu)\,l \ll 1$ (l is the PA cell length). Expression (1) illustrates a principal advantage of PA laser spectroscopy over spectrophotometric or intracavity ones, namely, linear dependence of the recorded signal on the absorptivity of the matter under study and input energy or power (for cw radiation).

The dependence of characteristics of the pressure pulse generated in PA cell on parameters of the exciting LR pulse and rates of relaxation processes in a gaseous medium was studied in detail in Refs. 3 and 8. Let us examine here the general expression describing relation between spectral sweep of the recorded electric signal $U(\nu)$, LR intensity $I(\nu, t)$, and spectral absorption coefficient of the gas under study $k(\nu_0 - \nu)$, where ν_0 is the frequency of the spectral line center. In most general case of nonlinear gas absorption, i.e., $k(\nu_0 - \nu) = k(\nu_0 - \nu, I)$, and nonmonochromatic radiation ($I = I(t, \nu_1 - \nu)$, where ν_1 is frequency of laser line center) the relation between the values of $U(t)$ and $W = \int_0^\tau I(t)\mathrm{d}t$ recorded experimentally is expressed by relation

$$A(I) = U/W = \frac{\alpha(P)\int_0^\tau \int_{-\infty}^\infty k(\nu_0 - \nu', I)\, I(\nu_1 - \nu', t)\, \mathrm{d}t\, \mathrm{d}\nu'}{\int_0^\tau \int_{-\infty}^\infty I(\nu_1 - \nu', t)\, \mathrm{d}t\, \mathrm{d}\nu'}, \qquad (2)$$

where τ is the LR pulse duration and $\alpha(P)$ is the gas pressure–dependent sensitivity of PA cell determined at calibrating. In the case of linear absorption, when $k(\nu, I) = k(\nu)$, and narrow LR spectrum, i.e., laser line width $\gamma_1 \ll \gamma$ (absorption line width) from Eq. (2) we obtain the principal relationship

$$A(\nu) = U(\nu)/W = \alpha(P)\, k(\nu) \qquad (3)$$

to determine $k(\nu)$ from the measured values of $U(\nu)$, W, and $\alpha(P)$ by high–resolution laser PA spectroscopy method.

A diagram of the laser PA spectrometer is shown in Fig. 1. The key elements of the device are the narrow–band frequency tunable laser and a system for measuring the radiation spectrum wavelength and width. One (or several, two, as a rule) PA cell with high–sensitive capacitor microphone built into the cell wall is used in the spectrometer. The PA spectrometers designed and employed at the IAO are equipped with the microphones of our own production. The signals from the microphone are amplified by wideband (in the case of gas excitation by single laser pulses) or selective (when operating with amplitudely modulated cw radiation) amplifiers and then recorded in the ordinary way.
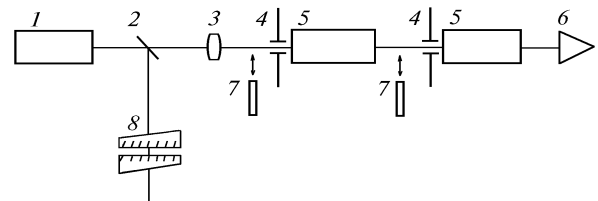

FIG. 1. A diagram of laser PA spectrometer: laser (1), light splitter (2), lens (3), diaphragms (4), cells (5), meter of the laser radiation energy (or power) (6), neutral attenuators of radiation (7), meter of wavelength and laser radiation spectrum width (8).

TABLE I. Main error sources at PA measurements of absorption coefficient with pulsed and cw lasers.

Error type	Relative error, %	
	pulsed laser	cw laser
1. Measurement error of an electric signal amplitude (depends on accuracy rating of oscillograph or voltmeter)	≤ 2	≤ 1.5
2. Measurement error of energy (pulsed regime) power (cw regime)	≤ 4 commercial calorimeters ≤ 1.5 precision calorimeters	≤ 1.5
3. Calibration error	10–20	5–10
4. Total error — absolute measurements — relative measurements	15–25 3.5–6	8–12 ≤ 3

One special feature of the PA method is the need for its calibration in order to obtain absolute values of $k(v)$. Table I presents the sources of errors arising at PA measuring absorption spectra with use of pulsed and cw lasers. It is seen that the calibration procedure is a main source of the measurement error in both cases. That fact stimulated development of dual−channel PA spectroscopy to measure physical dependencies like, for example, spectral line shape transformation due to pressure, temperature, strong electromagnetic field, and so on.[24]

Sensitivity is the most important characteristic of any spectroscopic method. In the absorption spectroscopy the sensitivity is determined by minimum detectable magnitude of the absorption coefficient k_{min} in cm^{-1}.

The PA method is one of the most sensitive methods of absorption spectroscopy. At small dimensions of PA cell (from 10 to 30 cm in length and about 10 cm^3 in volume) the reached sensitivity is about 10^{-9} to 10^{-10} cm^{-1}.

So, the use of dual−channel PA spectrometer with differential registration circuit[25] allowed one to obtain the value of $k_{min} \sim 10^{-9}$ cm^{-1} when measuring CH_4 and N_2O absorption in DF−laser generation lines. As seen from Eq. (3), the minimum detectable absorptivity, k_{min}, decreases with LR power (or energy) increase. The power of LR passing through the PA cell may increase from 10 to 100 times when the cell is located inside the laser cavity. Such design provides the lowest values of k_{min}. For example, the location of resonant PA cell inside CO_2−laser cavity allowed the authors of Ref. 26 to obtain $k_{min} = 1.8 \cdot 10^{-10}$ cm^{-1} when measuring C_2H_4 absorption.

The value of $k_{min} \sim 2 \cdot 10^{-9}$ cm^{-1} was obtained when measuring very weak H_2O absorption lines in the visible spectral range by means of cw dye laser and nonresonant PA cell inside the laser cavity.[20] It was not a limiting value, since no particular care was taken therewith to decrease mechanical vibration.

Table II illustrates the specifications of a series of laboratory PA spectrometers, which were designed at the IAO SB RAS since 1975 and used in execution of programs of fundamental and applied investigations into atmospheric optics.

2. HIGH−RESOLUTION STUDY OF ABSORPTION SPECTRA, BROADENING AND SHIFT OF H_2O SPECTRAL LINES IN THE VISIBLE REGION

The PA spectrometers of the visible region described in Table II were successfully used for obtaining reliable quantitative data on fine structure of H_2O and its isotopes absorption spectra. As well they were applied to study of broadening and shift of those H_2O absorption lines which fell inside the generation band of ruby laser and were the reference lines in lidar measurements of H_2O concentration in the atmosphere.

The first measurements of weak H_2O absorption spectra with $7 \cdot 10^{-4}$ cm^{-1} resolution were performed by means of PA spectrometer with cw dye laser and the PA cell located out of the laser cavity.[13,27] There were detected 282 lines of H_2O within the range 586.9 to 596.6 nm. It provided more detailed information as compared to the Tables of spectral lines by Moore and

coauthors.[28] The H_2O absorption spectrum was recorded experimentally at low pressure (of several Torrs), what allowed one to exclude the neighbour lines overlapping caused by collisional broadening.

The increase of sensitivity of the cw dye laser PA spectrometer up to $k_{min} \sim 2 \cdot 10^{-9}$ cm^{-1} due to locating of the PA cell inside the laser cavity[20] enabled one to measure still weaker absorption lines of H_2O and HDO. The use of frequency modulation method to measure absorption spectrum with registration of the first derivative of PA signal with respect to frequency resulted in increase of spectral resolution. Among 251 HDO lines from the range 16746 to 17012 cm^{-1} 222 lines were assigned, and 86 energy levels with rotational quantum numbers $J \geq 11$ and $K \leq 7$ in $5v_3$ band were determined. All those data significantly supplemented the available characteristics of H_2O and its isotops absorption lines in shortwave spectral region.

An example of efficient application of the dual−channel PA spectrometers was found in the first measurements of large shifts of H_2O absorption lines of (103) band by air pressure[16] which showed the value of shift coefficient for individual H_2O absorption line centered at 694.380 nm to be equal to (-0.76 ± 0.04) MHz/Torr. It gave the shift value of 0.019 cm^{-1} (at pressure difference of 750 Torr) which was comparable with Doppler linewidth. Based on the results obtained, the great importance of considering the reference H_2O absorption lines shift for solution of the inverse problem of lidar sounding of H_2O concentration at heights higher than 10 km was shown in Ref. 17 for the first time. The calculations performed for ruby laser radiation wavelength of 694.38 nm, which coincided with the corresponding H_2O absorption line maximum at standard atmospheric pressure and temperature, have shown the systematic error caused by ignoring the H_2O absorption line shift by air pressure to be from 10 to 12% at the sounding height $H \geq 10$ km. At $H = 20$ km this error increases up to 32%.

Study of broadening and shift of spectral lines of such trace molecules as H_2O, CO_2, NH_3, and CH_4 caused by other gases pressure are of great practical interest because these very gases determine optical radiation absorption in planetary atmospheres. Experimental data on shift and broadening coefficients provide information on parameters of intermolecular interaction potential and dynamics of collisions of molecules. The polarizability of a molecule in excited vibrational state and corresponding corrections to cross section of the excited molecule and buffer gas particles collision can be determined from the magnitude of lines shift of different vibrational states. The experimental data obtained by means of dual−channel laser PA spectrometry and spectrophotometry methods for a series of H_2O absorption lines in the visible and near−IR ranges ((201), (221), (202), (301), (103), and (402) bands) were analyzed by researchers of the IAO SB RAS in cooperation with colleagues from Department of Atmospheric Sciences of Research Center NASA, USA.[30] The values of polarizability α of H_2O molecule for a series of high vibrational states (Table III) were obtained from those data. An analysis of α values from Table III shows the vibrational excitation to lead to almost linear increase of α relative to V (the vibrational quantum number). Simple expression describing the V−dependence of α has been proposed in Ref. 30:

TABLE II. *Specifications of PA spectrometers of visible and IR ranges, developed at the IAO SB RAS.*

Specification	Laser type, operation mode					
	R6G cw PA cell outside cavity	R6G cw PA cell inside cavity	Ruby, pulsed	Nd:YAG, Nd-glass, pulsed	CO_2, pulsed and cw	YAG:TmCrHo, pulsed
Spectral range, μ	0.58−0.59	0.58−0.59	0.69	1.06	10.6	2.08−2.09
Wavelength tuning range, nm	~ 10	~ 10	~ 0.4	~ 2.0	Discrete tuning by lines of P and R branches	~ 1
Spectral resolution, cm^{-1}	$7 \cdot 10^{-4}$	$\sim 1 \cdot 10^{-3}$	$\sim 10^{-2}$	$5 \cdot 10^{-3}$	10^{-2}	$\sim 5 \cdot 10^{-2}$
Threshold sensitivity to absorption coefficient, cm^{-1}	$3 \cdot 10^{-8}$	$2 \cdot 10^{-9}$	$\sim 10^{-8}$	$\sim 10^{-8}$	$\sim 3 \cdot 10^{-8}$	$\sim 10^{-8}$
Power of cw radiation, mW	15	130				
Pulsed radiation intensity, W/cm^2			$\leq 5 \cdot 10^8$	$\leq 10^8$	$\leq 2 \cdot 10^7$	$10^6 - 10^7$
Laser pulse duration, nc			20−30	2−15	100−1000	~ 100
Subjects of investigation	H_2O and NO_2 absorption spectra; broadening and shifts of spectral lines by buffer gases pressure; shape of line contour inside outer electromagnetic field; measurements of vibrational relaxation times in H_2O.		Linear and nonlinear spectroscopy of vibrational−rotational transition in H_2O molecule; broadening and shifts of lines due to pressure; distortion of a contour in high−power field of resonant radiation; measurements of vibrational relaxation times in H_2O.	Absorption spectra of air and their dependence on the laser radiation intensity.	CO_2 and C_2H_4 resonance absorption and H_2O continual absorption as well as their dependence on the laser radiation intensity; measurements of times of vibrational relaxation in CO_2.	H_2O, CO_2, and air absorption spectra; shape of contour of individual spectral lines.

$$\alpha(V_1, V_2, V_3) = (14.96 + \alpha_1 V_1 + \alpha_2 V_2 + \alpha_3 V_3) 10^{-25} \text{cm}^3, \quad (4)$$

where $\alpha(V_1, V_2, V_3)$ is the polarizability of H_2O molecule in vibrational state (V_1, V_2, V_3); α_1, α_2, and α_3 are the coefficients describing the vibrational dependence on each quantum number. These coefficients can be determined from the experimental data on line shifts by the least−squares fitting method. They are

$\alpha_1 = 0.2700 \pm 0.0273$;

$\alpha_2 = 0.1780 \pm 0.0360$;

$\alpha_3 = 0.3900 \pm 0.0250$.

Note, that data on line shifts provide the simplest way to determine $\alpha(V)$ for different molecules.

TABLE III. *Polarizability of* H_2O *molecule* (α) *in excited vibrational states.*

Vibration type $(V_1 \, V_2 \, V_3)$	E_V , cm^{-1}	α, $\times 10^{-25}$ cm^3
0 0 0	0	14.69
3 0 1	13831	15.92
1 0 3	14319	16.07
4 0 1	16899	16.17

TABLE IV. *Coefficients of broadening* (γ) *and shifts* (Γ_{sh}) *of* H_2O *absorption lines of* $\nu_1 + 3\nu_3$ *band.*

Line center, cm^{-1}	Broadening gas	Γ_{sh}, cm^{-1}/atm ($\times 10^{-3}$)	γ, cm^{-1}/atm ($\times 10^{-3}$)
14397.364	air	− 19.3 ± 1.5	182.4 ± 4.5
	O_2	− 26.9 ± 2.0	131.7 ± 5.1
	CO_2	− 8.1 ± 1.5	205.2 ± 4.7
	N_2	− 17.0 ± 1.5	190.0 ± 4.5
	He	0 ± 1.5	48.1 ± 4.0
	Ne	− 4.6 ± 1.5	53.2 ± 4.0
	Ar	− 35.2 ± 1.8	106.4 ± 5.0
	Kr	− 42.6 ± 1.9	149.5 ± 5.6
	Xe	− 42.6 ± 1.9	184.9 ± 5.7
	CH_3−CO−CH_3	− 13.7 ± 2.0	293.9 ± 5.8
14400.328	air	− 13.2 ± 1.5	174.8 ± 4.6
	O_2	− 26.6 ± 2.0	144.4 ± 5.1
	CO_2	− 1.1 ± 1.5	225.5 ± 4.8
	N_2	− 9.1 ± 1.5	182.4 ± 4.3
	He	0 ± 1.5	27.9 ± 4.1
	Xe	− 38.0 ± 1.9	222.9 ± 5.7
	CH_3−CO−CH_3	+ 77.0 ± 2.0	516.8 ± 6.8
14400.782	air	− 16.5 ± 1.5	174.8 ± 4.0
	O_2	− 26.4 ± 2.0	134.3 ± 5.1
	CO_2	− 12.9 ± 1.5	276.1 ± 5.1
	N_2	− 13.4 ± 1.5	184.9 ± 4.3
	He	0 ± 1.5	30.4 ± 4.1
	Xe	− 42.1 ± 1.9	205.2 ± 5.7
	CH_3−CO−CH_3	0 ± 1.5	651.1 ± 6.7

The simplicity of the experiment with use of the dual−channel PA method and absorption cells of small volume allowed us to conduct the detailed measurements of broadening and shift coefficients of the H_2O absorption lines with the dye (R6G) and ruby lasers[30,31] for mixtures of H_2O with air and different atomic and molecular gases. Table IV presents the measurement results for H_2O lines of (103) band.

The results on H_2O absorption lines broadening and shifts induced by noble gases pressure (He, Ne, Ar, Kr, and Xe) are of great interest for further elaboration of the theory on collisional contour shape. Thus, the corresponding data (for (103) band) were used in analysis of contribution of the molecules relative motion trajectories curvature into shift magnitude at H_2O colliding with He and Ne.[32,33] After simple change of the PA cells construction, all the spectrometers developed occurred to be usable for study of the temperature dependence of molecular absorption spectra. The corresponding results are described in Ref. 34.

3. STUDY OF EFFECTS OF NONLINEAR INTERACTION OF LR WITH MOLECULAR GASES

A series of experiments was performed using PA spectrometers with high−power pulsed lasers of the visible and IR ranges to study nonlinearity of the laser radiation absorption at H_2O and CO_2 vibrational−rotational transitions. The detailed description of these experiments is in Refs. 6−10 and 35. The results of interest for the problem of high−power LR transfer through the atmosphere are presented in this chapter.

The decrease of a media resonance absorption coefficient at increase of optical radiation intensity is first and foremost due to spectroscopic effect of saturation. The threshold intensity of radiation I_s, which is a characteristic of the effect for vibrational−rotational transitions in molecular gases, depends on parameters of transition as well as on duration, spectrum width, and polarization of LR.

Observation of the saturation effect in vibrational−rotational transitions of atmospheric H_2O and CO_2 were performed with single− and two−channel PA spectrometers. The dependence of an electric signal amplitude at the PA cell microphone output on LR pulse energy at fixed duration and width of laser pulse was measured experimentally. Then the behavior of $k(I)$ was analyzed at a fixed wavelength of generation or at tuning the wavelength within the absorption line contour.[8] When tuning the generation wavelength of the ruby laser, the behavior of H_2O absorption line contour in strong resonance field of LR was studied, and the LR polarization was found to influence significantly the absorption line contour transformation at increase of LR intensity. The measurement results for LR of linear and circular polarization are presented in Figs. 2 and 3. They show that, in the case of linear polarization of LR interacting with vibrational−rotational transition in a dipole molecule, the transition saturation is observable at noticeably lower values of radiation intensity. Besides, these experiments have ascertained for the first time the phenomena of absence of an absorption line field broadening which should accompany the saturation effect according to the classical two−level model of an absorbing medium. The experimental results[8,10] were used in estimation of short laser pulses nonlinear transmission in an absorbing molecular atmosphere.[35,36]
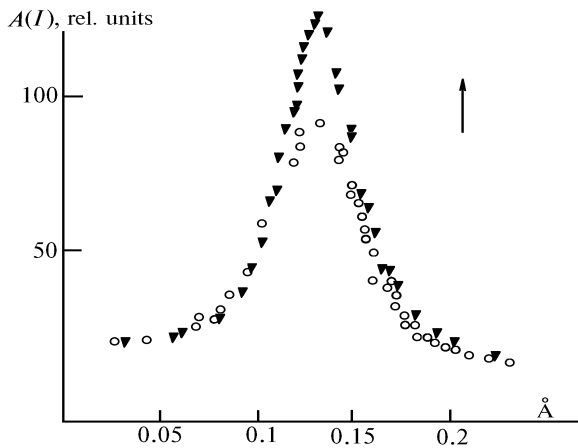
FIG. 2. *Spectral dependence of energy of linearly polarized radiation of ruby laser absorbed in* H_2O *line of* 694.38 nm.
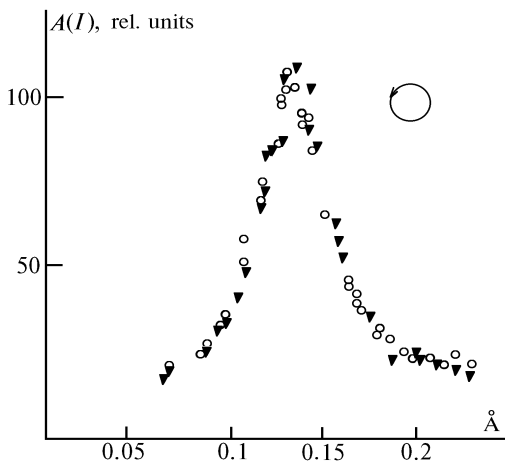

FIG. 3. *The same for radiation with circular polarization.*

Nonlinear I–dependence of absorptivity for vibrational–rotational transitions of CO_2 molecule was studied at fixed wavelengths of pulsed CO_2–laser radiation.[7] The obtained value $I_s \sim 0.25$ MW/cm^2 for P(20) line of CO_2 $10^00–0^001$ band in the air at pressure of about 100 Torr is in good agreement with theoretical estimations. Equality $I = I_s$ is easily achievable for pulsed CO_2–laser beams, therefore, the saturation effect in atmospheric CO_2 absorption lines should be taken into account when CO_2 lasers are applied to operation in the atmosphere.

The investigations into high–power LR field action on potential of intermolecular interaction and relaxation in gases also performed by PA spectroscopy methods are described in Refs. 11, 12, and 37. The "lightening" effect in far wing of an absorption line not attributed to violation of equilibrium distribution of population over vibrational–rotational states of molecular gas exposed to radiation was also discovered and studied in those works.

A theory of the effect[11] is based on the assumption that in a weak electromagnetic field the coefficient of a light absorption by gas at frequency ω is determined by classic potential of intermolecular interaction $V(R)$ where R is the distance between centers of masses of the colliding molecules.

In a high–power light field the potential $V(R)$ is connected with the field strength by relations

$$V = S\, p\, \rho_1\, \rho_2\, \hat{C}^{-1}\, H_{12}\, \hat{C}\,; \qquad (5)$$

$$i\,\hbar\,\frac{\partial \hat{C}}{\partial t} = [H_1 + H_2 + H_{12}(\xi,\, q(t)) + H_{1R}]\,\hat{C}\,; \qquad (6)$$

$$m\ddot{q} = -\,\partial V/\partial q\,, \qquad (7)$$

where t is the time, $\hbar$ is the Planck constant, ξ is an ensemble of quantum variables, H_1, ρ_1 and H_2, ρ_2 are Hamiltonians and Gibbs density matrices of the colliding molecules, H_{12} is Coulomb energy of intermolecular interaction, and $q(t)$ denotes the vector components of particles motion with reduced mass m relative to inertia center. H_{1R} is Hamiltonian of the absorbing molecule interaction with LR field, the appearance of which in the procedure of V computation results in function $V(I)$.

Solution of system of equations (5)–(7), based on the theory of perturbations relative to the H_{1R} in Eq. (6) and theoretical results from line wing theory,[12] shows that in high–power field

$$V(R) \rightarrow V_0(R)\,(1 - b\,I)\,, \qquad (8)$$

where b characterizes the intensity threshold $I_w = b^{-1}$ at which the lightening of the line wing begins. Theoretical estimations gave the value $I_w \propto (5–10)\cdot10^6$ W/cm^2 for the wing of H_2O (010) band and CO_2–laser radiation with 10.6 μm wavelength.

Corresponding experiment with mixture of H_2O vapor and N_2 gave the value $I_w \propto 2.0\cdot10^6$ W/cm^2 (see Fig. 4) being in satisfactory agreement with the theoretically estimated one.
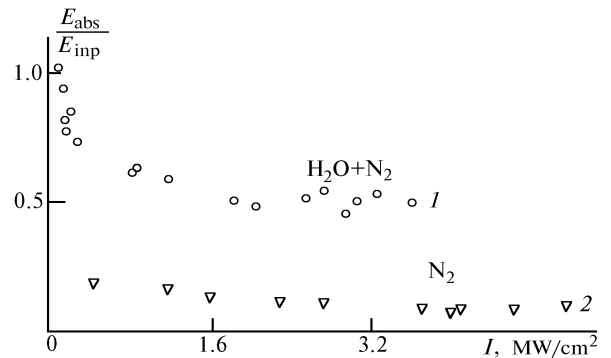

FIG. 4. *Radiation power dependence of ratio of laser radiation energy absorbed by gas* (E_{abs}) *to energy of the same radiation at PA cell input* (E_{inp}). 1) $H_2O–N_2$ *mixture* ($P_{H_2O} \sim 10$ Torr *and* $P_{N_2} \sim 750$ Torr) *and* 2) pure N_2 ($P_{N_2} \sim 100$ Torr).

One more consequence of intermolecular interaction potential V dependence on LR intensity should be a change of VT–relaxation time of gas at nonselective excitation. Actually, the probability of vibrational–transitional relaxation of an excited molecule is determined by expression[38]

$$w_{VT} \approx \left| x_{VV'} \int_{-\infty}^{\infty} \frac{V'(R)}{\hbar} \exp\left[\frac{i}{\hbar}(E_V - E_{V'})t\right] dt \right|^2 , \quad (9)$$

where $x_{VV'}$ is the matrix element of $x = r - r_e$, r is a deviation of the distance between vibrating atoms in a molecule from the equilibrium; E_V and $E_{V'}$ are the energies of vibrational states V and V', respectively; $V'(R) \sim \alpha V(R)$, where $1/\alpha$ is a width of a potential well.

In accordance with Ref. 8, in a high−power light field the decrease of w_{VT} and increase of $\tau_{VT} \sim w_{VT}^{-1}$ should be expected at decreasing of $V(I, R)$. In the case of resonant excitation of molecules by intense LR, we observe acceleration of VT−relaxation due to gas heating as well as starting the VV and VV' exchange processes at quick populating of high vibrational state. It results in deviation of the population distributing between vibrational states from an equilibrium.[39] At a molecule excitation by high−power LR far from resonance the VT−relaxation should depend inversely on I.

Figure 5 presents the experimental results of determining the I−dependence of τ_{VT} for H_2O and CO_2 molecules. Decreasing of ratio $\tau_{VT}(I)/\tau_{VT}^0$ was noted at resonant excitation of vibrational−rotational transition in CO_2 molecule exposed to CO_2−laser radiation at $I \sim I_s \simeq 0.4$ MW/cm² (τ_{VT}^0 is the time of VT−relaxation in a weak field). An increase of the ratio takes place at interaction of the same laser radiation with H_2O vapors. The value of intensity at which this effect is noticeable, correlates well with I_w value, i.e., the threshold intensity of the lightening effect in an absorption line wing. The correlation of behavior of a molecular gas spectral and relaxation parameters in high−power LR field was observed for the first time in a series of experiments conducted at the IAO SB RAS.
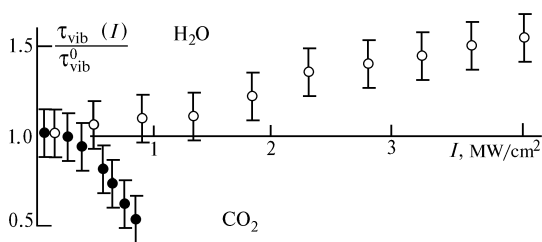

FIG. 5. *Dependence of vibrational relaxation in H_2O and CO_2 on intensity of CO_2−laser radiation at CO_2 resonant excitation and H_2O nonresonant one.*

4. MEASUREMENTS OF VIBRATIONAL RELAXATION TIME USING LASER PA SPECTROMETERS

Investigation of relaxation of selectively excited vibrational states of molecules in gases is actual for physics of gas lasers, physics of molecular interaction, and description of processes of nonlinear interaction between laser radiation and a matter.

In the process of the PA spectroscopy instrumentation development, the peculiarities of an acoustic signal generation in PA cell under low pressures were studied in detail in Refs. 3, 8, 13, and 15. The results obtained

enabled us to propose two methods to measure relaxation time of excited vibrational−rotational states. The first one[3] is based on the fact that the PA spectrometers sensitivity at low pressures $P \leq 5$ Torr is determined by VT−relaxation in a gas and deactivation of vibrationally excited molecules on the cell walls. Hence, τ_{VT} can be found from the dependence of the PA spectrometer sensitivity α on gas pressure in the cell, if τ_d (deactivation time of excited molecules on the wall) and τ_t (heat relaxation time) values are known.

As was shown in Ref. 3, the PA cell sensitivity is

$$\alpha(P) = \alpha'(P)\,\varepsilon(P), \quad (10)$$

where $\varepsilon(P)$ is a characteristic of membrane elasticity determined at the microphone calibrating, and

$$\alpha'(P) = f(\tau_{VT}, \tau_d, \tau_t). \quad (11)$$

Practically, the method is reduced to measuring $\alpha'(P)$ at low pressure, computing τ_d and τ_t according to Refs. 3 and 8, and then solving equation (11) for τ_{VT}.

Explicit expressions for the function $f(\tau_{VT}, \tau_d, \tau_t)$ for different correlations between duration of exciting pulse τ and times τ_{VT}, τ_d, and τ_t are presented in Ref. 8.

By the above−described method, vibrational relaxation times of ν_2 vibration of CH_4 molecule in mixtures with air and Ar as well as relaxation times of high vibrational states $4\nu_1 + \nu_3$, $\nu_1 + 3\nu_3$ in H_2O vapor were measured using PA spectrometers of visible and IR ranges.[3,8,14]

One more approach to τ_{VT} determination is proposed in Ref. 15 based on dependence of phase shift of natural vibrations of the microphone membrane on low pressure variations of the gas under study in the cell. This method may be realized in the cell of large diameter, thus excluding additional errors caused by acoustic waves reflection from walls of PA cell. Besides, this way does not require the diffusion coefficient of a vibrationally excited molecule and probability of deactivation at molecules collisions with the cell walls be known. As a rule, these parameters precision is not high what restricts the applicability of the method to τ_{VT} determination by the character of $\alpha(P)$ function.

The expression obtained in Ref. 15 for phase shift of natural vibrations of the membrane in PA cell of large volume is

$$\tan\varphi = \omega\,\tau_{VT}(3 - \omega^2\tau_{VT}^2) / (1 - 3\,\omega^2\tau_{VT}^2), \quad (12)$$

where $\omega = (\omega_0^2 - \beta^2)^{1/2}$, $\omega_0 = \sqrt{K/ms}$ is the frequency of natural vibrations of the microphone membrane, K is the membrane elasticity coefficient, m is the mass, and s is the membrane surface; $\beta = B/ms$ (B is the coefficient of damping) usually satisfies the condition $\beta \ll \omega_0$ so $\omega \approx \omega_0$.

Thus, expression (12) enables one to determine τ_{VT} from measuring $\tan\varphi$. The value of τ_{VT} of H_2O molecule vibrational state $\nu_1 + 3\nu_3$ was measured for the first time in Ref. 40 by the above−mentioned method.

The PA methods allow us to measure with confidence total time of excited vibrational state relaxation due to collision of molecules in the atmosphere (without relaxation channels selection) even for very weak transitions owing to high sensitivity of laser−excited PA spectrometer. The total relaxation time of an excited state is an important parameter of molecular gaseous media optics because it

determines the time of appearance of inhomogeneities in refraction index in a laser beam propagation path.

CONCLUSION

All the examples described above manifest the PA method of laser spectroscopy to be promising for the research programs on atmospheric optics. One more avenue of the PA methods development is local gas analysis with laser and nonlaser radiation sources.[2,3,5] Study of physical processes of PA signals generation and further elaboration of the spectroscopic PA methods resulted in appearance of nonlaser PA gas analizers at the IAO SB RAS[22]; technique for investigation of plants gas—exchange dynamics at variations of environmental conditions (pressure, gas composition of air, and temperature)[21]; sensitive meters of low—energy LR[8]; and, methods for investigation of linear and nonlinear absorption of LR energy by gas—aerosol media.[41]

The program of further development of PA methods and their applications being under realization at the IAO SB RAS includes the following lines:

— elaboration of methods increasing PA spectrometers sensitivity and measurement selectivity;

— expansion of PA spectroscopy instrumentation aplicability into UV range;

— development of PA instrumentation for measurements of multifrequency LR interaction with gases;

— improvement of PA methods to study absorption in multiphase media;

— improvement of methods and software for solution of inverse problems of PA spectroscopy and gas analysis.

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REFERENCES

1. V.E. Zuev, Yu.S. Makushkin, and Yu.N. Ponomarev, *Spectroscopy of the Atmosphere* (Gidrometeoizdat, Leningrad, 1987), 247 pp.

2. O.D. Gorelik and B.B. Sakharov, *Photo—Acoustic Effect in Physicochemical Measurements* (Komitet Standartov, Moscow, 1969), 186 pp.

3. A.B. Antipov, V.A. Kapitanov, Yu.N. Ponomarev, and V.A. Sapozhnikova, *Photo—Acoustic Technique in Laser Spectroscopy of Molecular Gases* (Nauka, Novosibirsk, 1987), 129 pp.

4. G.A. West, J.J. Barrett, D.R. Siebert, and K.V. Reddy, Rev. Sci. Instrum. **54**, 797—817 (1983).

5. M.W. Sigrist, ed., *Air Monitoring by Spectroscopic Techniques* (J. Wiley and Sons, Inc. New York Chichester—Brisbane—Toronto—Singapore, 1994), 531 pp.

6. A.B. Antipov and Yu.N. Ponomarev, Kvant. Elektron., No. 6, 1345—1349 (1974).

7. B.G. Ageev, Yu.N. Ponomarev, and L.K. Chistyakova, Izv. Vyssh. Uchebn. Zaved. SSSR, ser. Fizika, No. 10, 49—51 (1982).

8. B.G. Ageev, Yu.N. Ponomarev, and B.A. Tikhomirov, *Nonlinear Photo—Acoustic Spectroscopy of Molecular Gases* (Nauka, Novosibirsk, 1987), 128 pp.

9. V.P. Lopasov, Yu.N. Ponomarev, and B.A. Tikhomirov, Kvant. Elektron. **9**, No. 8, 1724—1727 (1982).

10. V.E. Zuev, Yu.N. Ponomarev, and B.A. Tikhomirov, Dokl. Akad. Nauk SSSR **277**, No. 2, 347—350 (1984).

11. B.G.Ageev, E.P.Gordov, Yu.N.Ponomarev, S.D.Tvorogov, and L.K. Chistyakova, Dokl. Akad. Nauk SSSR **268**, No. 5, 1105—1107 (1983).

12. B.G. Ageev, E.P. Gordov, Yu.N. Ponomarev, and S.D. Tvorogov, Izv. Akad. Nauk SSSR, ser. Fizika **49**, No. 3, 459—465 (1985).

13. V.A. Kapitanov, "Photo—acoustic spectroscopy of atmospheric gases and gaseous impurities in 590 μm region," Candidate's Dissertation in Physical and Mathematical Sciences, Tomsk State University, Tomsk (1982), 173 pp.

14. A.B. Antipov, V.A. Kapitanov, and Yu.N. Ponomarev, Opt. Spekstrosk. **50**, 563—565 (1981).

15. V.A. Kapitanov and B.A. Tihkomirov, Proc. SPIE **2205**, 509—514 (1993).

16. Yu.N. Ponomarev and B.A. Tihkomirov, Opt. Spekstrosk. **58**, No. 4, 947—948 (1985).

17. V.V. Zuev, Yu.N. Ponomarev, A.M. Solodov, B.A. Tikhomirov, and O.A. Romanovskii, Opt. Lett., No. 7, 318—320 (1985).

18. V.V. Lazarev and Yu.N. Ponomarev, Opt. Lett. **17**, No. 18, 1283—1285 (1992).

19. V.V. Lazarev, Yu.N. Ponomarev, V.N. Stroinova, and B.A.Tihkomirov, Atmos. Oceanic Opt. **5**, No. 9, 582—586 (1992).

20. B.V. Bondarev, V.A. Kapitanov, S.M. Kobtsev, and Yu.N. Ponomarev, Opt. Atm. **1**, No. 10, 18—24 (1988).

21. B.G. Ageev, T.P. Astafurova, Yu.N. Ponomarev, et al., Atmos. Oceanic Opt. **7**, No. 7, 528—530 (1994).

22. *Photo—Acoustic Analyzer of Multicomponent Gas Mixtures,* Atmos. Oceanic Opt. **5**, No. 9, 654—655 (1992).

23. V.A. Kapitanov, M.Yu. Kataev, A.A. Mitsel', et al., Atmos. Oceanic Opt. **5**, No. 4, 243—248 (1992).

24. Yu.N. Ponomarev, Infrared Phys. **29**, Nos. 2—4, 525—533 (1989).

25. T.E. Deaton, P.A. Depatie, and T.W. Walker, Appl. Phys. Lett. **26**, 300—310 (1975).

26. F.J.M. Harren, F.G.C. Bijnen, J. Reus, et al., Appl. Phys. B. **50**, 137—145 (1990).

27. A.B. Antipov, A.D. Bykov, V.A. Kapitanov, et all., J. Mol. Spectrosc. **89**, 449—459 (1981).

28. C.E. Moore, M.G.J. Minnaert, and J. Houtgast, *Tables of Spectral Lines of the Atmosphere from 2950 to 8770 A* (Covt. Print off., Washington, 1966), 276 pp.

29. A.D. Bykov, V.A. Kapitanov, S.M. Kobtsev, and O.V. Naumenko, Atm. Opt. **3**, No. 2, 133—140 (1990).

30. B.E. Grossman, E.V. Browell, A.D. Bykov, et al., Atm. Opt. **3**, No. 7, 617—630 (1990).

31. E.A. Korotchenko, V.V. Lazarev, Yu.N. Ponomarev, and B.A. Tikhomirov, Atm. Opt. **3**, No. 11, 1076—1079 (1990).

32. A.D. Bykov, V.V. Lazarev, Yu.N. Ponomarev, et al., Atmos. Oceanic Opt. **7**, No. 9, 651—657 (1994).

33. A.D. Bykov, N.N. Lavrent'eva, and L.N. Sinitsa, Atmos. Oceanic Opt. **5**, No. 9, 587—594 (1992).

34. V.V. Lazarev and Yu.N. Ponomarev, Atmos. Oceanic Opt. **6**, No. 8, 530—532 (1993).

35. Yu.N. Ponomarev, Infrared Phys. **32**, 377—384 (1991).

36. A.A. Mitsel' and Yu.N. Ponomarev, *Optical Models of Molecular Atmosphere* (Nauka, Novosibirsk, 1988), 128 pp.

37. B.G. Ageev, O.Yu. Nikiforova, Yu.N. Ponomarev, et al., Atm. Opt. **2**, No. 1, 37—39 (1989).

38. V.N. Kondrat'ev and E.E. Nikitin, *Kynetics and Mechanism of Gas—Phase Reactions* (Nauka, Moscow, 1974), 558 pp.

39. S.A. Akhmanov and N.I. Koroteev, *Methods of Nonlinear Optics in Light Scattering Spectroscopy* (Nauka, Moscow, 1981), 554 pp.

40. V.A. Kapitanov, O.Yu. Nikiforova, Yu.N. Ponomarev, et al., Atmos. Oceanic Opt. **7**, No. 11 (1994) (to be published).

41. B.G. Ageev, A.A. Zemlyanov, A.M. Kabanov, and Yu.N. Ponomarev, Atmos. Oceanic Opt. **5**, No. 2, 88—90 (1992).