21. R. Lang and K. Kobayshi, "External optical feedback effects on semiconductor injection laser properties," IEEE J. Quantum Electron., **QE-16**, No. 3, 347-355 (1980).
22. P. Spano, S. Piazzolla, and M. Tamburrini, "Theory of noise in semiconductor lasers in the presence of optical feedback," IEEE J. Quantum Electron., **QE-20**, No. 4, 350-357 (1984).
23. R. W. Tkach and A. R. Chraplyvy, "Regimes of feedback effects in 1.5 μm-distributed feedback lasers," J. Lightwave Technol., **LT-4**, No. 11, 1655-1661 (1986).
24. A. P. Bogatov, P. G. Eliseev, O. A. Kobildzhanov, and V. R. Madgazin, "Suppression and spectral splitting of the amplitude noise due to mode beating in single-frequency injection laser," IEEE J. Quantum Electron., **QE-23**, No. 6, 1064-1070 (1987).
25. H.-J. Bachert, A. P. Bogatov, Yu. V. Gurov, P. G. Eliseev, O. G. Okhotnikov, G. T. Pak, M. P. Rakhval'skii, and K. A. Khairetdinov, "Radiofrequency spectra of mode beats and intensity fluctuations of an injection laser with an external dispersive cavity," Kvantovaya Élektron. (Moscow), **8**, No. 9, 1957-1961 (1981).
26. A. B. Zhuravlev, G. T. Pak, E. L. Protnoi, and N. M. Stel'makh, "Dispersion of the refractive index and radiofrequency spectra of intermode beats of a heterolaser in an external dispersive cavity," Pis'ma Zh. Fiz., **11**, No. 22, 1362-1365 (1985).
27. H. Sato, T. Fujita, and K. Fujito, "Intensity fluctuation in semiconductor lasers coupled to external cavity," IEEE J. Quantum Electron., **QE-21**, No. 1, 46-51 (1985).
28. R. F. Kazarinov, C. H. Henry, and R. A. Logan, "Longitudinal mode self-stabilization in semiconductor lasers," J. Appl. Phys. **53**(7), 4631-4644 (1982).

MULTIFREQUENCY LASER PROBING

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A method is developed for processing the results of measuring gain or absorption by multiple sounding of gaseous media. The accuracy of the determined parameters of gaseous media is analyzed as a function of the accuracy with which the gain or absorption is measured. The method was developed by solving model problems and used to reduce the measured values of the gain in media containing CO and CO_2 *molecules. Recommendations are made for diagnostics of equilibrium and nonequilibrium gaseous media containing CO and* CO_2, *and conditions are stipulated with respect to the probing system and the measurement accuracy needed in measurements of the gain and absorption indices from which the parameters of the gaseous media are determined.*

INTRODUCTION

A great variety of methods are used for the diagnostics of gaseous media [1]. Of particular interest are measurements of the parameters in active media and contactless laser measurements of the concentrations of various components in the atmosphere, in the exhausts of motors and turbines, and in the commercial waste products. One simple and sufficiently effective diagnostic method is that of resonant amplification or absorption of a probing signal passing through the investigated gas. This makes it possible to understand the physics of the phenomena in the active media, optimize the working parameters, and determine the energy characteristics of laser systems. The use of tunable lasers that emit on individual vibrational—rotational transitions of molecules yields the spectral distribution of the amplification/absorption index a_{nJ} in the gas and permits measurements of the temperature, concentrations, and populations of individual levels [2]. The use of tunable lasers ensures high parameter-measurement accuracy, but encounters the problem of the correctness of the experimental measurements and of reliability of the resultant data as functions of the accuracy with which a_{nJ} is measured. To this end it

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is necessary to solve the inverse problem of determining the parameters of the medium from the measured distribution of a_{nJ}, and it is obligatory in this case to estimate the accuracy of the obtained solutions. Since the errors of the determined gas parameters are very sensitive to the accuracy with which the amplification/absorption indices are measured, it is expedient to process the measured values of a_{nJ} by using the methods for solving ill-posed problems [3]. This makes it possible to develop a general procedure for reducing the results of indirect measurements in laser spectroscopy [2].

The progress achieved in the development of tunable lasers operating on vibrational—rotational transitions, and of semiconductor and dye lasers, makes this problem topical, can expand greatly the range of applicability of this method, and makes possible unique measurements of molecule absorption spectra, investigations of energy transfer between molecules, studies of the dynamics of chemical reactions, and others. In addition, the method of resonance laser absorption can turn out to be the most universal and promising for control of the environment.

The aim of the present paper is development of a multifrequency sounding method using tunable stabilized CO and CO_2 lasers, development of software for the reduction of the experimental results, and investigation of specific laser systems.

1. DESCRIPTION OF PROCEDURE

The theoretical premises underlying the mechanism whereby inversion is produced in diatomic or triatomic molecular gases have been developed long ago and are well known [4]. The expression for the amplification/absorption index at the line center of an individual vibrational—rotational transition can be written, by starting from these premises, in the form of a linear combination of two functions that depend on quantum and macroscopic parameters whose specific forms are determined by the molecular constants of the investigated gas component (CO, CO_2, HF, N_2O, etc.):

$$a(n, n', J, J', T, p) = \varphi_2 (n, n', J, J', T, p) N_n - \varphi_1 (n, n'J, J', T, p) N_{n'}, \tag{1}$$

where N_n and $N_{n'}$ are the vibrational populations of the upper and lower levels; J and J′ are the numbers of the rotational sublevels; T and p are the temperature and pressure of the gas. (For a gain expressed in this form it is assumed that the rotational and translational degrees of freedom are in equilibrium).

For the P mode of the transitions of the CO molecules and for the P and R modes of the transitions of the CO_2 molecules (for the bands $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$) the functions φ_i ($i = 1, 2$) can be written in the form

$$\varphi_i (n, n', J, J', T, p) = \xi(n, J, T, p) B_i (n) \cdot \exp[- B_i (n) m (m + 2i - 3)/T],$$

$$\xi(n, J, T, p) = \sigma_{CO (CO_2)} \cdot \lambda^3_{n,J\mp 1 \rightarrow n',J} \cdot A_{n,n'} \sqrt{\mu_{CO (CO_2)}/2R} \cdot |2m + 1| \cdot$$

$$H(a)/(4\pi T)^{3/2},$$

$B_i(n)$ are the rotational constants of the vibrational levels that correspond to the quantum number n (which must be treated for CO_2 molecules as a multiple index: $n = 00^01$ and $n' = 10^00$ or 02^00). For CO we have $B_1(n) = B_2(n - 1) \simeq 2.795 - 0.025 \cdot n$(K) and for CO_2 $B_2(00^01) = 0.55702$ K, $B_I(10^00) = 0.56299$ K, B_I $(02^00) = 0.56182$ K, $m = -J$.

For the P mode, $m = J + 1$ for the R mode $\sigma_{CO} = 1$, $\sigma_{CO_2} = 2$.

$\lambda_{n,J\pm 1 \rightarrow n',J}$ is the transition wavelength ("—" — P mode, "+" — R mode). For the P mode of the CO molecules we have $\lambda_{n,J-1 \rightarrow n',J} = 1/(E_{n,J-1} - E_{n-1,J})$,

$$\begin{aligned} E_{n,J} = {} & \omega_e (n + \frac{1}{2}) - \omega_e x_e (n + \frac{1}{2})^2 + \omega_e y_e (n + \frac{1}{2})^3 - \omega_e z_e (n + \frac{1}{2})^4 \\ & + \omega_e a_e (n + \frac{1}{2})^5 - \omega_e b_e (n + \frac{1}{2})^6 + \ldots + [B_e - a_e (n + \frac{1}{2}) \\ & + \gamma_e (n + \frac{1}{2})^2 - \delta_e (n + \frac{1}{2})^3 + \ldots] J (J + 1) - [D_e - \beta_e (n + \frac{1}{2}) \\ & + \pi_e (n + \frac{1}{2})^2 - \ldots] J^2 (J + 1)^2 + [H_e - \eta_e (n + \frac{1}{2}) + \ldots] J^3 (J + 1)^3. \end{aligned}$$

(The values of the spectroscopic constants of the last expression can be found in [5]).

For the P- and R-modes of the transitions of the bands $00^01 \rightarrow 10^00$ and $00^01 \rightarrow 02^00$ of the CO_2 molecule we have

TABLE 1

n(n′)	$B_{n(n')}$, cm^{-1}	$D_{n(n')}$, cm^{-1}	$H_{n(n')}$, cm^{-1}
00°I	0,387I4I40	I,33034·I0^{-7}	0,I7·I0^{-I3}
I0°0	0,390I8893	I,I4952·I0^{-7}	I,9I·I0^{-I3}
02°0	0,39048230	I,57I6I·I0^{-7}	2,33·I0^{-I3}

TABLE 2

	P-mode		R - mode	
	00°1 → 10°0	00°1 → 02°0	00°1 → 10°0	00°1 → 02°0
a, c^{-I}	0,I902	0,203	0,I542	0,I57
b, c^{-1}	-8.875·I0^{-4}	-9,5·I0^{-4}	I,I25·I0^{-3}	I,4I·I0^{-3}

$$1/\lambda_{n,J\mp1\to n',J} = \omega_{n\to n'} + [B_n(m+1) - B_{n'}(m-1)]m -$$
$$- [D_n(m+1)^2 - D_{n'}(m-1)^2]m^2 + [H_n(m+1)^3 - H_{n'}(m-1)^3]m^3,$$
$$\omega_{00^\circ1\to10^\circ0} = 980{,}9586\ \text{см}^{-1},\ \omega_{00^\circ1\to02^\circ0} = 1063{,}7346\ \text{cm}^{-1}$$

B, D, and H are listed tabulated in [6].

$A_{n,n'}$ are Einstein coefficients (their values for the CO molecule are given in [7])

$A_{n,n'}(J) = a + b\cdot J$ — for the CO_2 molecule [8].

μ_{CO} and μ_{CO_2} are the molecular weights of the molecules CO and CO_2,

R is the universal gas constant,

H(a) is the Voigt function (at the line center). Its value can be calculated with high accuracy ($\leq$0.09%) from the approximate equations [9]

$a = \Delta\nu_L\sqrt{\ln 2}/\Delta\nu_D$ — Voigt-function parameter

$\Delta\nu_L = \sum_i \xi_i \Delta\nu_L{}^i$ — Lorentz linewidth.

(For CO_2 molecules we can use the expression [10]

$$\Delta\nu_L = p\cdot\gamma_{CO_2-CO_2}(J)\,[\xi_{CO_2}\left(\frac{300}{T}\right)^{n_{CO_2-CO_2}} + \sum_i \xi_{x_i}\left(\frac{300}{T}\right)^{n_{CO_2-x_i}} \frac{\gamma_{CO_2-x_i}(J)}{\gamma_{CO_2-CO_2}(J)}], \tag{2}$$

where ξ_{x_i} is the molar concentration of the component x_i, and $\gamma_{CO_2\text{-}x_i}$ is the width of the Lorentz line (in $cm^{-1}\cdot atm^{-1}$) broadened by interaction with the gas component x_i. In [10] is given also a brief survey of the available experimental data on $\gamma_{CO_2\text{-}x_i}(J)$ and $n_{CO_2\text{-}x_i}$. A similar expression can be used for the CO molecules — a survey of the experimental data is given in [7]).

$\Delta\nu_D = \sqrt{8RT\ln 2/\mu_{CO(CO_2)}}\,/\lambda_{n,J\mp1\to n',J}$ is the Doppler linewidth.

Note that Eq. (1) can be used to process the measured amplification/absorption indices in the case when the line contours corresponding to different transitions do not overlap. If overlap does take place, the gain is given by expressions of type (1) summed over all the transitions that contribute to the change of the intensity of the probing radiation (in this case, of course, it is necessary to take into account in the Voigt function the deviation of the frequency from the line center).

Comparison of the calculation of the absorption indices in pure CO_2 determined from the equations above with the measured [8] absorption indices for different values of J and p, and the measured temperature dependences of the absorption indices [11], show that the difference is only 3-4%, which can be regarded as fully satisfactory within the accuracy of γ and $A_{nn'}$ (2-3% for each quantity).

The reduction itself of the measurement results consists of solving the inverse problem, i.e., of calculating the populations N_n of the vibrational levels and of the gas temperature T from the aggregate of the measured amplification/absorption indices $a_{nJ}{}^{exp}$. This problem, however, turns out to be quite sensitive to the accuracy of the $a_{nJ}{}^{exp}$ measurement. Thus, in the simplest case, three measurements of a_{nJ} for different J and for one n suffice formally to determine the three unknowns N_{n-1}, N_n, and T when p is known. However, attempts to reduce the experimental $a_{nJ}{}^{exp}$ for real CO and CO_2 media and to solve model problems have shown that a 10% error in the gain can lead to unreliable temperature and population values that differ from the true one by several times. This situation is altogether typical of the solutions of a number of inverse problems [3], so that it is necessary either to measure a_{nJ} with extra high precision, or use a statistical reduction of a large number of $a_{nJ}{}^{exp}$ measurements and carry out the solution by the methods of ill-posed problems [3] with an unavoidable estimate of the errors of the calculated parameters.

We have reduced the measured distribution of the amplification (absorption) indices by the rather universal method of interpreting the results of indirect measurements — the least squares method. According to this method, the vibrational populations N_n and the temperature T are approximately estimated by choosing a set of these quantities that minimizes the sum of the squares of the deviations

$$R(N, T) = \sum_{(n,J)_{exp}} [a_{nJ}(T) - a_{nJ}^{exp}]^2, \tag{3}$$

where $a_{nJ}{}^{exp}$ are the measured values, $a_{nJ}(T)$ is defined by Eq. (1), and N is the vector of the vibrational populations that must be determined, with a total number n of components. (It will be assumed throughout that the gas pressure p is known). The summation is over all the transitions for which the amplification (absorption) indices have been measured. It is assumed here and below that the primary reduction of the measurement results has already been performed, and that Eq. (3) contains the averaged values of $a_{nJ}{}^{exp}$.

It is known that the determination of the minimum of (3), for fixed T, by setting up a system of normal equations and equating to zero the partial derivatives with respect to the variables N_n, encounters frequently serious difficulties due to the large stipulation numbers of the obtained matrices, for example if the sets of functions φ_1 and φ_2 for the different J are close and linearly dependent. This can lead in the calculations to loss of accuracy, and frequently simply to meaningless results. There are also known numerical methods which not only point to the appearance of large stipulation numbers, but are also sufficiently effective when account is taken of the input information, the roundoff errors, and the linear dependence of the basis functions. It is stated in [12] that in the general least-squares problem the most reliable method of calculating the coefficients, capable also of revealing a linear dependence of the basis functions, is based on a matrix factorization called singular expansion.

It will be more convenient hereafter to write the minimization problem in matrix notation

$$R(N, T) = \|\varphi(T) N - \vec{a}\|^2, \tag{4}$$

where $\varphi(T)$ is a rectangular m × n matrix such that the i-th component of the vector $\varphi(T)N$ coincides with the theoretical expression for the i-th transition; m is the total number of transitions for which the amplification (absorption) index has been measured; n is the dimensionality of the population vector N (the total number of vibrational levels needed for a theoretical calculation of a_{nJ}, $\boldsymbol{a}$ is the vector of the measured gains with total number of components m; $\|\ldots\|$ is the Euclidean length (norm) of a vector in m-dimensional vector space R_m:

$$\|x\| = \sqrt{(x^T, x)} = \sqrt{\sum_{i=1}^{m} x_i^2},$$

and x^T is the row-vector transpose of a column vector. The problem of finding N and T reduces then to finding

$$\min_{(N, T)} R(N, T) \tag{5}$$

The minimum of (5) with respect to $N \in R_n$ and T should be determined under the conditions that the components of the vector N be nonnegative, arbitrarily designated hereafter by

$$N > 0 \tag{6}$$

and that T belong to a temperature interval whose position is determined by the experimental conditions, i.e., by reasonable physical estimates.

In a specific realization of the calculations, Eq. (4) was minimized with respect to N at fixed T, followed by one-dimensional minimization with respect to T. The minimization with respect to N was with the aid of a singular expansion of the matrix φ, i.e., with the aid of a representation in the form: $\varphi = U\sum V^T$, where U is an orthogonal ($U^{-1} = U^T$) m × m matrix; V is an orthogonal n × n matrix; $\sum$ is a rectangular m × n matrix of singular numbers and its elements are $\sigma_{ij} = \sigma_i\delta_{ij}$ (δ_{ij} is the Kronecker symbol and $\sigma_i \geq 0$ are the singular numbers of the matrix φ).

The algorithm, program, and the capabilities of such a representation are described in [12-14].

For any fixed T, the solution of the problem (5) without allowance for (6) can be expressed in terms of a pseudo-inverse (in the Moore—Penrose sense [12-14]) matrix φ^+ defined by

$$\varphi^+ = V\Sigma^+U^T \ ,$$

where $\sum^+$ is an n × m matrix with elements $\sigma_{ij}{}^+ = \sigma_i{}^+\delta_{ij}$,

$$\sigma_i^+ = \begin{cases} 1/\sigma_i, & \sigma_i \geqslant \tau \\ 0 \ , & \sigma_i < \tau \end{cases}, \quad \tau = \sigma_{\max}\,\chi,$$

$\sigma_{\max}$ is the maximum singular number of the matrix φ; χ is the relative error that reflects the accuracy of the initial data (or of the computation accuracy).

Thus, the formal solution of the problem (5) for fixed T, without allowance for the condition (6), is given by

$$N_0(T) = \varphi^+(T)\vec{a}$$

(the so-called normal pseudo-solution [3]). Note that if the matrix φ has a rank smaller than n (rank $\varphi < n$) or if $\sigma_i < \tau$ for even one singular number, the solution is in general not single valued:

$$N(T) = N_0(T) + V \sum_{\sigma_i<\tau} c_i e_i \, ,$$

where c_i are arbitrary constants and $e_{ij} = \delta_{ij}$. Separation of a single-valued solution calls in this case for additional conditions. In particular, the solution with minimum length is determined by the vector N_0 (see [12, 14] for details).

To solve the problem (5) it is necessary next to obtain the minimum, with respect to T, of the function

$$r(T) = \min_{N \in R_n} R(N, T) = \|[\varphi(T)\varphi^+(T) - E_m]\vec{a}\,\|^2, \tag{7}$$

where E_m is an m × m unit matrix.

The minimum of (7) is obtained numerically by any one-dimensional algorithm (we used the FMIN algorithm and program of [12]).

The vector $N_0(T)$ constructed above may not ensure satisfaction of the condition (6) for all T, while the function r(T) may have several local minima in the specified temperature interval. Calculations for a number of model problems have shown that the "false" minima correspond to those N which have negative components. The condition (6) is thus necessary to monitor the physical nature of the obtained N_n and T, and permit in a number of cases to find the correct temperature interval in which the minimum of (7) is to be sought. Solution of the problem (5) with inequality-type constraints reduces to solution of a sequence of least-squares problems (possibly of smaller dimensionality) and is quite clear from the algorithmic viewpoint, but writing this solution in compact analytic form is a complicated task (it is necessary in fact to analyze the position of the vector $\varphi^+(T)a$ relative to a polyhedral angle defined by condition (6), and consider the possibility of setting the corresponding components of the solution equal to zero).

The least squares method is quite universal and requires practically no a priori information on the solution. The only such information is on the location of the temperature interval in which the minimum of (7) is sought, but it can be used mainly to shorten the computation of min r(T). Frequently, however, this information on the solution exists and it is desirable to use it for a more accurate determination of N and T. For CO_2 systems, for example, this additional information can be the assumption that the vibrational temperatures of the second and first modes are equal ($T_1 = T_2 = T$), and for CO systems it can be the population ratio that can be computed from known pumping rates, V—V and V—V′ exchange and V—T relaxation, and the Boltzmann distribution of the populations for equilibrium systems.

We examine the solution of (5) using additional information on the relation between the components of the vector **N**. In R_n space all the vectors having specified component ratios lie on a straight line passing through the origin, and are described by the unit vector $\xi \in R_n(\xi^2 = 1)$. One can require that the solution be closest to this straight line and that the sum of the squares of the deviations (4) not exceed a specified value ϵ^2. The problem reduces then formally to finding the minima, with respect to $N \in R_n$ and T, of the expression

$$R_1(N, T) = \|N - \vec{\xi}(\vec{\xi}^T, N)\|^2_n,$$

under the conditions

$$\|\varphi N - \vec{a}\|^2 \leq \epsilon^2,$$

or

$$N > 0,$$

where $\|\ldots\|$ is the norm in R_n space.

Using a singular expansion of the matrix φ we can express the problem in the following equivalent form: find

$$\min_{(z \in R_n, T)} R_1(z, T),$$

where

$$R_1(z, T) = \|z - \vec{\zeta}(\vec{\zeta}^T, z)\|^2_n,$$

under the conditions $\|\Sigma \mathbf{z} - \mathbf{d}\| \leq \epsilon$ and $V\mathbf{z} > 0$.

We have introduced here the notation

$$\vec{\zeta} = V^T\vec{\xi}\ (\vec{\zeta}^2 = 1),\quad \mathbf{z} = V^T\mathbf{N},\quad \mathbf{d} = U^T\vec{a}.$$

Using the method of Lagrange multipliers, we can reduce the problem to finding the absolute extremum (disregarding the condition N > 0) of the function

$$\Phi(z, \lambda, T) = \|z - \vec{\zeta}(\vec{\zeta}^T, z)\|^2_n + \lambda(\|\Sigma z - d\|^2 - \epsilon^2).$$

The minimum with respect to $z \in R_n$ is realized on a vector z_0 with components

$$z_{0k} = \frac{\lambda}{\lambda\sigma_k^2 + 1}\left(\sigma_k d_k + \zeta_k \frac{\sum\limits_{i=1}^{n} \frac{\sigma_i d_i \zeta_i}{\lambda\sigma_i^2 + 1}}{1 - \sum\limits_{i=1}^{n} \frac{\zeta_i^2}{\lambda\sigma_i^2 + 1}}\right),\ k = 1, 2, \ldots, n$$

where the parameter λ is defined as the solution of the equation

$$\sum_{i=1}^{n} [\sigma_i z_{0i}(\lambda) - d_i]^2 = \epsilon^2$$

The remaining minimization with respect to T is realized, as before, by any one-dimensional algorithm. The condition (6) is also met by solving a sequence of problems of the type indicated above, using the algorithms of [14].

We estimate now the accuracy of the parameters N and T. We assume that N and T undergo no statistical fluctuations and that the components of the vector a are random with a certain (as a rule, unknown) distribution, where the deviations from the mean can have a systematic character (this can be due to inaccurate adjustment, to a systematic error in the determination of the gain when measuring the radiation intensity and due to the spatial inhomogeneity of the sounded region, or to other causes).

We assume also that the problem (5)-(6) can be solved exactly in a sufficiently wide range of the components of the vector a. The conditions that (4) be a minimum with respect to N and T can be written in the form

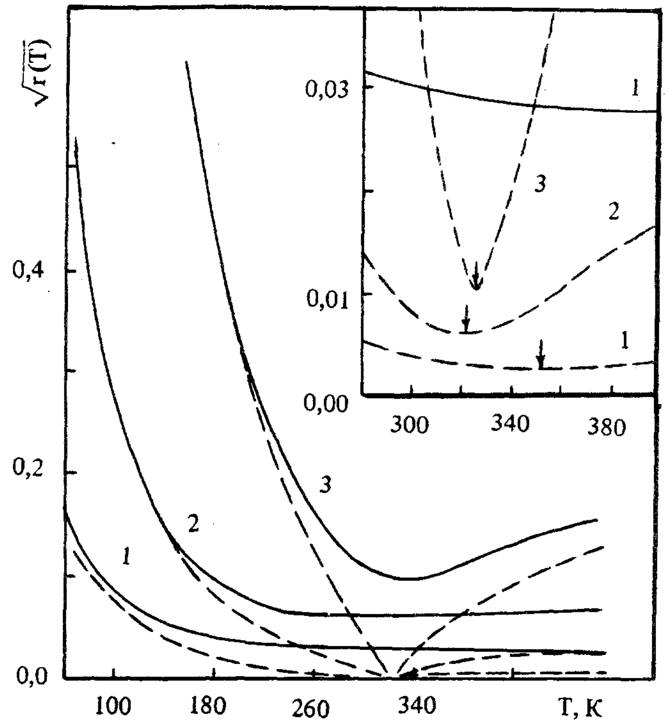

Fig. 1

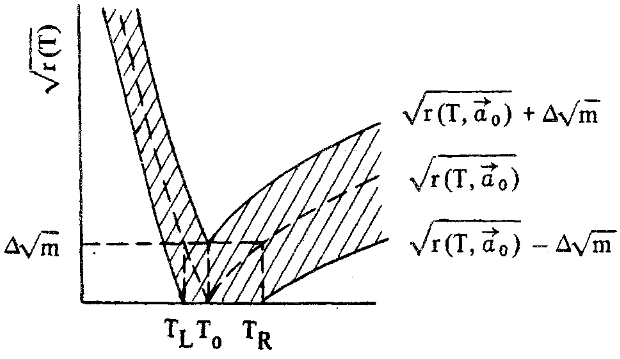

Fig. 2

Fig. 1. Dependence of $\sqrt{r(T)}$ on the temperature for different numbers of probe lines in four vibrational bands 10-9, 12-11, 14-13, 16-15: 1) J = 9, 10, 11 (3 lines in each band, 2) J = 9, 10, 11, 12, 13 (5 lines in each band), 3) J = 9, 10,..., 18 (10 lines in each band). Solid lines – gain measured with relative accuracy 0.1; dashed – with relative accuracy 0.01. Inset – region of exact solution at 325.4 K in enlarged scale. The arrows mark the positions of the minima of the curves.

Fig. 2. The values of $\sqrt{r(T, a)}$ are located within the shaded region.

$$\varphi^T(\varphi N - \vec{a}) = 0$$

$$N^T \frac{\partial\varphi^T}{\partial T}(\varphi N - \vec{a}) = 0 \qquad (8)$$

These equations determine N and T implicitly as functions of $\boldsymbol{a}$. Substitution of these functions in (8) transforms them into identities. We apply a small shift $\Delta\boldsymbol{a}$ and expand the left-hand sides of the obtained identities in series accurate to terms of first order of smallness. We obtain

$$\varphi^T\left(\frac{\partial\varphi}{\partial T} N\,\Delta T + \varphi\,\Delta N - \overrightarrow{\Delta a}\right) + \frac{\partial\varphi^T}{\partial T}(\varphi N - \vec{a})\,\Delta T = 0,$$

$$N^T \frac{\partial\varphi^T}{\partial T}\left(\frac{\partial\varphi}{\partial T} N\,\Delta T + \varphi\,\overrightarrow{\Delta N} - \overrightarrow{\Delta a}\right) + \left(N^T \frac{\partial^2\varphi^T}{\partial T^2}\,\Delta T + \overrightarrow{\Delta N}^T \frac{\partial\varphi^T}{\partial T}\right)(\varphi N - \vec{a}) = 0,$$

Recognizing that $\|\varphi N - \boldsymbol{a}\|$ is a minimum, meaning that each component of the vector $\varphi N - \boldsymbol{a}$ is small, we neglect the second terms in the above two equalities. The resultant relations

$$\varphi^T\left(\frac{\partial\varphi}{\partial T} N\,\Delta T + \varphi\,\overrightarrow{\Delta N} - \overrightarrow{\Delta a}\right) = 0,$$

$$N^T \frac{\partial\varphi^T}{\partial T}\left(\frac{\partial\varphi}{\partial T} N\,\Delta T + \varphi\,\overrightarrow{\Delta N} - \overrightarrow{\Delta a}\right) = 0$$

coincide with the conditions for the minimum of the function

$$R_2(\overrightarrow{\Delta N}, \Delta T) = \left\|\frac{\partial\varphi}{\partial T} N\,\Delta T + \varphi\,\overrightarrow{\Delta N} - \overrightarrow{\Delta a}\right\|^2$$

with respect to $\overline{\Delta N}$ and ΔT [N and T satisfy Eq. (8)]. Introducing the $m \times (n+1)$ matrix ψ by adding from the left the column $(\partial\varphi/\partial T)N$ in the matrix φ and the vector $\overrightarrow{\Delta x}$ ($\Delta x_1 = \Delta T$, $\Delta x_i = \Delta N_{i-1}$, $i = 2, 3, \ldots, n+1$) we can express the function R_2 in the form

$$R_2(\overrightarrow{\Delta x}) = \|\psi\,\overrightarrow{\Delta x} - \overrightarrow{\Delta a}\,\|^2 \tag{9}$$

An estimate of the accuracy of the solution of the problem (5)-(6), for a known experimental error $\overrightarrow{\Delta a}$ can thus be obtained by minimizing (9) with respect to $\overrightarrow{\Delta x}$. Equation (9) is minimized by the same method as (5). The procedure is even simpler, since there is no condition such as (6) and there are no nonlinear arguments of type T.

Solution of model problems [2] using the procedure described above has shown that it is indeed possible in this manner to reconstruct in a number of cases the parameters (1) from the specified values of $a_{nJ}^{\exp}$ and to estimate their accuracy. In some cases, however, it is impossible to obtain meaningful results, frequently in fact in experimental modeling of real situations. The causes may be the low accuracy of $a_{nJ}^{\exp}$ (~10%) a small number of lines within the limits of one vibrational band, or when the probe lines are located in the region of maximum gains. The character of the r(T) dependence which is minimized to determine the parameter T is shown in Fig. 1 for various dispositions of the probe lines and for different accuracies of the gain measurement. (The calculation was carried out under operating conditions of a probing CO laser, viz., gas temperature $T_0 = 325.4$ K and gain $a \simeq 0.4\ \mathrm{m}^{-1}$ at the maxima of the vibrational bands [2]. The figure shows clearly the presence of a minimum of r(T) when the gain is measured with high accuracy (dashed lines). At lower accuracy (solid lines) the minimum is not as strongly pronounced and is shifted farther away from the exact solution or is altogether nonexistent—solid curve 1 (more accurately, the minimum on the right-hand boundary of any specified temperature interval). The absence of a minimum of r(T) means in fact that the proposed procedure cannot solve the problem and the range of its validity is in question.

The question can be answered by considering the behavior of the function $r(T, \boldsymbol{a})$ introduced in (7). Let us list briefly the salient points of this analysis (it is described in detail in [2]).

1. The function $r(T, \mathbf{a}_0)$ has an ascending branch $T < T_0$, a descending one $T > T_0$, and a minimum equal to zero at $T = T_0$ ($\boldsymbol{a}_0$ is the vector of the exact values of the gain corresponding to the temperature T_0 and the population N_0, i.e. $\boldsymbol{a}_0 = \varphi(T_0)N_0$).

2. If the gain contains errors, $\boldsymbol{a} = \boldsymbol{a}_0 + \Delta\boldsymbol{a}$ with $\Delta = \max\limits_{1 \leqslant i \leqslant m} |\Delta a_i|$, the values of $r(T, \boldsymbol{a})$ are bounded from above and from below:

$$\sqrt{r(T, \vec{a}_0)} + \Delta\sqrt{m} \geqslant \sqrt{r(T, \vec{a})} \geqslant \begin{cases} \sqrt{r(T, \vec{a}_0)} - \Delta\sqrt{m}, & T \notin [T_L, T_R] \\ 0, & T \in [T_L, T_R] \end{cases},$$

T_L and T_R are the two solutions of the equation $r(T, \boldsymbol{a}_0) = \Delta^2 m$.

The geometric meaning is that the values of $\sqrt{r(T, \boldsymbol{a})}$ are located within the region shown shaded in Fig. 2.

3. A limit of $r(T, \boldsymbol{a}_0)$ exists as $T \to \infty$. If $r(T, \boldsymbol{a})$ is always to have a minimum with respect T, it suffices to require satisfaction of the condition

$$\sqrt{r(T_*, \vec{a}_0)} - \Delta\sqrt{m} > \Delta\sqrt{m} \tag{10}$$

for a certain $T_* > T_R$ (and, in particular, for infinite T_*). Indeed, since any function $\sqrt{r(T, \boldsymbol{a})}$ passes not higher than the point $(T_0, \Delta\sqrt{m})$ and is always larger than the function $\sqrt{r(T, \boldsymbol{a}_0)} - \Delta\sqrt{m}$ $(T > T_R)$ this condition suffices for the existence of a minimum of (7), so that in this case Eq. (5) will always have a solution.

In the simplest case when the amplification/absorption index is measured within one vibrational band with a set of quantum numbers from J to J + m, we have

$$r(\infty, \vec{a}_0) = \|[\varphi(T)\varphi^+(T)|_{T\to\infty} - E_m]\vec{a}_0\|^2 = \sum_{i=1}^{m}\Big[\frac{2J+2i-1}{S}\sum_{j=1}^{m}(2J+2j-1)a_{0j} - a_{0i}\Big]^2,$$

$$S = \sum_{i=1}^{m}(2J+2i-1)^2.$$

(This expression was derived neglecting the wavelength and characteristic-temperature differences.)

Next, neglecting the difference between the factors $2J + 2i - 1$, which is permissible at not too large m, and using (10), we obtain

$$\Delta < \frac{1}{2}\sqrt{\frac{r(\infty, \vec{a}_0)}{m}} \cong \frac{1}{2}\sqrt{\frac{1}{m}\sum_{i=1}^{m}\Big[a_{0i} - \frac{1}{m}\sum_{j=1}^{m}a_{0j}\Big]^2}, \tag{11}$$

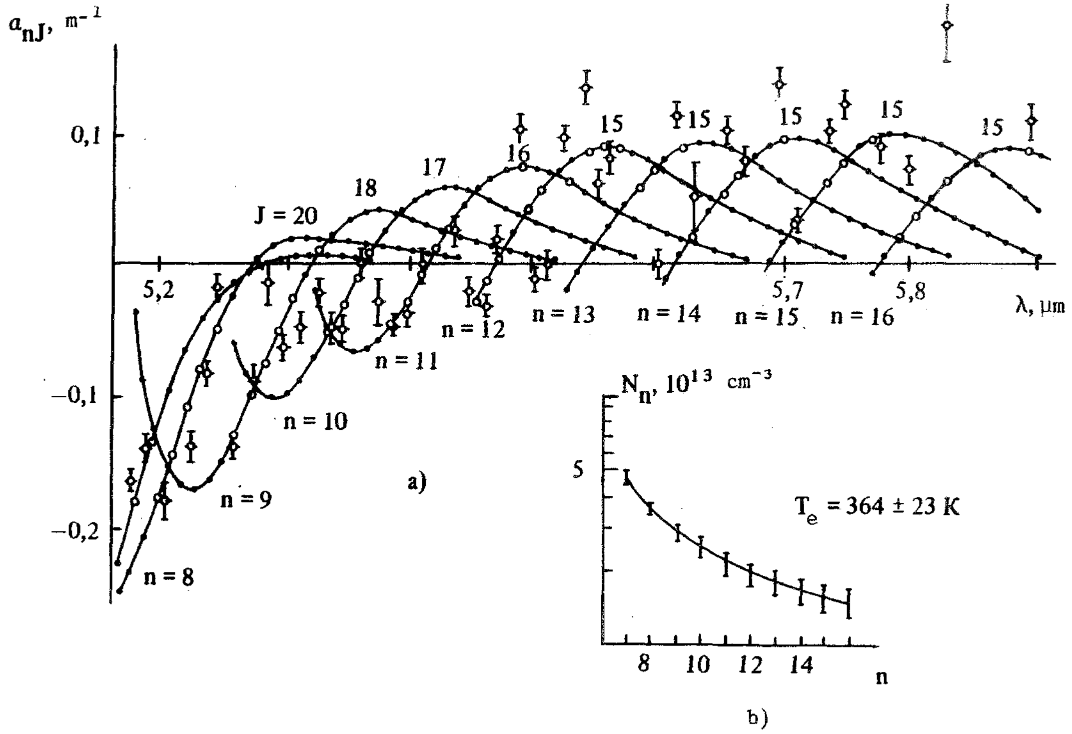

Fig. 3. Measured gain and absorption of an electric-discharge CO laser: a) measured a_{nJ} — circles with vertical and horizontal error bars; b) values of $N_n + \Delta N_n$ obtained by reducing a_{nJ}^{exp}.

Thus, for a minimum of r(T, $\boldsymbol{a}$) to exist, and hence to be able to use the proposed procedure, it suffices to have the absolute accuracy of the gain measurement within the vibrational band not higher than half the square root of their variance. (Although the use of the term "variance" is not at all correct here, since the values a_{0j} describe different physical quantities — the gains at different vibrational—rotational transitions - the structure of the resultant expression is characteristic enough to justify the use of this term).

Computations show that the upper bound defined by (11) is overestimated by 1.5-2 times, owing to the simplifying assumptions made, and that although this indeed a rough estimate, the range of permissible values of Δ is not very large and agree with the relative 5-7% accuracy of the measured a_{nJ}^{exp} (for the maximum values of a_{nJ} within the vibrational band).

The estimate (11) ensures the existence of a minimum of the r(T, $\boldsymbol{a}$) curve, but says nothing about the accuracy with which the temperature is determined from this curve. Returning to Fig. 1, we note that the values of T_L and T_R are natural estimates of the lower and upper bounds of T. It can be shown that T_L and T_R are the exact lower and upper bounds of all possible minima of the r(T, $\boldsymbol{a}_0 + \Delta\boldsymbol{a}$) curves, and the errors $\Delta\boldsymbol{a}_{L(R)}$ can have distributions such that the minima are reached at the points T_L and T_R. (In other words, for any T_* for which $T_L \le T_* \le T_R$, there exists an error distribution such that $\Delta\boldsymbol{a}_*: \|\Delta\boldsymbol{a}_*\| \le \Delta\sqrt{m}$ is realized at the point T_*.)

Clearly, the actual accuracies will depend on the numbers and dispositions of the proble lines within the vibrational bands, on the gain measurement accuracy, and also on the spectral distribution of a_{nJ}. The possible accuracy with which the gas parameters determined must therefore be analyzed for specific systems for which the gain distribution can be estimated, at least roughly. For the medium in an electric-discharge CO laser such an analysis was carried out in [2]. It was shown that when approximately 8-10 probe lines are used and the gain is determined accurate to ~5% one can expect T to be determined with accuracy not worse than 20%.

2. USE OF METHOD

A. Active Media of Electric-Discharge Lasers

To investigate the active media of gas-discharge lasers and to check on the functionality of the described method, we used the electric-discharge tubes of the regular-production ILGN-706 (CO) and GL-509 (CO_2) lasers. Both tubes are identical

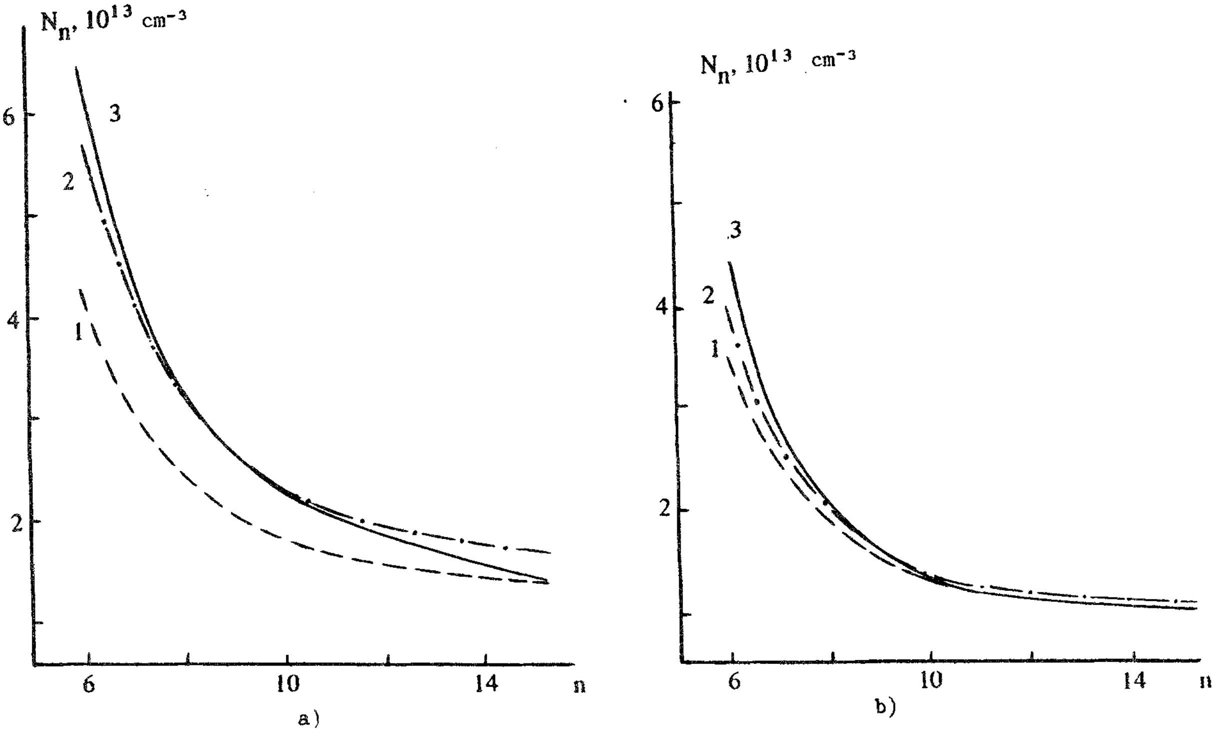

Fig. 4. Distribution of the vibrational populations of the CO molecule. 1) 10 mA, 17.5 kV; 2) 20 mA, 10 kV; 3) 30 mA, 8 kV; $\Delta N_n \approx 0.5 \cdot 10^{13}$ cm^{-3}. a) T_0 = 293 K, T_e = 410 ± 30 K; b) T_0 = 267 K, T_e = 364 ± 23 K.

in structure and consist of a central tube 15 mm in diameter and 150 mm long, surrounded by a cooling jacket with stubs connecting it to the reserve volume. The ends of the tubes are closed by gallium-arsenide windows making a Brewster angle with the tube axis.

The probing lasers generated on ~50 individual P-mode vibrational–rotational lines of the CO molecules at wavelengths 5.2-6.1 μm (CO laser) and on ~40 P- and R-mode lines of CO_2 at wavelengths 9.2-9.7 and 10.2-10.8 μm (CO_2 laser). The high amplitude stability (better than 1%) permitted measurements to be made without a reference signal.

The measured gain/absorption indices for the CO–Xe–N_2–He (17:30:43:290) mixture at a cooling temperature 267 K are marked in Fig. 3a by circles with vertical and horizonal error bars (for a_{nJ} and the wavelength, respectively). It can be seen that a CO laser with such a mixture can operate at wavelengths ≥5.3 μm.

The use of the reduction method described in the first part made it possible to determine the populations of the vibrational levels N_n of the CO molecule and the experimental temperature T_e of the gas mixture (shown in Fig. 3b). The value of T_e agrees within the limits of error with the gas temperature measured by probe methods and with the calculated estimates of this value. The solid curves in Fig. 3a show the distribution of the gains, calculated from these T_e and N_n. The circles on the solid curves mark the positions of the probe lines, n is the vibrational quantum number, and the points on the curves are tagged by the rotational quantum numbers. It can be seen that in general the gains calculated in this manner describe correctly the variation of the experimental values.

Figure 4 shows the distributions, obtained in similar fashion, of the CO molecules over the vibrational levels for two cooling-liquid temperature and three values of the discharge current, obtained in similar fashion. It can be seen that at a cooling temperature 267 K the populations are somewhat smaller than at 293 K, although the measured gains are approximately equal. In addition, the errors of the population curves in Fig. 4b and the curves for 10 and 30 mA in Fig. 4a coincide, meaning that the measured a_{nJ} are not accurate enough for the investigation of effects such as the influence of the discharge current on the population of the vibrational levels, even though this accuracy is sufficient to show that the gas temperature on the tube axis is different and is about 100° higher than the coolant temperature.

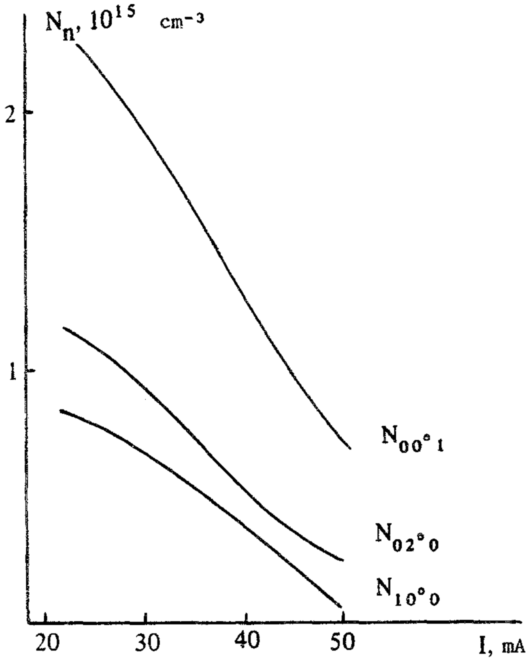

Fig. 5. Dependences of the CO_2 vibrational-level population on the discharge current.

The gains in a CO_2—Xe—air—He (25:30:40:135) mixture were similarly measured at a cooling-liquid temperature 291 and at discharge currents 20, 30, 40, and 50 mA. Reduction of the measurement results yielded $T_e = 440 + 30$ K, which depended little on the discharge current. The populations of the levels $00^{0}1$, $02^{0}0$ and $10^{0}0$ as functions of the discharge current are shown in Fig. 5.

B. Active Media of CO Gasdynamic and Chemical-Gasdynamic Lasers.

The use of a electric-discharge probing laser to investigate the gas parameters of CO gasdynamic lasers (GDL) and CO chemical-gasdynamic lasers (CGDL) introduces, in addition to the above measurement-accuracy problems, complications due to the possible disparity of the probe-laser wavelength region and the region of nonzero gain of the probed medium. Let us consider, for example, the operation of a CO GDL.

Operation of this system requires large degrees of expansion ($\geq$150), so that the translational temperatures in the cavity region are low. This shifts the spectral distribution of the gains into the region of small J. The calculated distributions of a_{nJ} for this case are shown in Fig. 6. (The calculation was performed by a procedure given in [15]. The temperature at the entrance to the nozzle was 2000 K, the pressure 100 atm, the CO-molecule fraction 0.133, and the nozzle expansion factor 280. The calculated gas temperature and pressure in the cavity region were 49 K and 4.4 torr, respectively.)

It is seen from the figure that the maximum values of a_{nJ} occur at $n = 5$, $J = 6$ ($\lambda \simeq 4.963$ μm). Analysis of the lasing lines of the probing electric-discharge CO laser shows that only ten out of almost fifty of its lines can be used for diagnostics (the selection criterion was $a_{nJ} \geq 0.1$ m^{-1}).

The gains corresponding to these lines are marked in Fig. 6 by circles. It can be seen that the probe-line locations are not most favorable, and that diagnostics of the gas yields the gas temperatures and the populations of levels 7, 8, 9, and 10. In view of the low pressure, the line overlap can be disregarded here. Results of modeling the temperature-accuracy problem are shown in Fig. 7.

Solution of this problem has shown that nonnegative populations are realized in the narrow temperature interval from 30 to 60 K. The values of Δ that take T out of this interval were taken therefore to be its limits, as reflected in Fig. 7 by the horizontal lines at $\approx$22 and 39% for the left- and right-hand limits, respectively. It can be seen from the figure that for $\Delta \approx 0.02$ m^{-1} one can expect to determine the temperature with accuracy $\approx$20%, which is quite low when the value of the temperature itself is considered.

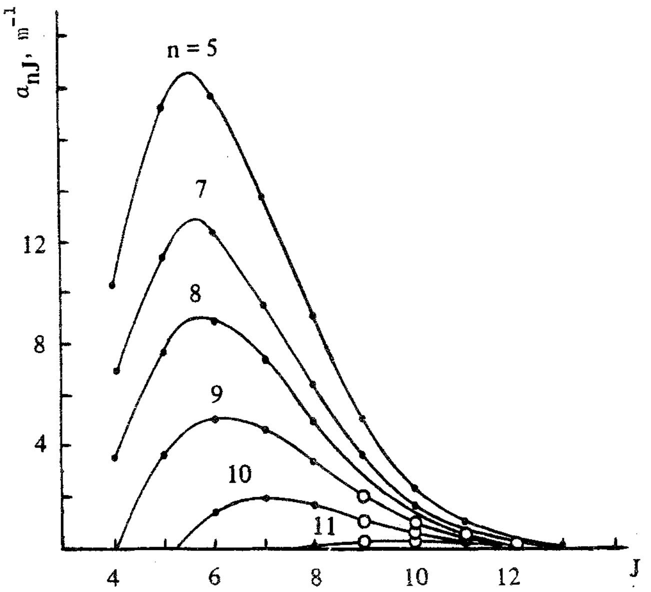

Fig. 6. Distribution of the gains with respect to the rotational quantum numbers for a CO GDL.

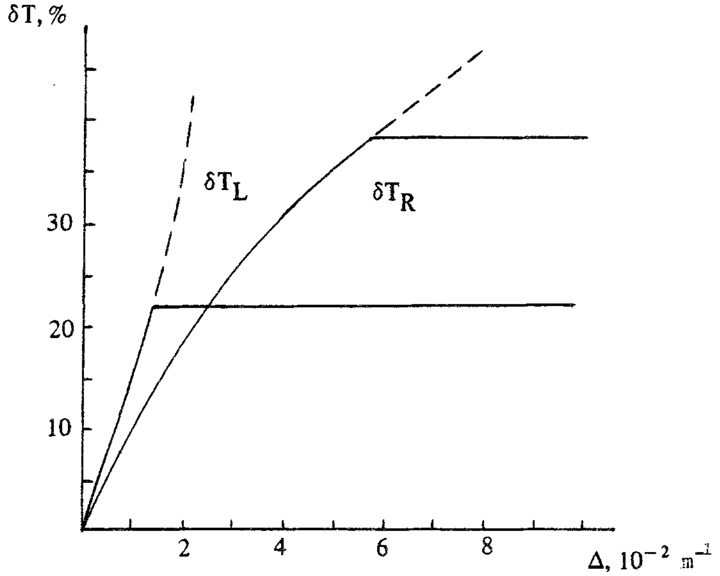

Fig. 7. Accuracy of the determined temperature in a CO GDL as a function of the gain-measurement accuracy, using eight probing lines: (n, J) = (8, 11), (8,12), (9, 9), (9, 10), (9, 11), (10, 9), (10, 10), and (10, 11).

We examine similarly the probing of the active medium of a CO CGDL. The calculated values of the populations, temperature, pressure, and CO concentration were taken from [4] ($T = 365$ K, $p = 38.3$ torr, $CO_2 = 0.004$). The distribution of the gains is shown in Fig. 8, where the circles mark transitions that can be used for probing. In our case the probing lines of the electric-discharge laser are much more favorably placed relative to the spectral-distribution contours. One can expect therefore to determine with high accuracy the temperature and the vibrational populations N_n with n from 6 to 14.

It is seen from Fig. 9 that to measure in this case the translational temperature with accuracy not worse than 5-10% it suffices to measure the gain for three lines within one vibrational–rotational band. The measurement accuracy need not be high, 0.01-0.03 m^{-1} (curves 3), but to this end it is necessary to choose correctly the positions of the probe lines, otherwise the accuracy is much worse (curves 1 and 2). Since curves 3 and 4 practically coincide it is useless, if only the temperature is determined by the indicated method, to increase the number of probe lines (from three to six in this case). This increase does

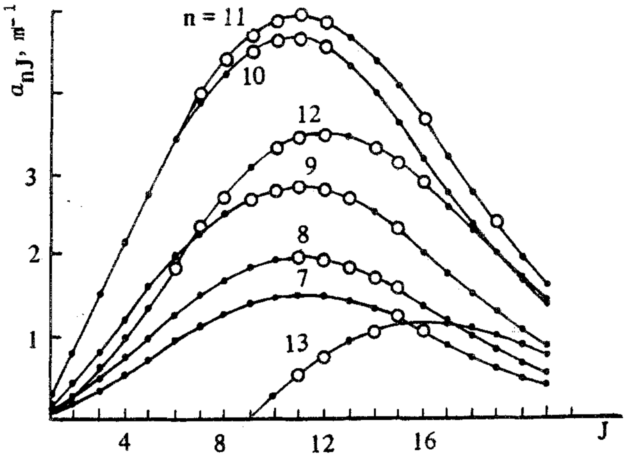

Fig. 8. Distribution of gains with respect to the rotational quantum numbers for CO CGDL.

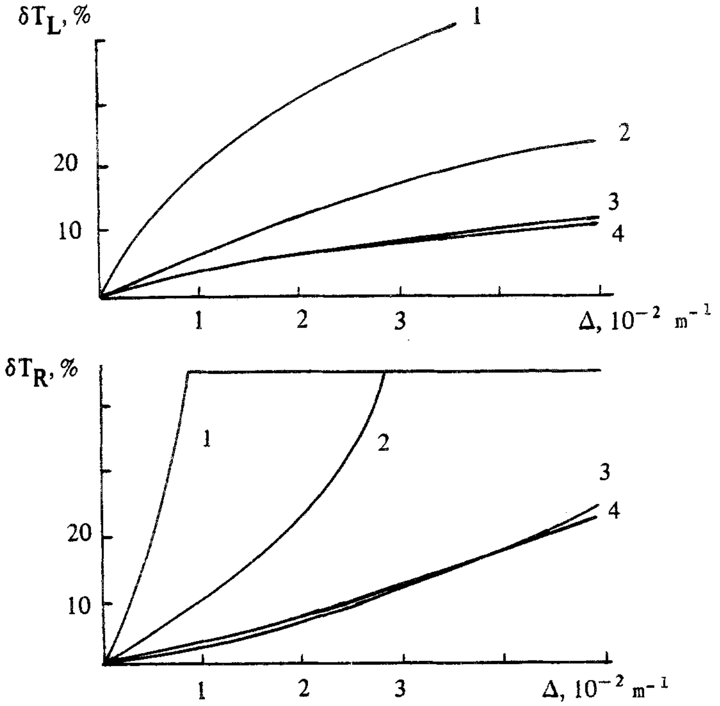

Fig. 9. Accuracy of determined CO CGDL temperature vs the accuracy of the gain measurements using various probing lines: 1) n = 11, J = 10, 11, 12; 2) n = 11; J = 9, 11, 13; 3) n = 11, J = 9, 11, 16; 4) n = 10, J = 9, 11, 16, n = 11, J = 9, 11, 16.

not improve the accuracy, but doubles the measurement time. (If the populations must also be measured, it is naturally necessary to use all the available values of n).

C. Measurement of Parameters of Gaseous Media Containing CO_2 Molecules

The use of the proposed procedure to determine the parameters of gaseous media containing CO_2 molecules has a number of distinctive features connected with the specific conditions under which the measurements are made. Of greatest interest at present are contactless measurements of equilibrium media (atmosphere, engines, combustion products, probing of high-pressure chambers) and nonequilibrium media (active media of CO_2-molecule gas lasers). For a medium in full equilibrium (with mode temperatures equal to the gas temperature), at room temperature, the population of the 00^01 level differs

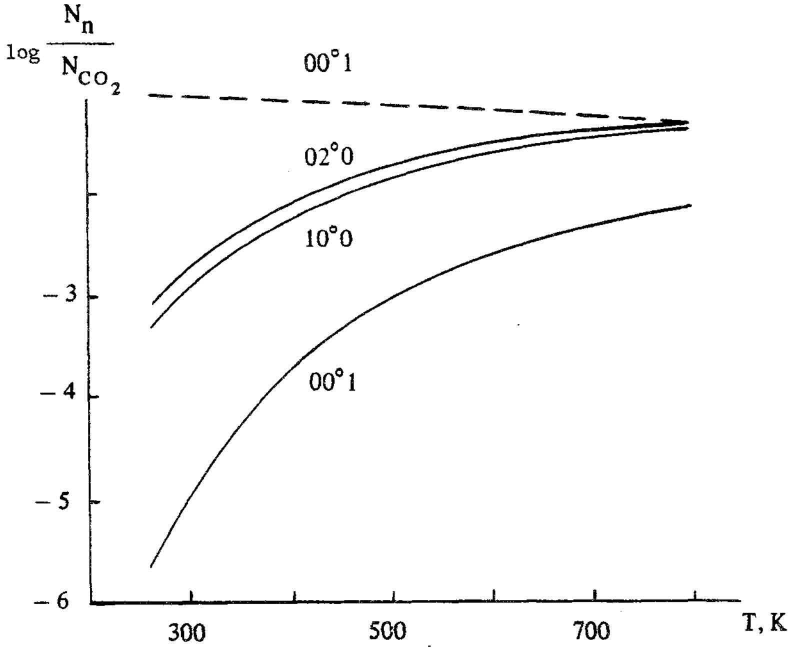

Fig. 10. Temperature dependence of the relative populations of vibrational levels. Dashed line — T_3 = 1500, $T_2 = T_1 = T$; solid lines — complete equilibrium $T_3 = T_2 = T_1 = T$).

from those of the 10^00 and 02^00 levels by two orders. The absorption index given by Eq. (1) is in this case a linear combination of functions φ_1 and φ_2 (which are approximately equal in value for fixed J), with coefficients (populations of the levels $N_{00^\circ 1}$, $N_{10^\circ 0}$, and $N_{02^\circ 0}$) whose values differ by a factor of 100. Clearly, $N_{00^\circ 1}$ can then be reliably determined only if the absorption is measured with accuracy not worse than 1%. Otherwise only the population of the lower level ($N_{10^\circ 0}$ and/or $N_{02^\circ 0}$) and the temperature can be determined. When the temperature is raised to ~1000 K the population difference becomes smaller (Fig. 10).

As the temperature is raised, however, line overlap comes into play (especially at pressures on the order of atmospheric or higher), and it is necessary either to take into account the contribution of the higher levels whose spectral characteristics (e.g., collision broadening) are not sufficiently well known at present, or else choose practically nonoverlapping lines for the probing (see e.g. [10, pp. 56-59]).

The full-equilibrium conditions make it possible to determine the $N_{00^\circ 1}$ population also when the measurement accuracy is insufficient for this direct determination by the proposed procedure. Indeed, if T and $N_{10^\circ 0}$ are determined with sufficient accuracy, then $N_{00^\circ 1}$ can be determined from the relation

$$N_{00^\circ 1} = N_{10^\circ 0} \exp(-1382{,}6/T).$$

It was assumed in the problems considered above that the partial pressures of the gases in the mixture. Frequently, however, it is necessary to determine the concentration of a small admixture of CO_2 in a gas whose composition is known (the CO_2 concentration in air, in the combustion products of gases containing mainly N_2 and O_2). Some modification of the proposed procedure allows this problem to be solved.

Indeed, if the ratio of the main components of the gas (N_2, O_2, CO, etc.) and the pressure p are known, and it is necessary to determine only the temperature and the concentration of a small but unknown CO_2 impurity in the gas, we can use the fact that the Voigt-function parameter (more accurately, the Lorentz width of the line) depends little on the CO_2 concentration. The problem can then be solved by iteration: the Voigt-function parameter is initially calculated by assuming zero CO_2 concentration, calculating T and $N_{10^\circ 0}$ (or $N_{02^\circ 0}$) by the described procedure and then, taking the equilibrium of the medium into account, calculate the first approximation of the concentration ξ'_{CO_2} using

$$\xi'_{CO_2} = N_{10^\circ 0}\, kT \exp(1997{,}3/T)/(Q_V^{-1} p),$$

where Q_v^{-1} is the partition function. The iteration cycle is then repeated with this value of ξ'_{CO_2} (redefining the concentration ξ_{x_i} in Eq. (2) by using the relations

$$\xi'_{x_i} = (1 - \xi'_{CO_2})\xi_{x_i}, \quad i = 1, \ldots, n$$

where ξ_{x_i} stands the concentration of the gas components (N_2, O_2, CO, etc., with the exception of CO_2, assumed to be specified, and $\sum_{j=1}^{n} \xi_{x_i} = 1$) calculating a new value of ξ'_{CO_2}, etc.

Clearly, at small values of ξ_{CO_2} the Voigt-function parameter changes insignificantly, so that ξ_{CO_2} is obtained after a few iterations. The accuracy of ξ_{CO_2} is determined mainly by the accuracy with which the temperature is determined from the measured absorption, or only by the accuracy of the absorption index if the temperature is known.

CONCLUSION

The method developed for reducing the measured gain or absorption by multifrequency laser probing is closely related to the analysis of time-dependent series, and to the theory of nonlinear spectral analysis [16]. Modern methods of this theory (particularly the maximum-entropy and maximum-likelihood methods) are widely used in radar, seismology, sonar, or to determine the motion of the earth's poles. The approach developed above permits effective utilization of multifrequency laser probing in laser-media diagnostics and in the investigation of kinetic phenomena. The method was used in practice to determine the parameters of specific gaseous media containing CO and CO_2 molecules (temperature, concentration and populations of vibrational levels). It was tested by solving model problems. Recommendations were developed for diagnostics of equilibrium and nonequilibrium gaseous media containing CO and CO_2 molecules. Requirements were stipulated for the probing system and for the required accuracy with which anJ must be measured to determine the parameters of gaseous media.

The method was used to obtain the experimental distributions of a_{nJ} of active CO and CO_2 media in gas-discharge, gasdynamic, and chemical lasers.

Our results allow us to recommend the method for extensive use in the reduction of data obtained by indirect measurements in physical experiments, especially in problems involving environment control.

LITERATURE CITED

1. W. Demptröder, Laser Spectroscopy, Springer, N.Y. (1981).
2. N. M. Vyazovetskii, A. I. Didyukov, V. Yu. Kirko, Yu. A. Kulagin, and L. A. Shelepin, "Determination of the parameters of gaseous media from measurements of the spectral distribution of the gains," FIAN Preprint No. 221, Moscow (1988).
3. A. N. Tikhonov and V. Ya. Arsenin, Methods of Solving Ill-Posed Problems [in Russian], Nauka, Moscow (1974).
4. V. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kinetic Processes in Gases, and Molecular Lasers [in Russian], Nauka, Moscow (1980).
5. A. W. Mantz, J.-P. Maillard, Won B. Roth, and K. N. Rao, "Ground state molecular constant of $^{12}C^{16}O$," J. Mol. Spectrosc., **57**, 155-159 (1975).
6. L. S. Rothman and L. D. G. Young, "Infrared energy levels and intensities of carbon dioxide. II," JQSRT, **25**, 505-524 (1981).
7. Yu. V. Konev, I. V. Mochetov, V. G. Pevgov, and V. F. Sharkov, "Analysis of kinetic processes that determine the parameters of CO lasers," Preprint No. 2821, Atomic Energy Inst., Moscow (1977).
8. V. V. Nevdakh, "Spontaneous emission probabilities and collisional line widths of $00^01 \rightarrow [10^00, 02^00]_{I,II}$ lasing transitions in the CO_2 molecule," Kvantovaya Élektron. (Moscow), **11**, No. 8, 1622-1627 (1984).
9. V. P. Kuprya, "Calculation of the values Voigt function at the line center," Opt. Spektrosk., **55**, No. 6, 1113-1114 (1983).
10. O. V. Achasov, N. N. Kudryavtsev, S. S. Novikov, R. I. Soloukhin, and N. A. Fomin, Diagnostics of Nonequilibrium States in Molecular Lasers [in Russian], Nauka i Tekhnika, Minsk (1985).
11. A. M. Robinson and N. Sutton, "High temperature absorption in the 10.4-μm band of CO_2," Appl. Opt., **18**, No. 3, 379-385 (1979).
12. G. C. Forsythe, M. A. Malcolm, and C. B. Moler, Computer Methods for Mathematical Computations, Prentice-Hall, Englewood Cliffs, N.J. (1977).
13. G. N. Wolkinson and S. Rainsch, Handbook of Algorithms in ALGOL Language [Russian translation], Nauka, Moscow (1986).
14. C. L. Lawson and R. J. Hanson, Solving Least Squares Problems, Prentice-Hall, Englewood Cliffs, N.J. (1974).
15. A. I. Didyukov, V. Yu. Kirko, Yu. A. Kulagin, and L. A. Shelepin, in: Trudy FIAN, 144, 107-123, Moscow (1984).
16. S. Haykin (ed.), Nonlinear Methods in Special Analysis, Springer-Verlag, Berlin—Heidelberg—New York—Tokyo (1983).