LASER PATH GAS ANALYSIS OF THE ATMOSPHERE USING INFRARED DOUBLE-RESONANCE SPECTROSCOPY

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A new method is proposed for laser monitoring of the atmospheric pollution: path multicomponent molecular diagnostics using IR double-resonance saturated absorption spectroscopy. The essence of this method is preliminary excitation of a selected vibrational-rotational level of detected molecules and application of the procedure of differential absorption on an adjacent "hot" transition. With the help of the HITRAN−92 database, a search has been conducted for vibrational-rotational transitions suitable for the application of the proposed method to simple molecules. Formulas for the determination of concentrations of the detected molecules have been derived. Sensitivity of measurements by the proposed method has been estimated and a comparison with the traditional method of differential absorption has been made. Altitude and temporal dependences of the saturation intensity of the vibrational-rotational transition have been calculated. Saturation conditions on the path with consideration for the spatial orientation of a pumping beam and its initial focusing have been determined.

1. INTRODUCTION

The increase of accuracy, sensitivity, and selectivity of the methods for remote sensing of gas pollutants in the atmosphere is necessary for the development of ecological monitoring of the environment. Traditional methods of optical gas analysis,[1] based on the linear absorption of radiation, in some practical cases are inefficient. In particular, serious problems arise in quantitative analysis of a gas mixture when the absorption spectra of many components overlap: traditional methods of experimental data inversion are very sensitive to random measurement errors. This leads to the fatal decrease of accuracy in determining concentrations of examined gases.[2−5]

In some cases this problem can be solved using special smoothing procedures (for example, regularization methods[2,3]) and selecting molecular lines suitable for sensing by smooth tuning of spectrometer frequency.[4,5] However, when many absorption bands overlap (which is typical, for example, of heavily polluted air and exhausts of jet engines) these methods are inapplicable. Alternatives in these cases are new methods of laser gas analysis based on nonlinear and nonstationary optical effects (see, for example, Refs. 6−8).

One of the ideas promising for gas analysis is bench marking of levels, that is, preliminary selective radiation excitation of molecular energy states, has received widespread use in nonlinear spectroscopy.[9] This method permits to select optically the detected component from a complex gas mixture and to measure its concentration. The best known methods based on bench marking of levels are the methods of laser-induced fluorescence (LIF) and photoacoustic spectroscopy (PAS). However, their use for remote sensing of the atmosphere is limited by fast collisional deactivation (LIF) and necessity of taking samples (PAS).[1]

In the present paper a new variant of the path laser gas analysis of atmospheric components is proposed harnessing double IR-resonance. The method is based on preliminary laser excitation of selected vibrational-rotational states of detected molecules and using the differential absorption on an adjacent transition. This method essentially improves the potentialities of the path IR laser gas analysis, which is especially important for monitoring of pollutants having small concentrations in the real atmosphere and of gas flows having complex chemical composition.

2. IDEA OF THE METHOD

Let us consider the system of three sequential vibrational-rotational levels $|0> − |1> − |2>$ (cascade or Ξ configuration) coupled with double IR resonance and belonging to the detected molecules of the given type

(Fig. 1).   Let the spectral line of the transition $|0> - |1>$ be strongly overlapped by lines of other substances, which makes the use of the traditional method of differential absorption inefficient in this region. The line center of the adjacent transition of the examined molecules $|1> - |2>$, as a rule, is noticeably detuned from the frequency of the transition $|0> - |1>$ (for example, toward red spectral range on intramode transitions due to anharmonizm of vibrations). However, under standard conditions there is no sense to use the "hot" transition $|1> - |2>$ for sensing because of small equilibrium population of the level $|1>$. This situation changes for significant population of this level, which essentially intensifies the absorption line $|1> - |2>$ against the "parasitic" background of others molecular lines and continuum.   Table I gives the parameters of some vibrational-rotational transitions[10] suitable for implementation of this method in case of simple molecules.
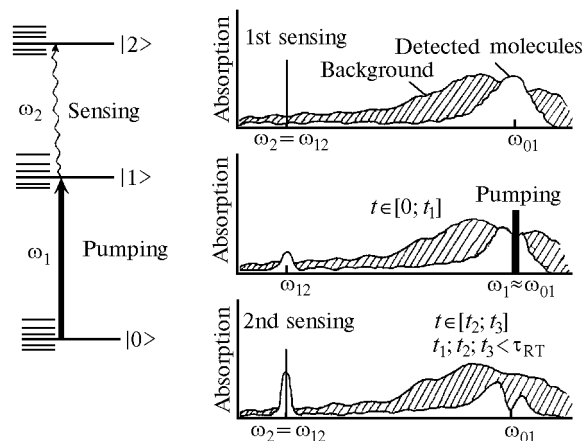

FIG. 1. Scheme of vibrational-rotational levels $|0> - |1> - |2>$ and sequence of measurements.

TABLE I. Parameters of some double vibrational-rotational resonances in simple molecules.[10]

Gas	ν, cm^{-1}	S, cm/mol	$|R|^2/g''$, D^2	γ_{air}, cm^{-1}·atm^{-1}	e'', cm^{-1}	$V'' \rightarrow V'$	$Q'' \rightarrow Q'$
O_3	1052.8484	$4.20 \cdot 10^{-20}$	$1.784 \cdot 10^{-2}$	0.7773	87.1499	$000 \rightarrow 001$	$14,0,14 \rightarrow 15,0,15$
–	1002.7370	$4.82 \cdot 10^{-22}$	$3.362 \cdot 10^{-2}$	0.0773	1139.99805	$001 \rightarrow 002$	$15,0,15 \rightarrow 14,0,14$
SO_2	530.2970	$7.08 \cdot 10^{-21}$	$1.056 \cdot 10^{-2}$	0.1520	129.0000	$000 \rightarrow 010$	$20,0,20 \rightarrow 21,1,21$
–	2478.7377	$5.79 \cdot 10^{-23}$	$2.143 \cdot 10^{-4}$	0.1520	659.2490	$010 \rightarrow 111$	$21,1,21 \rightarrow 20,1,20$
NO_2	758.85188	$1.08 \cdot 10^{-21}$	$8.533 \cdot 10^{-4}$	0.0670	88.5195	$000 \rightarrow 010$	$14,0,14^+ \rightarrow 14,1,13,+$
–	1617.4120	$3.26 \cdot 10^{-21}$	$4.713 \cdot 10^{-2}$	0.0670	847.3729	$010 \rightarrow 011$	$14,1,13^+ \rightarrow 15,1,14,+$
N_2O	2236.2235	$1.00 \cdot 10^{-18}$	$3.17 \cdot 10^{-2}$	0.0768	100.5525	$00^00 \rightarrow 00^01$	R(15)E
–	2206.6880	$2.27 \cdot 10^{-23}$	$3.588 \cdot 10^{-2}$	0.0762	2336.7759	$00^01 \rightarrow 00^02$	R(16)E
NO	1903.1231	$6.04 \cdot 10^{-20}$	$9.085 \cdot 10^{-3}$	0.0602	105.2920	$X\frac{1}{2},0 \rightarrow X\frac{1}{2},1$	R(7.5)e
–	1903.1338	$6.04 \cdot 10^{-20}$	$9.089 \cdot 10^{-3}$	0.0602	105.3850	$X\frac{1}{2},0 \rightarrow X\frac{1}{2},1$	R(7.5)f
–	1877.7256	$1.42 \cdot 10^{-23}$	$2.004 \cdot 10^{-2}$	0.0580	2008.5070	$X\frac{1}{2},1 \rightarrow X\frac{1}{2},2$	R(8.5)E
–	1877.7360	$1.42 \cdot 10^{-23}$	$2.005 \cdot 10^{-2}$	0.0580	2008.6100	$X\frac{1}{2},1 \rightarrow X\frac{1}{2},2$	R(8.5)F
CO	2172.7588	$4.64 \cdot 10^{-19}$	$6.280 \cdot 10^{-3}$	0.0599	107.6423	$0 \rightarrow 1$	R(7)
–	2149.4885	$2.67 \cdot 10^{-23}$	$1.254 \cdot 10^{-2}$	0.0598	2280.40234	$1 \rightarrow 2$	R(8)
HCl	2944.9138	$5.03 \cdot 10^{-19}$	$2.952 \cdot 10^{-3}$	0.0718	62.6219	$0 \rightarrow 1$	R(2)
–	2856.9330	$7.49 \cdot 10^{-25}$	$5.323 \cdot 10^{-3}$	0.0624	3007.4853	$1 \rightarrow 2$	R(3)

N o t e . Only basic isotopomers of molecules are given. The lower transition is selected for reasons of its maximum integral intensity in the corresponding vibrational-rotational band. Here, ν is the transition center, S is the integral intensity, R is the matrix element of dipole moment of transition, g'' is the statistical weight of the lower level, γ_{air} is the collisional halfwidth of line in the air, e'' is the total energy of the lower level, and V, Q are the vibrational and rotational quantum numbers of transition.

Measurements consist of three stages (see Fig. 1). The path of length L in the atmosphere is sensed at first on the frequency $\omega_1 = \omega_{12}$ to obtain the equilibrium transmission $\tau(\omega_2, L)$. As a rule, the main contribution to this quantity comes from the background absorption − resonant and nonresonant absorption of radiation by molecules of H_2O, CO_2, and others and from the aerosol absorption. After that

sufficiently intense laser pulse at the frequency $\omega_1 \approx \omega_{01}$ excites the vibrational-rotational transition $|0> - |1>$; in so doing, the population inversion is created on the level $|1>$ (in general, on inhomogeneous path).

For high degree of saturation, the population of the level $|1>$ is approximately equal to half the equilibrium population of the ground level $|0>$. After excitation of the detected molecules, the transition

$|1\rangle - |2\rangle$ is sensed once more at the same frequency $\omega_1 = \omega_{12}$. As a result, the nonequilibrium transmission $\tau(\omega_2, L)$ is determined. A time delay between exciting and sensing pulses should be less than the characteristic collisional relaxation time of population of the level $|1\rangle$. Repeated sensing of the transition $|1\rangle - |2\rangle$ at the frequency ω_2 can be performed in the process of saturation of the transition $|1\rangle - |2\rangle$ given that this process has already proceeded in the stationary regime.

The essence (and necessary requirement) of the suggested approach is that the pumping radiation changes the absorption spectrum of only one (detected) component of the mixture near ω_2, but the absorption of other components remains unchanged. This circumstance permits us to cut off the undesirable background by the differential absorption method: the ratio of the values of transmission τ/τ_0 depends only on the nonequilibrium population of the level $|1\rangle$. As shown below, this population can be calculated and related with the concentration of the detected molecules under certain conditions.

3. BASIC EQUATIONS

Because several vibrational-rotational transitions $|0\rangle - |1\rangle$ with close frequencies may interact with the high-power laser radiation, the excitation stage should be modeled with consideration for this peculiarity. Population kinetics of the ith pair of vibrational-rotational levels $|0\rangle$ and $|1\rangle$ in the pumping radiation field will be described by the following equations[11] (implying that the pumping pulse duration is larger than the phase and vibrational relaxation times of the examined levels):

$$\frac{dn_0^i}{dt} = - W_{01}^i n_0^i + W_{10}^i n_1^i + \frac{1}{\tau_{R_0}} (N_0 q_{R_0}^i - n_0^i),$$

$$\frac{dn_1^i}{dt} = W_{01}^i n_0^i - W_{10}^i n_1^i + \frac{1}{\tau_{R_1}} (N_1 q_{R_1}^i - n_1^i), \qquad (1)$$

$$W_{10}^i = \frac{g_0^i}{g_1^i} W_{01}^i, \quad W_{01}^i = \frac{\sigma_{01}^i(\omega_1, z)\, I(z, t)}{\hbar \omega_{01}^i},$$

$$\sigma_{01}^i(\omega_1, z) = \frac{g_1^i}{g_0^i} \frac{c^2\, \pi^2\, A_{10}^i}{(\omega_{01}^i)^2} G(\omega_1 - \omega_{01}^i),$$

$$q_{R_0}^i = g_0^i \exp(- E_{R_0}^i / k_B\, T) / Q_R(T),$$

$$q_{R_1}^i = g_1^i \exp(- E_{R_1}^i / k_B\, T) / Q_R(T),$$

where W_{01}^i and $\sigma_{01}^i(\omega_1, z)$ are the probability of the induced vibrational-rotational transition $|0\rangle - |1\rangle$ per unit time and the corresponding absorption cross section at the point of the path with coordinate z; g_0^i, g_1^i, τ_{R_0}, τ_{R_1}, $e_{R_0}^i$, $e_{R_1}^i$, $q_{R_0}^i$, and $q_{R_1}^i$ are the statistical weights, characteristic times of rotational (rotational-translational) relaxation, energies, and relative

populations of rotational sublevels $|0\rangle$ and $|1\rangle$; A_{10}^i is the first Einstein coefficient of the vibrational-rotational transition $|0\rangle - |1\rangle$; $T(z)$ is the air temperature distribution over the path; $Q_R(T)$ is the rotational statistical sum; N_0 and N_1 are the current populations of the vibrational states $|0\rangle$ and $|1\rangle$ (summed over all rotational sublevels); $G(\omega_1 - \omega_{01}^i)$ is the spectral profile of the absorption line $|0\rangle - |1\rangle$ normalized by unity; c is the light velocity; k_B is the Boltsmann constant; $\hbar = h / 2\pi$ is the Planck constant.

Populations of the vibrational levels are described by the following equations for the closed two-level system:

$$\frac{dN_0}{dt} = - W_{01} N_0 + W_{10} N_1 + \frac{1}{\tau_{VT}} (N_0^e - N_0), \qquad (2)$$

$$\frac{dN_1}{dt} = W_{01} N_0 - W_{10} N_1 + \frac{1}{\tau_{VT}} (N_1^e - N_1),$$

$$N_0 + N_1 = N_0^e + N_1^e = N = \text{const},$$
$$N_0(t = 0) = N_0^e, \quad N_1(t = 0) = N_1^e,$$

where W_{01} and W_{10} are the probabilities of induced emission and absorption on the vibrational transition $|0\rangle - |1\rangle$ per unit time, τ_{VT} is the characteristic time of vibrational-translation relaxation, N_0^e and N_1^e are the equilibrium populations.

In the quasistationary approximation $dn_0^i / dt = = dn_1^i / dt = 0$ at $\tau_{R_0} \approx \tau_{R_1} = \tau_R$ the probabilities W_{01} and W_{10} have the form[12]

$$W_{01} = \sum_i \frac{q_{R_0}^i\, W_{01}^i}{1 + (W_{01}^i + W_{10}^i)\, \tau_R},$$

$$W_{10} = \sum_i \frac{q_{R_1}^i\, W_{10}^i}{1 + (W_{01}^i + W_{10}^i)\, \tau_R}.$$

The summation is done over all vibrational-rotational transitions interacting with the pumping radiation. The population of the vibrational level $|1\rangle$ is described by the linear inhomogeneous equation

$$\frac{dN_1}{dt} + (W_{01} + W_{10} + \frac{1}{\tau_{VT}}) N_1 = \frac{N_1^e}{\tau_{VT}} + W_{01} N,$$

whose exact solution can be written as

$$N_1(t) = \exp\left[- \frac{t}{\tau_{VT}} - \Phi(t) \right] \times$$

$$\times \left\{ N_1^e + \int_0^t \left[\frac{N_1^e}{\tau_{VT}} + W_{01}(t) N \right] \exp\left[\frac{t}{\tau_{VT}} + \Phi(t) \right] dt \right\},$$

$$\Phi(t) = \int_0^t [W_{01}(t) + W_{10}(t)]\, dt. \qquad (3)$$

Quasistationary population of the ith vibrational-rotational level $|1\rangle$ after termination of the pumping pulse with duration t_p to the base is

$$n_1^i(z, t_p) = \frac{N_0\, q_{R_0}^i + N_1\, q_{R_1}^i\, (\eta^i + \tilde{\tau})}{\tilde{g}^i + \tilde{\tau} + \eta^i} =$$

$$= N(z)\, \varphi[z, t_p, I(z)], \qquad (4)$$

$$N(z) = \xi(z)\, p(z)\,/\,[k_B\, T(z)],$$

$$\varphi[z, t_p, I(z)] = \frac{q_{V_0}\, q_{R_0}^i + q_{V_1}\, q_{R_1}^i\, (\eta^i + \tilde{\tau})}{\tilde{g}^i + \tilde{\tau} + \eta^i}\,,$$

$$q_{V_0}(z) = \exp\left(-\,E_{V_0}/k_B\, T\right)/Q_V(T),$$

$$q_{V_1}(z) = \exp\left(-\,E_{V_1}/k_B\, T\right)/Q_V(T),$$

$$\eta^i = \frac{1}{W_{01}^i\, \tau_{R_1}}\,, \quad \tilde{\tau} = \tau_{R_0}/\tau_{R_1}\,, \quad \tilde{g}^i = g_0^i/g_1^i.$$

In the given formulas $p(z)$, $N(z)$, and $\xi(z)$ are the total pressure and the absolute and relative concentrations of the molecules of the detected gas; E_{V_0} is the vibrational energy of the level $|0\rangle$, and $Q_V(T)$ is the vibrational statistical sum.

Considering that the attenuation of the sensing radiation at ω_2 on the ith adjacent transition $|1\rangle - |2\rangle$ is described by Bouguer's law, to determine the concentration of the detected molecules we use the following formulas:

$$\ln\frac{\tau(\omega_2, L)}{\tau_0(\omega_2, L)} = -\int_0^L \sigma_{12}^i(\omega_2, z)\, n_1^i(z, t_p)\, dz, \qquad (5)$$

$$\sigma_{12}^i(\omega_2, z) = \frac{g_2^i}{g_1^i}\,\frac{c^2\,\pi^2\,A_{21}^i}{(\omega_{12}^i)^2}\, G(\omega_2 - \omega_{12}^i),$$

where $\sigma_{12}^i(\omega_2, z)$ is the absorption cross section, A_{21}^i is the first Einstein coefficient, and $G(\omega_2 - \omega_{12}^i)$ is the spectral profile of the absorption line. On the basis of Eqs. (3)–(5), given that the ratio τ/τ_0 and distributions $p(z)$, $T(z)$, and $I(z)$ along the path are known, we can obtain the average relative concentrations of the detected molecules on the path. The minimum detectable concentration in this method in general depends on the pumping intensity (degree of saturation of the transition $|0\rangle - |1\rangle$) and for $\xi(z) = \text{const}$ can be written as

$$\xi_{\min} = \frac{\min\left\{\ln\dfrac{\tau_0(\omega_2, L)}{\tau(\omega_2, L)}\right\}}{\max\left\{\displaystyle\int_0^L \dfrac{\sigma_{12}^i(\omega_2, z)\,\varphi(z, t_p, I)\, p(z)}{[k_B T(z)]}\, dz\right\}}\,. \qquad (6)$$

Let us consider the important limiting case of high degree of saturation at each point of the path, in which the formulas for the concentration do not depend on the pumping intensity. Assuming that $\eta^i \ll 1$ for $g_0^i \approx g_1^i$, $\tau_{R_0} \approx \tau_{R_1}$, and $N(z) \approx N_0(z) \gg N_1(z)$ we have

$$n_1^i(z, t_p) = n_1^s = \frac{N_0\, q_{R_0}^i + N_1\, q_{R_1}^i\, \tilde{\tau}}{\tilde{g}^i + \tilde{\tau}} \approx N q_{V_0}\, q_{R_0}^i/2.$$

In this case the sensitivity of the method is also maximum because $\varphi = \varphi_{\max} = q_{V_0} q_{R_0}^i/2$. In Table II the results are given of calculations of the minimum detectable concentration of ozone n_3^{16} by the proposed method ($\xi_{\min}^{\text{new}}$, Eq. (6)). For comparison, the data are presented calculated by the traditional method of differential absorption on the lower transition $|0\rangle - |1\rangle$ ($\xi_{\min}^{\text{trad}}$). The parameters of transitions were borrowed from Table I. The values of $\xi_{\min}^{\text{trad}}$ were calculated by the same formula (6) with substitutions $\tau \to \tau_{\text{on}}$, $\tau_0 \to \tau_{\text{of}}$, $\sigma_{12}^i n_1^i \to \sigma_{01}^i n_0^i$ (the subscripts "on" and "of" correspond to the analytic and reference sensing frequencies in the classical method of differential absorption).

TABLE II. *Minimum detectable concentration (ppmV) of the ozone* n_3^{16} *by the proposed method ($\xi_{\min}^{\text{new}}$) and by the traditional method of differential absorption on the lower transition* $|0\rangle - |1\rangle$ *($\xi_{\min}^{\text{trad}}$).*

L, km	$\Delta\tau/\tau_0 = 0.01$		$\Delta\tau/\tau_0 = 0.5$	
	$\xi_{\min}^{\text{new}}$	$\xi_{\min}^{\text{trad}}$	$\xi_{\min}^{\text{new}}$	$\xi_{\min}^{\text{trad}}$
0.1	0.2432	0.2434	16.7728	16.1670
0.5	0.0486	0.0469	3.3546	3.2334
1	0.0243	0.0234	1.6773	1.6167
5	0.0049	0.0047	0.3555	0.3233
10	0.0024	0.0023	0.1677	0.1617

N o t e . Horizontal homogeneous path of length L and the Lorentz profile of the absorption line at $T = 296$ K and $\Delta\tau = \tau_0 - \tau$ were taken. The parameters of transitions were borrowed from Table I. The values ($\xi_{\min}^{\text{new}}$) correspond to the case of full saturation of the transition $|0\rangle - |1\rangle$ and ($\xi_{\min}^{\text{trad}}$) correspond to the case of absence of spectral lines of other components near the analytic and reference sensing frequencies.

For simplicity of calculations, the homogeneous horizontal path and the Lorentz profile of the absorption line were chosen. The parameter $\Delta\tau/\tau_0$ (where $\Delta\tau = \tau - \tau_0$) in the table characterizes the sensitivity of recording instrumentation to the transmission variation. As expected, $\xi_{\min}^{\text{new}} \approx \xi_{\min}^{\text{trad}}$, that is, the new method is highly competitive with the traditional one by its sensitivity. At the same time, its selectivity is much higher. We note that the values $\xi_{\min}^{\text{trad}}$ were obtained for the ideal case of absence of

absorption lines of other gas components in the ranges of analytic and reference sensing frequencies.

However, as an analysis on the basis of Ref. 10 has shown, in the range $1052.74–1053 \, cm^{-1}$ (near the center of the transition $|0>-|1>$ of n $_3^{16}$) there are 3 lines of SO_2, 2 lines of CO_2, and 2 lines of PH_3; moreover, the intensities of SO_2 and CO_2 lines increase with the increase of the temperature. For enhanced concentrations of SO_2 and CO_2 in a hot mixture (typical example is the jet of an engine) the problem of determination of O_3 concentration in this spectral range by the traditional differential absorption method will be ill-posed. The proposed method is free from this disadvantage, because the decrease of the transmission $\Delta\tau = \tau - \tau_0$ is caused by the selective excitation of the detected gas O_3.

It should be noted that complete saturation of the transition $|0>-|1>$ at each point of the path is difficult to achieve for long paths, because the pumping radiation intensity decreases as the radiation propagates along the path due to attenuation and divergence. To achieve saturation in these cases, special measures are required, for example, selection of the path geometry (if, of course, we have this opportunity) or initial focusing of the pumping beam.

4. ROLES OF THE PATH GEOMETRY AND FOCUSING OF THE PUMPING RADIATION

Influence of the initial path altitude and its zenith angle on saturation can be understand if we consider that the intensity of saturation of the transition $|0>-|1>$ depends on the pressure and temperature. From Eq. (1) or (4) we easily derive

$$I_S^i = \hbar \, \omega_{10}^i / [(1 + \tilde{g}^i) \, \sigma_{10}^i(\omega_1, z) \, \tau_R(z)]. \quad (7)$$

In the above formula the characteristic times of relaxation of levels $|0>$ and $|1>$ are assumed identical and equal to τ_R. The subscript i will be omitted further, and $\tilde{g}^i \approx 1$. The following dependences of τ_R and collisional halfwidth of the absorption line γ on the pressure and temperature are assumed:

$$\tau_R(z) = \tau_R^0 / p(z) \, [T^*/T(z)]^m,$$
$$\gamma(z) = \gamma^0 \, p(z) \, [T^*/T(z)]^n, \quad (8)$$

where T^* is the reference temperature (at which τ_R^0 and γ^0 are measured, usually $T^* = 296$ K), m and n are the exponents of temperature dependence of τ_R and γ (usually, $n = -m \approx 0.5$).

In the case of resonance $\omega_1 = \omega_{01}$ with the Lorentz line $|0>-|1>$ from Eqs. (7)–(8) we have

$$I_S(z) = I_{S0} \, p^2(z) / p_0^2 \, [T^*/T(z)]^{n-m},$$

$$I_{S0} = \frac{\hbar \, \omega_{01}^3 \, \gamma^0}{c \, A_{10} \, \tau_R^0} \, p_0^2 \left(\frac{T^*}{T_0}\right)^{n-m}, \quad (9)$$

where p_0, T_0, and I_{S0} are the pressure, temperature, and intensity of saturation of the transition $|0>-|1>$ at the initial point of the path ($z = 0$). Thus, in this case the saturation intensity of the transition decreases quadratically with the decrease of the pressure and increases as $\sim T^{-1}$ with the decrease of the temperature.

For the Voigt line profile the quantity I_S is more complex function of z

$$I_S(z) = \frac{\hbar \, \omega_{01}^3 \, \gamma^0}{\pi \, A_{10} \, G_{V0}(z)} \, p(z) \, [T^*/T(z)]^{0,5}, \quad (10)$$

owing to the fact that $G_{V0}(z)$ is the resonance value of the Voigt function (in centimeters) and depends on the pressure and temperature. Here and further we use the approximations $1/\tau_R \approx c\gamma$ and $n = -m \approx 0.5$. Dependences of I_S on the altitude in the atmosphere for the Lorentz (Eq. (9)) and Voigt (Eq. (16)) line profiles for different values of the broadening coefficient γ^0 are shown in Fig. 2. It can be seen that at altitudes up to ~ 20 km the saturation intensity decreases quadratically as the pressure decreases, which is caused by the Lorentz line shape.
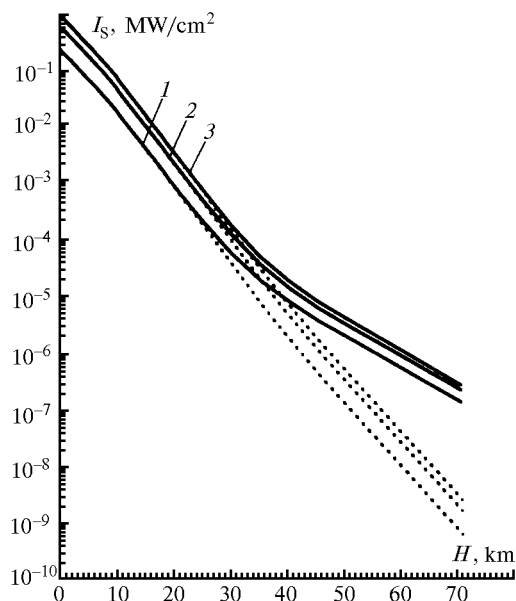

FIG. m Vertical profile of the intensity saturation I_S of vibrational-rotational transition for different collisional line widths γ^0 at $n \approx m = 0.5$ and middle-latitudinal winter model of the atmosphere: $A_{10} = 10 \, s^{-1}$, $\omega_{01}/2\pi c = 1000 \, cm^{-1}$, $\gamma^0 = 0.05$ (1), 0.08 (m), and $0.1 \, cm^{-1} \cdot atm^{-1}$ (3). Solid lines are for the Voigt line profile and dashed lines are for the Lorentz line profile. The Doppler width in the Voigt profile corresponds to the ozone molecule.

At high altitudes the saturation intensity is small and changes insignificantly as the altitude increases further. This is caused by the fact that the line profile becomes Doppler one. Because the Doppler line profile

does not depend on pressure, the above-indicated variations are caused by the temperature variations. In Fig. 3 the dependences of the saturation intensity of the vibrational-rotational transition on the temperature are shown for an altitude of 18 km and different values of the broadening coefficient. The curves illustrated by Fig. 3 were calculated for the jet of a supersound passenger aircraft (SPS−2).
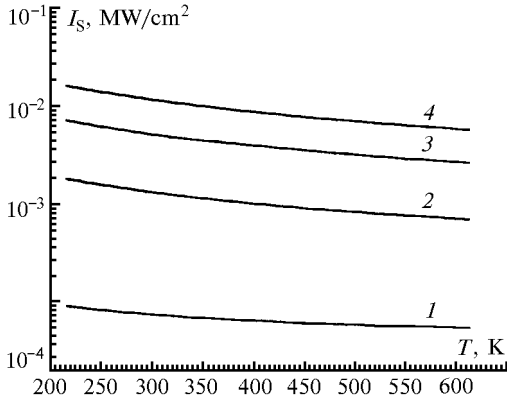

FIG. 3. Dependence of the saturation intensity of the vibrational-rotational transition on the temperature for different collisional widths $\gamma^0 = 0.01$ (1), 0.05 (m), 0.1 (3), and 0.15 cm^{-1}·atm^{-1} (4) . Middle-latitudinal winter model of the atmosphere at $m = 18$ km. Other parameters of calculation are the same as in Fig. 1.

The attenuation coefficient of radiation of the frequency ω_1 in general depends on I

$$\alpha(I) = \sum_{j,k} \alpha_{jk}(I) + \alpha_{ns}(I) < \sum_{j,k} \alpha_{jk}^0 + \alpha_{ns}^0 = \alpha^0,$$

where α_{ns} is the coefficient of nonselective attenuation, α_{jk} is the coefficient of selective attenuation for the jth line of the kth gas, α^0 is the linear (nonsaturated) coefficient. Summation is done over all lines of all the components absorbing radiation of frequency ω_1. However, in many cases of diagnostics of minor gas components in the atmosphere the pumping beam attenuation will be primarily caused by the background gases with small absorption cross sections and high concentrations (H_2O, CO_2, and N_2) and hence will be linear in a wide range of radiation intensities. Then, considering the attenuation, initial focusing, diffraction, and turbulent broadening of a single-mode Gaussian beam, for the axial pumping intensity distribution over the path we have[13]

$$I(z) = I_0 \exp\left[-\int_0^z \alpha^0(z)\, dz \right] \bigg/ B(z, \theta),$$

$$B(z, \theta) = (1 - z/F)^2 + \Omega^{-2}\left(1 + \frac{4}{3}\frac{a^2}{\rho_0^2}\right), \qquad (11)$$

$$\rho_0 = [1.45\, C_n^2(z = 0)\, k^2\, X(z, \theta)]^{-3/5},$$

where F is the initial curvature radius of the beam wavefront, $\Omega = k^2/z$ is the Fresnel parameter of laser aperture (k is the wave vector and a is the initial beam radius by the intensity); q_n^2 is the structural characteristic of the refractive index fluctuations, $u(z, \theta)$ is the equivalent distance.[14]

To achieve the complete saturation of the transition $|0> - |1>$ at each point of the path, the condition $I(z) \gg I_S(z)$ should be satisfied, where $I(z)$ and $I_S(z)$ are given by Eqs. (7)−(11). Let us simplify this inequality for limiting cases of nonresonant and resonant absorption of the Lorentz lines. We also assume that the temperature is constant but the air pressure in the atmosphere is described by the barometric formula

$$p(z) = \exp(-\beta\, z\, \cos\theta), \quad \beta \approx \mu g/(k_B T),$$
$$0 \le \theta \le \pi/2,$$

where μ is the average molecular mass of the air, g is the acceleration of gravity, and θ is the zenith angle of the path.

1. The main contribution to α_0 comes from wings of the Lorentz absorption lines of foreign gases. In this case

$$\alpha^0(z) = \alpha_0^0\, p^2(z)/p_0^2,$$

$$\alpha_0^0 = \frac{2\pi^2\, c^3\, p_0^2}{k_B T} = \sum_{j,k} \frac{A_{jk}\, \xi_k\, \gamma_{jk}^0}{\omega_{jk}^2\, (\omega_1 - \omega_{jk})^2},$$

where $\alpha_0^0 = \alpha^0$ ($z = 0$) is the absorption coefficient at the initial point of the path, ω_{jk}, A_{jk}, and γ_{jk}^0 are the frequency of the line center, the Einstein coefficient, and the coefficient of collisional broadening of the jth line of the kth gas, ξ_k is the relative content of the kth gas in the mixture (also considered independent of z). For the radiation intensity distribution along the path, we have

$$I(z) = \frac{I_0 \exp\left\{ -\dfrac{\alpha_0^0}{2\beta \cos\theta}[1 - \exp(-2\beta\, z\, \cos\theta)] \right\}}{B(z, \theta)}.$$

For $2\beta z \cos\theta \ll 1$ (nearly horizontal paths and initial sections of any paths), we obtain $I(z) = I_0 \exp(-\alpha_0^0 z)/B(z, \theta)$. When e. p$(-2\beta z \cos\theta) \ll 1$ (end sections of long nearly vertical paths), the distribution of the beam intensity along the path is determined solely by the function $B(z, \theta)$

$$I(z) = I_0 \exp\left\{ -\frac{\alpha_0^0}{2\beta \cos\theta} \right\} \bigg/ B(z, \theta) = \text{const}/B(z, \theta).$$

For saturation of the transition $|0>-|1>$ at each point of the path, the condition

$$I_{S0} \exp(-2\beta z \cos\theta) \ll$$

$$\ll \frac{I_0 \exp\left\{-\frac{\alpha_0^0}{2\beta \cos\theta}[1-\exp(-2\beta z \cos\theta)]\right\}}{B(z,\theta)}. \qquad (12)$$

should be satisfied. For $T \geq 200$ K, $\theta \geq 0$, and $z \leq 1$ km we have $2\beta z \cos\theta \leq 0.0348 \ll 1$; at $\theta \approx 0$ and $z \geq 70$ km the condition e. p $(-2\beta z \cos\theta) \leq 0.088 \ll 1$ is satisfied. Thus, in majority of practical cases (not too long slant paths) the decrease of the saturation intensity of the transition due to the pressure decrease with the increase of the altitude is insignificant.

2. The main contribution to α^0 comes from the resonant absorption of the Lorentz lines of foreign gases. In this situation the absorption coefficient does not depend on the pressure and therefore on z

$$\alpha(z) = \text{const} = \alpha_0^0 = \frac{c}{2k_B T} \sum_{j,k} \frac{A_{jk}\, \xi_k}{\gamma_{jk}^0}.$$

For saturated absorption of the transition $|0>-|1>$ at each point of the path the condition

$$I_{S0} = \exp(-2\beta z \cos\theta + \alpha_0^0 z) \ll I_0 / B(z,\theta). \qquad (13)$$

should be satisfied. As can be seen from inequalities (12)–(13), initial focusing of the pumping beam can be used to compensate for the attenuation and divergence when $z \leq F$ or to achieve the complete saturation of the transition $|0>-|1>$ of the detected molecules at the short section of the path near the beam waist $z \approx F$. This method is very efficient under conditions of localization of the examined gas in a relatively small volume (smoke plume, aircraft jet, and so on). It is well to bear in mind that the intensity in the region of waist cannot exceed $I_{\max} = I_0 / B_{\min} \approx I_0 / B(F, \theta)$.
In conclusion, we note that more detailed analysis require questions of the background absorption stability upon excitation of the detected molecules, optimal selection of the pumping and sensing frequencies, and correct description of the beam propagation under nonstandard atmospheric conditions (for example, in the aircraft jet).

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