

ON THE ACCURACY OF REMOTE SOUNDING OF CARBON MONOXIDE USING THE SECOND HARMONIC OF A TEA-CO₂ LASER RADIATION

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The effect of a finite width of a laser pulse radiation on the effective coefficient of differential absorption of CO is studied for the case of sounding by a long-path absorption technique with the use of the second harmonic TEA-CO₂ laser. It is shown that under laser mixture pressure ~ 1 atm the neglect of the effect of spectral averaging can result in the errors in determining the absorption coefficient and, hence, CO concentration of 10 to 100 %. Nontraditional method is proposed for processing data of sounding to eliminate these errors. The errors in determining the CO, which are caused by the sounding radiation line shift, are also estimated.

Use of the second-harmonic generation of a tunable CO₂-laser radiation for sounding carbon monoxide (CO) by a differential absorption method (DIAL) over long paths using a mirror reflector has been shown to be efficient many times.¹⁻⁴ The second-harmonic emission lines, first, 2*9R (18) (Refs. 1 and 2) and then 2*9P (24) (Refs. 3 and 4) coincident with the CO absorption lines of approximately equal intensities centered at 2154.596 and 2086.322 cm⁻¹, respectively, were used in experiments. The second harmonics on the adjacent lines 2*9R(16) and 2*9R(28) centered at 2151.976 and 2082.558 cm⁻¹, respectively, were chosen as reference frequencies of radiation.

Carbon monoxide concentration is determined from data of long-path absorption DIAL sounding measurements with a reflector by the known relation⁵

$$\rho[\text{ppm}] = \frac{1}{K [\text{cm}^{-1} \cdot \text{atm}^{-1}] z} \ln \frac{P_0(\nu_{on}) \eta_{on} P(\nu_{off}, z)}{P_0(\nu_{off}) \eta_{off} P(\nu_{on}, z)}, \quad (1)$$

where $K = K(\nu_{on}) - K(\nu_{off})$ is the CO differential absorption coefficient averaged over the path of the length z ; $P_0(\nu_i)$ is the power of radiation incident on the atmosphere at frequencies ν_i ; $P(\nu_i, z)$ is the recorded signal power at the exit from the atmospheric channel at frequencies ν_i ; $i = on$ or off (on and off an absorption line), η_{on} and η_{off} are the calibration constants of a laser system.

It is well known that if a mirror reflector is used in the measurement arrangement the requirements imposed on the laser transmitter output power are most weak. Therefore in such a measuring scheme it is possible to use low-pressure cw CO₂ lasers in spite of low efficiency of the radiation frequency doubling of such lasers (e.g., it is shown in Ref. 3 that the efficiency of frequency doubling normally achieved with the nonlinear crystals of ZnGeP₂ or CdGeAs₂ of several hundred per cent is quite sufficient for sounding CO along a 1-2 km path). High-power pulsed laser transmitters must be used for remote methods of sounding CO using reflection of sounding radiation from topographic targets or, all the more, from aerosols distributed along the path. The efficiencies of frequency

doubling in ZnGeP₂ or CdGeAs₂ crystals can reach several tens per cent for pulsed TEA-CO₂ lasers with a generation pulse duration of 200 ns (Ref. 3). In this case, the efficiency of frequency doubling is known to increase with increase of the TEA-CO₂ laser power which, in turn, is directly related to the lasing medium pressure P_{las} . The laser transmitters based on the frequency-doubled tunable pulsed TEA-CO₂ lasers can be considered sufficiently effective for remote sounding of CO at $P_{las} = 200$ Torr. In this case the emission linewidth of such a transmitter, even in the single-mode generation, becomes comparable to a CO absorption linewidth. As known, this causes incorrectness of sounding results due to the effects of the laser emission instrumental function $I(\nu_i - \nu)$ (the emission line contour shape with central frequency ν_i). In this paper we deal with two aspects of this problem in application to remote sounding of CO. These are the effect of a finite linewidth of sounding radiation caused by the lasing medium pressure P_{las} on the measurement accuracy of CO content and the sensitivity of a measurement system.

For the case of a finite linewidth of the laser $\Delta\nu_{las}$ the differential absorption coefficient $K_{eff}(\rho, z)$ can be represented as an effective value averaged over the laser emission spectrum

$$K_{eff}(\rho, z) = \frac{1}{2\rho z} \ln \frac{\int I(\nu_{off} - \nu) T^2(\nu, \rho, z) d\nu}{\int I(\nu_{on} - \nu) T^2(\nu, \rho, z) d\nu}, \quad (2)$$

where $I(\nu_i - \nu)$ is the spectral distribution of the laser emission power, and $T^2(\nu, \rho, z)$ is the square of a medium transmission along the path z

$$T^2(\nu, \rho, z) = \exp \{-2K(\nu)\rho z - 2\beta(\nu)z\}. \quad (3)$$

Here $\beta(\nu)$ is the volume coefficient of "interfering" gases. In Eq. (2) we assume that the following conditions hold:

$$\text{a) } \eta = 1, \text{ b) } P_0(\nu_{on}) = P_0(\nu_{off}), \text{ and c) } \int I(\nu_i - \nu) d\nu = 1.$$

As can be seen from Eqs. (2) and (3) the effective absorption coefficient K_{eff} depends on the sought concentration ρ , the path length z , and on the interfering absorption if it is not compensated for. The ρ and z dependences of K_{eff} result from the finite linewidth $\Delta\nu_{\text{las}}$ of the laser emission. At $I(\nu_i - \nu) \rightarrow \sigma(\nu_i - \nu)$ it follows from Eqs. (2) and (3) that $K_{\text{eff}}(\rho, z) \rightarrow (K_{\text{on}} - K_{\text{off}}) + (\beta_{\text{on}} - \beta_{\text{off}})$ and when $K_{\text{off}} \ll K_{\text{on}}$ and $\beta_{\text{on}} - \beta_{\text{off}} \ll K_{\text{on}}$ we obtain $K_{\text{eff}}(\rho, z) \rightarrow K$, i.e., we come to the classical definition of the absorption coefficient in the differential absorption method.

The larger the emission linewidth $\Delta\nu_{\text{las}}$, the stronger is the ρ and z dependences of K_{eff} . For the first time we have studied this problem for paths with a distributed reflector in Ref. 6.

Let us consider the problem on the error in the CO determination from sounding data, due to the error in assigning the absorption coefficient value in formula (1). In contrast to the case, of monochromatic radiation the effective coefficient of differential absorption depends on the unknown concentration of CO (see Eqs. (2) and (3)) and this can cause an uncertainty of sounding data inversion by formula (1) under conditions of strong CO variations. Strong variations of the CO content are typical of an industrial center where the CO concentration can change by more than two orders of magnitude, i.e., from the background values ~ 0.1 ppm to the values of 10 ppm characterizing a strongly polluted urban atmosphere,⁵ especially during industrial emergency events. Moreover, the calculations of the CO absorption coefficient made

based on the atlas of spectral data HITRAN (version 1991) showed that there was water-vapor absorption in the vicinity of the CO line centers at 2154.596 and 2086.322 cm^{-1} .

Figure 1 depicts horizontal profiles of the effective values for the CO differential absorption coefficient calculated by formulas (2) and (3) (solid lines) for three values of $\rho_{\text{CO}} = 0.1, 1, \text{ and } 10$ ppm for a pair of frequencies 2086.327 and 2082.558 cm^{-1} . The dots in the figure show K_{eff} corrected for the interfering H_2O absorption. The model of the atmosphere used here is the mid-latitude summer.⁷ The errors in determining $K_{\text{eff}}(z)$, without any corrections for absorption by H_2O (or, what is the same, systematic errors in reconstructing the CO concentration) are shown by dashed line assuming that the most typical CO concentration is ~ 1 ppm. The effective absorption coefficients were calculated for the Voigt emission line contour allowing for the $\sqrt{2}$ -fold broadening with radiation frequency doubling. It can be seen that the error in determining K_{eff} within the range of CO concentrations of 0.1 to 10 ppm can reach (at $z = 6$ km and $P_1 = 760$ Torr) 60 % taking into account the interfering H_2O absorption (curve with crosses) and 100 % without consideration for the H_2O absorption. When P_{las} (and, correspondingly, $\Delta\nu_{\text{las}}$) decreases the error in determining K_{eff} naturally, decreases and does not exceed 30 % (at $P_{\text{las}} = 250$ Torr) even without the account for H_2O absorption.

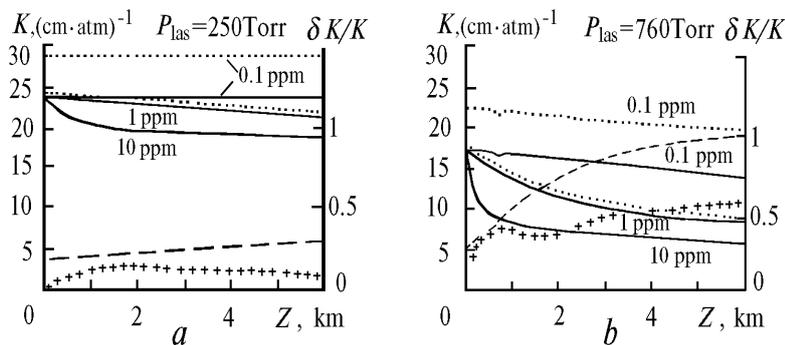


FIG. 1. Effective differential CO absorption coefficient (dots and solid curves) and relative error $\delta K/K$ (dashed curves and crosses) as functions of the path length (z is the path length to the reflector) and of the mean CO pressure along the path for the pair of lines at 2086.326 and 2082.558 cm^{-1} [$2 \cdot 9P(24) - 2 \cdot 9P(26)$]. These dependences were calculated for following CO_2 -laser medium pressures P_{las} : a) 250 and b) 760 Torr. Solid curves and curves formed of crosses are constructed with and, dotted and dashed ones without taking into account the selective H_2O absorption. (The background concentration of H_2O was taken to be $1.8 \cdot 10^4$ ppm).

Depicted in Figs. 2a and b are analogous results for a pair of lines at 2169.270–2166.960 cm^{-1} ($2 \cdot 9R(30) - 2 \cdot 9R(28)$). The emission line $2 \cdot 9R(30)$ is within the CO absorption line (2169.198 cm^{-1}). The advantage of this pair is essentially weaker (by two orders of magnitude) interference of absorption than by other gases as well as the possibility of simultaneous sounding of two atmospheric pollutions, i.e., NH_3 and CO at the fundamental frequencies and their second harmonics, respectively. However, here too the relative error in determining K_{eff} in the range of CO concentrations from 0.1 to 10 ppm increases with P_{las} increase and reaches 85 % for a 2 km-long path at $P_{\text{las}} = 760$ Torr.

Thus, one important conclusion can be drawn from Figs. 1 and 2. If no efforts are being applied to narrow the emission spectrum (e.g., by introducing dispersion elements into the laser cavity), then the effect of the CO concentration and of the path length z on the effective absorption coefficient becomes stronger with the increase of the laser mixture pressure P_{las} . Thus, for large ρ_{CO} the value K_{eff} first quickly (along short paths) and then slowly decreases with increasing z . In this case the difference between K_{eff} and quasimonochromatic absorption coefficient K can reach, for the line pair $2 \cdot 9R(30) - 2 \cdot 9R(28)$ (see Fig. 2), 70 ($P_{\text{las}} = 250$ Torr, $\rho_{\text{CO}} = 10$ ppm) to 300 % ($P_{\text{las}} = 760$ Torr, $\rho_{\text{CO}} = 10$ ppm).

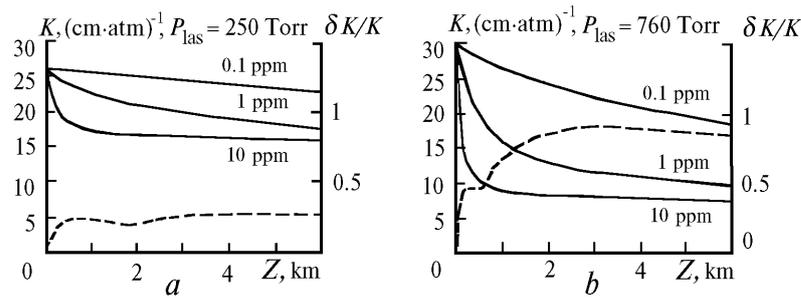


FIG. 2. Effective differential CO absorption coefficient and relative error $\delta K/K$ (dashed curves) as functions of the path length and the mean CO pressure along the path for the pair of lines at $2169.270-2169.960 \text{ cm}^{-1}$ [$2*9R(30)-2*9R(28)$].

To eliminate a systematic error in reconstructing the gas concentration ρ_{CO} from the laser sounding data it is necessary to employ the iteration method for solving the equation

$$\rho = \frac{\tau}{2K_{\text{eff}}(\rho)z}, \quad (4)$$

where τ is the measured optical depth of the double path. In this case we must be aware of the line shape of a pulsed sounding radiation. One of the methods for solving this equation can be a graphic one.

Figure 3a depicts the calculated dependences of τ

$$\tau(\rho_{CO}) = \ln \frac{\int I(v_{\text{off}} - v) T_{\text{off}}^2(v, \rho, z) dv}{\int I(v_{\text{on}} - v) T_{\text{on}}^2(v, \rho, z) dv} \quad (5)$$

on the gas concentration ρ_{CO} for two values of P_{las} equal to 1 and 760 Torr (the pair of lines $2*9P(24)-2*9P(26)$,

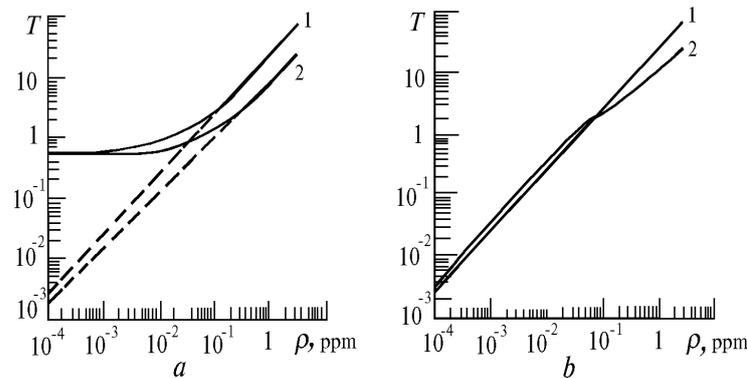


FIG. 3. Total optical depth $\tau = 2K\rho z$ as a function of the CO concentration for the path length of 5 km. Dashed lines are calculated without taking into account selective H_2O absorption: 1) $P_{\text{las}} = 1$ Torr and 2) $P = 760$ Torr. a) Pair of lines $2*9P(24)-2*9P(26)$, b) the pair of lines $2*9R(30)-2*9R(28)$.

Let us now examine the problem on the effect of the emission spectrum width on the concentration sensitivity of a measuring system. Let the minimum detectable concentration (MDC) ρ_{min} be taken as the concentration sensitivity. To determine the MDC the formula⁵

$z = 5 \text{ km}$) with H_2O (solid lines) and without taking into account H_2O (dashed lines) absorption. It can be seen that the function $\tau(\rho_{CO})$ saturates at small ρ_{CO} values due to the effect of the interfering H_2O absorption. In Fig. 3 b no "saturation" for the pair of $2*9R(30)-2*9R(28)$ lines is observed.

Curves presented in Fig. 3 can be used for reconstructing ρ_{CO} from the sounding data. To do this, it is necessary to put the measured value τ on the ordinate axis and to draw a horizontal line until it crosses the curve $\tau(\rho_{CO})$. The intersection point gives the value of the sought concentration. If the measurement error $\Delta\tau$ of the optical depth is known, we can find the error $\Delta\rho$ using the same plot. It should also be noted that measured τ value can differ from that obtained in Eq. (5) by the value $A = \frac{1}{2} \ln [P_0(v_{\text{on}})\eta_{\text{on}}/P_0(v_{\text{off}})\eta_{\text{off}}]$ (see Eq. (1)), which is a calibration constant of the laser system. When calculating τ by formula (5) we assume that $A = 0$. In actual situations the value A can also be nonzero. In this case one must check the curves in Fig. 3 taking into account A .

$$\rho_{\text{min}} = \frac{0.02}{2Kz} \quad (6)$$

is often used where the value of minimum detectable logarithm of the signal ratio is taken to be 0.02 which is

typical, following Ref. 5, of the majority of systems for digital data recording and processing. Before using this formula, we determine the limits of Eq. (6) applicability. It is easy to show that expression (6) is valid: in the absence of the effect of interfering absorption (a) and provided that K is independent of ρ and z (b). In Figs. 1 and 3a for the line pair 2*9P(24)–2*9P(26) the aforementioned results reveal strong effect of the interfering H₂O absorption, therefore for this pair of lines condition (a) does not hold. This fact is clearly demonstrated in Fig. 3a in which the optical depth at small ρ_{CO} is saturated. If Eq. (6) is rewritten in the form

$$\rho_{\min} = \frac{\tau_{\min}}{2Kz} \tag{6a}$$

then using Eqs. (6) and (6a) we obtain $\tau_{\min} = 0.02$, i.e., the minimum detectable optical depth is 0.02 while τ at small values of ρ_{CO} in Fig. 3a cannot be smaller than ~ 0.5 . Condition (b) strictly holds only when laser measurement is carried out with a very narrow spectrum ($\Delta v_{\text{las}} \ll \gamma_0$, where γ_0 is the absorption linewidth). In this case, by taking $\tau_{\min} = 0.02$ one obtains ρ_{\min} from the curve $\tau(\rho)$. Thus, for the pair 2*9R(30)–2*9R(28) when $\Delta v_{\text{las}} \ll \gamma_0$ (curve 1 in Fig. 3b) $\rho_{\min} \sim 6 \cdot 10^{-4}$ ppm. When $\Delta v_{\text{las}} \sim \gamma_0$, condition (b) is violated and criterion (6) gives incorrect estimates of the MDC, both under- and overestimations of ρ_{\min} are possible.

Taking into account the above-said we can make use of a more rigorous criterion for estimating MDC developed in Refs. 8 and 9. For the experimental arrangement under consideration the MDC is estimated from the relations

$$L = B[\bar{T}^2(\rho = 0) - \bar{T}^2(\rho)] \geq L_0; \tag{7}$$

$$B = \frac{P_{\text{off}} \eta}{[\sigma_{\text{on}}^2 + \sigma_{\text{off}}^2 \eta^2 \bar{T}^2(\rho = 0) + \sigma_{\eta}^2 P_{\text{off}}^2 \bar{T}^2(\rho = 0)]^{1/2}}; \tag{8}$$

$$\bar{T}^2 = \frac{\int I(v_{\text{on}} - v) \exp(-2\beta_{\text{on}}(v)z) \exp(-2K_{\text{on}}(v)\rho z) dv}{\int I(v_{\text{off}} - v) \exp(-2\beta_{\text{off}}(v)z) \exp(-2K_{\text{off}}(v)\rho z) dv} \tag{9}$$

The value L is the information distance in the space of the unknown parameter ρ ; B represents a generalized index of the signal-to-noise ratio; \bar{T}^2 is the squared medium transmission along the path z for a given pair of frequencies v_{on} and v_{off} ; $\eta = P_0(v_{\text{on}})\eta_{\text{on}}/P_0(v_{\text{off}})\eta_{\text{off}}$ is the calibration constant of the measuring system; β_{on} and β_{off} are the coefficients of interfering absorption on and off the absorption line, σ_{on} , σ_{off} , and σ_{η} are the measurement errors of the signals P_{on} and P_{off} and of the system constant η .

Criterion (7) has a probabilistic sense that for a gas concentration found from expression (7) it is possible to determine the probability of detecting the gas concentration ρ with this device

$$P = \frac{1}{2} \left[1 + \Phi \left(\frac{L}{2\sqrt{2}} \right) \right], \tag{10}$$

where $\Phi(x)$ is the integral of errors $\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$.

The value P is called the probability of detection. When $L = 1$, $P \sim 0.7$; $L = 2$, $P = 0.84$; and $L = 3.3$, $P = 0.95$.

Determine the relationship between expressions (6) and (7). Let $I(v_i - v) = \delta(v_i - v)$ be the delta-function (monochromatic case), $\beta_{\text{on}} = \beta_{\text{off}}$. Then for $2K\rho z \ll 1$ from Eq. (7) we obtain

$$L = B[1 - e^{-2K\rho z}] \approx 2BK\rho z \geq L_0,$$

from which we have

$$\rho_{\min} = \rho_0 = \frac{L_0}{2BKz}, \tag{11}$$

where $K = K_{\text{on}} - K_{\text{off}}$.

If $L_0/B = 0.02$ then Eq. (11) is reduced to Eq. (6). Then for $B = 50$, $L_0 = 1$, ρ_{\min} found from Eq. (6) can be interpreted as the MDC, whose detection probability is 0.7. We use the threshold value $L_0 = 3.3$ for which $P = 0.95$. In what follows the value $B = 100$ characterizing higher measurement accuracy is used.

Depicted in Figs. 4a, and b are the calculational results for ρ_{\min} obtained using formulas (7)–(9) with $B = 100$ for two pairs of lines considered in this paper. It can be seen that for the first pair, the sensitivity decreases with the P_{las} increase. In this case, due to the interference of H₂O absorption, ρ_{\min} increases from $4 \cdot 10^{-4}$ to $6 \cdot 10^{-4}$ ppm at $P_{\text{las}} = 1$ Torr, $L = 1$ and from $7 \cdot 10^{-4}$ to 10^{-3} ppm at $P_{\text{las}} = 760$ Torr, $L = 1$. As was shown above, the detection reliability P was equal to 0.7 for $L = 1$. If we need for higher reliability of the MDC estimates ($P = 0.95$), then we have values $1.7 \cdot 10^{-3}$ and $3 \cdot 10^{-3}$ ppm for ρ_{\min} at $P_{\text{las}} = 1$ and 760 Torr, respectively.

For the second pair, the interfering absorption is absent, and the emission spectrum broadening has much weaker effect on the MDC estimate. In this case, in contrast to the first pair of lines, one can observe quite opposite situation, i.e., with the increase of Δv_{las} the value ρ_{\min} decreases (sensitivity increases). This is accounted for by the fact that the emission line $v_{\text{on}} = 2169.270 \text{ cm}^{-1}$ is shifted relative to the CO absorption line by 0.072 cm^{-1} (of the order of the CO line half-width γ_0).

The following conclusions can be drawn from this study. First, the increase of the transmitter power makes it possible to substantially increase the sounding path length (up to 10 km) using a topographic target, the sensitivity of CO sounding can both decrease (for resonance interaction) due to the effect of the instrumental function of the laser radiation source and increase (for nonresonance interaction) if the power increase is caused by a simple enhancement of the pressure of a TEA-CO₂ laser active medium. Second, a conventional techniques for processing the sounding data obtained using the low-pressure and, all the more, high-pressure TEA-CO₂ laser can give significant errors in determining ρ_{CO} under conditions of strong CO variations typical of the urban atmosphere due to the industrial and/or automobile atmospheric emissions. The technique

proposed in this paper for processing the data requires that the spectral composition of sounding pulse radiation is known. It should be noted that the aforementioned

problems are missing in coherent lidars based on heterodyne reception of sounding radiation due to narrow stabilized emission lines used.¹⁰

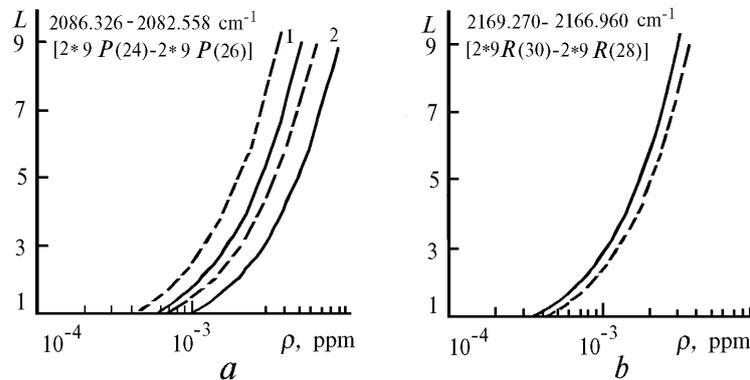


FIG. 4. The information distance L as a function of the CO concentration at the path length of 5 km. Dashed curves stands for $P_{\text{las}} = 1$ Torr and solid curves $P_{\text{las}} = 760$ Torr. Without (1) and with (2) H_2O absorption taken into account. The pair of lines $2^*9P(24)-2^*9P(26)$ (a) and $2^*9R(30)-2^*9R(28)$ (b).

It should be noted here that of the two pairs of lines $2^*9P(24)-2^*9P(26)$ and $2^*9R(30)-2^*9R(28)$ preference should be given to the second pair due to the absence of interfering absorption (a) and the larger value of the differential absorption coefficient (b), and possibility of using this pair of lines for sounding NH_3 (c).

In closing the discussion we should like to point one more source of errors in determining CO from the sounding data obtained with a high-pressure TEA- CO_2 laser. The collisional shift of the emission line grows with increase of the working laser mixture pressure. The shift estimated by the authors of Ref. 11 based on the literature data for different transitions of P - and R -branches of the $9.4 \mu\text{m}$ band is $0.0075-0.009 \text{ cm}^{-1}$. The range of the collisional shift variations depends on the composition of the lasing gas mixture. The value of shift is doubled with the frequency doubling. Moreover, the CO absorption line center is also displaced due to the collisional shift. If these shifts have opposite signs, the total shift can be significant that inevitably would lead to variations in the effective absorption coefficient. Preliminary estimates of K_{eff} made taking into account only the emission line shift give the following results. For both these pairs the maximum calculational error K_{eff} reaches $\sim 27\%$ for $P_{\text{las}} = 250$ Torr, $z = 5$ km, and $\rho_{\text{CO}} = 10$ ppm, when $P_{\text{las}} = 760$ Torr the calculational errors are 33 and 14% for the line pairs $2^*9P(24)-2^*9P(26)$ and $2^*9R(30)-2^*9R(28)$, respectively.

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