GAS ANALYSIS OF THE ATMOSPHERE BY THE DIFFERENTIAL ABSORPTION METHOD USING CO_2 LASERS WITH DIFFERENT LASING LINE WIDTHS

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The possibility of using CO_2 *lasers, with different lasing line widths for gas analysis of the atmosphere by the differential absorption method has been investigated. A technique for determining the concentration of gaseous components of the atmosphere has been proposed in the case of single-frequency sounding. The calculated effective absorption coefficients of some gases in the spectral regions of the first and second harmonics of the* CO_2 *laser are presented. It is shown that the* CO_2 *lasers with different lasing line widths made feasible the determination of the background values of concentration of carbon dioxide, ammonia, and water vapor in the case of single-frequency sounding. In the region of the second harmonic of the* CO_2 *laser, the proposed technique can be used to eliminate the interfering effect of the water vapor absorption in sounding of* OCS *and* NO *and to detect simultaneously the background values of concentration of carbon monoxide and water vapor in the case of sounding at the second harmonic of the lasing line of the* CO_2 *laser* 9R18 *with different spectral widths.*

In the traditional bifrequency differential absorption method, in which measurements are performed on a path with a specular reflector, the concentration of gaseous components of the atmosphere is reconstructed on the basis of the well-known formula[1]

$$n(t) = \frac{\alpha(\nu_2) - \alpha(\nu_1)}{K(\nu_1) - K(\nu_2)} \qquad (1)$$

by its averaging over time t. Here $n(t)$ is the concentration of an examined gas averaged over the time of reading a series of counts, $\alpha(\nu_i)$ and $K(\nu_i)$ are the radiation extinction coefficients and preliminary calculated radiation absorption coefficients on ($i = 1$) and off ($i = 2$) the absorption line. In the case of the finite laser line width, the absorption coefficient can be defined as an effective value averaged over the laser lasing spectrum[2]

$$K_{\rm eff}(\nu_1, z, \Delta\nu) = \frac{\int\limits_{-\infty}^{\infty} I(\nu_1, \Delta\nu) T^2_{\rm ma}(\nu_1, z)\, K_0(\nu_1)\, d\nu}{\int\limits_{-\infty}^{\infty} I(\nu_1, \Delta\nu) T^2_{\rm ma}(\nu_1, z)\, d\nu}, \qquad (2)$$

where $K_0(\nu_1)$ are the undistorted values of the monochromatic absorption coefficients, $I(\nu_1, \Delta\nu)$ is the instrumental function defined as the spectral distribution of the sounding laser radiation power, $T^2_{\rm ma}(\nu_1, z)$ is the square of the atmospheric transmission given by the formula

$$T^2_{\rm ma}(\nu_1, z) = \exp\left[-2\int\limits_0^z \alpha_{\rm ma}(\nu_1, z)\, dz'\right] \qquad (3)$$

in the case of allowing for the molecular absorption by the examined gas, where

$$\alpha_{\rm ma}(\nu_1, z) = K_0(\nu_1)\, n(z). \qquad (4)$$

Numerical modeling and sounding of the atmospheric gaseous components were performed in Refs. 3 and 4 with the use of CO_2 lasers. The effect of the finite laser line width on the accuracy of measuring of the atmospheric gaseous components was also studied,[4] including the case of sounding at the second harmonic of the CO_2 lasers.[5]

The purpose of this paper is to investigate the possibility of application of the CO_2-lasers with different lasing line widths depending on the pressure of gas mixture to gas analysis by the differential absorption method in single-frequency sounding. In this case, the gas concentration $n(t)$ is given by the formula

$$n(t) = \frac{\alpha(\nu_1, \Delta\nu_1) - \alpha(\nu_1, \Delta\nu_2)}{K(\nu_1, \Delta\nu_2) - K(\nu_1, \Delta\nu_1)}, \qquad (5)$$

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where ν_1 is the sounding radiation frequency, and $\Delta\nu_1$ and $\Delta\nu_2$ are the lasing line widths.

Calculations were made for a horizontal sounding path 5 km long with the use of the spectral parameters of absorption lines of atmospheric gases borrowed from Atlas HITRAN–91 (see Ref. 6) for the meteorological model of the atmosphere at mid-latitudes in summer.[7] Spectral profiles of absorption and laser lines were assumed to be Voigt ones.

In the spectral region of the first harmonic of the CO_2 laser, we investigated the behavior of the parameter K_{eff} as a function of the pressure of laser gas mixture in the absorption lines of the following atmospheric gases: CO_2, NH_3, H_2O, and O_3, being coincident with the following lasing lines of the CO_2 laser: 9R20, 9R30, 10R20, and 9P14.

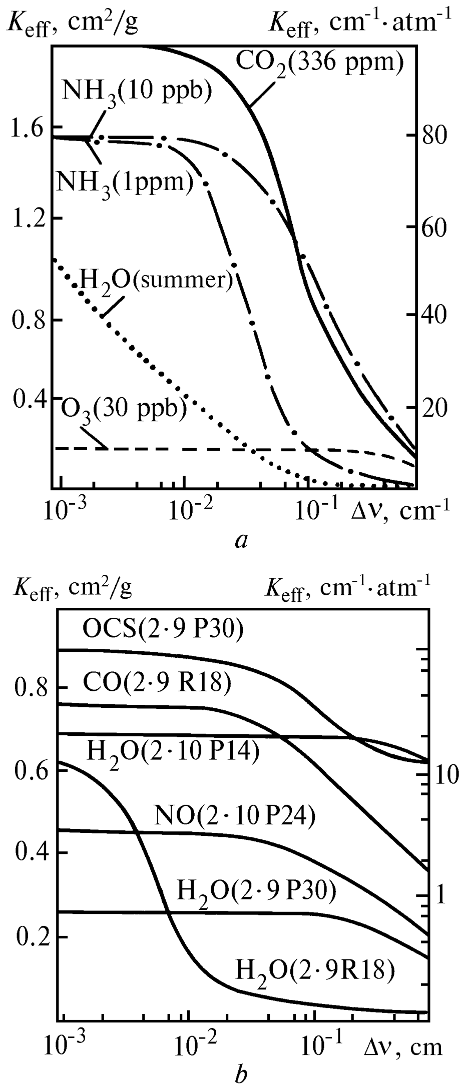

FIG. 1. Dependence of the effective absorption coefficients of the indicated gases on the CO_2*–laser line width in the spectral regions of the first (a) and second (b) harmonic of the* CO_2 *laser.*

Figure 1*a* shows the dependence of the efficient absorption coefficients of the above gases on the CO_2-laser line width. For convenience, the values of the effective absorption coefficients of carbon dioxide and water vapor are shown on the left ordinate, in cm^2/g, and the values of the effective absorption coefficients of ammonium and ozone – on the right ordinate, in $cm^{-1}\cdot atm^{-1}$. It is seen from the figure that the effective differential absorption coefficient is more than 1 cm^2/g when the pressure of gas mixture of the CO_2 laser changes from 0.002 (the lasing line width $\Delta\nu = 0.001\ cm^{-1}$) to 1–2 atm ($\Delta\nu = 0.1\ cm^{-1}$), which makes feasible the detection of the background level of concentration of carbon dioxide.

The differential absorption coefficient is equal to about 20 $cm^{-1}\cdot atm^{-1}$ when $\Delta\nu$ changes from 0.001 to 0.1 cm^{-1} and the NH_3 concentration is 10 ppb, and it is equal to 65 $cm^{-1}\cdot atm^{-1}$ when the NH_3 concentration is 1 ppb.

Analogous calculations have shown that the differential absorption coefficient of water vapor is equal to 0.95 cm^2/g (see Fig. 1*a*), which makes feasible the determination of the background level of water vapor concentration in summer.

The above technique is efficient only in the case of isolated intense absorption lines of atmospheric gases. In the case of interference of many absorption lines, this technique is inefficient. This is illustrated by Fig. 1*a* in which the dependence is shown of the parameter K_{eff} of ozone, whose absorption spectrum is nonselective in character, on the laser line width. It can be seen from Fig. 1*a* that the effective absorption coefficient of ozone is virtually independent of the CO_2-laser line width.

As is well known, a major problem in search for optimal wavelengths of sounding of gaseous atmospheric components in the spectral region of the second harmonic of the CO_2 laser is the interfering effect of the water vapor absorption. In some cases, as was demonstrated in Ref. 8, lasers based on different isotopic compositions must be used in the bifrequency differential absorption method to reduce this effect. This is rather complicated engineering problem. The use of the CO_2 lasers based on the parent isotope with different pressures of gas mixture makes feasible the reconstruction of the gas concentration without regard for the interference effect of the water vapor absorption.

Figure 1*b* shows the dependence of the effective absorption coefficients (in $cm^{-1}\cdot atm^{-1}$) of OCS (lasing line 2·9P30), CO(2·9R18), and NO(2·10P24) on the CO_2-laser line width in the spectral region of the second harmonic of the CO_2 laser when the concentration of the examined gases is 1 ppm. In addition, the dependence of K_{eff} of water vapor (in cm^2/g) on the laser line width is also shown for the same lasing lines (indicated in parenthesis). As is seen from Fig. 1*b*, the use of the CO_2 lasers with different pressures of gas mixture makes feasible the determination of OCS, CO, and NO concentration at a level of 1 ppm, because the effective differential absorption coefficients of OCS, CO, and NO are equal to 71, 25, and 1.2 $cm^{-1}\cdot atm^{-1}$, respectively.

Our calculations have shown that when the laser line width changes from 0.001 to 0.1 cm^{-1}, the effective absorption coefficient of H_2O remains unchanged only for the second harmonics of the lasing lines of the CO_2 laser 9P30 and 10P24 (sounding of OCS and NO, respectively), which fall within the wings of the water vapor absorption lines. This means that, in spite of large values of K_{eff}, the interfering effect of the water vapor absorption can be ignored, and the NO concentration can be determined without correction of measurements by way of simultaneous reconstruction of H_2O and NO (see Ref. 4). In the case of sounding of OCS, we obviate the need for the CO_2 lasers based on different isotopic compositions suggested in Ref. 8.

In the case of sounding of CO at the second harmonic of the lasing line of the CO_2 laser 9R18, the interfering effect of the water vapor absorption can be eliminated by way of an increase in the laser line width with the use of high-pressure lasers. As is seen from Fig. 1*b*, the parameter K_{eff} of H_2O decreases sharply with an increase in $\Delta\nu$. This is explained by the fact that, as our calculations[8] have shown, the lasing line 2·9R18 falls practically at the center of the H_2O absorption line. However, starting from $\Delta\nu = 0.03$ cm^{-1}, the parameter K_{eff} of H_2O remains practically unchanged, whereas the effective absorption coefficient of CO decreases by an order of magnitude, which makes feasible the determination of the background level of the CO concentration. At the same time, when the laser line width increases from 0.001 to 0.01–0.02 cm^{-1}, the parameter K_{eff} of CO remains practically unchanged (see Fig. 1*b*), whereas the differential absorption coefficient of H_2O is equal to 0.55 cm^2/g, that is, sufficient for determination of atmospheric humidity. Thus, our calculations have shown that the use of the second harmonic of the lasing line of the CO_2 laser 9R18 with different spectral widths makes feasible simultaneous sounding of water vapor and carbon monoxide.

Finally, the following main conclusions can be drawn from the results of our calculations:

– the use of the CO_2 lasers with different lasing line widths makes feasible the determination of the background levels of carbon dioxide, ammonium, and water vapor concentration in single-frequency sounding; in so doing, in the case of sounding of carbon dioxide, in comparison with the traditional bifrequency differential absorption method, we need no *a priori* knowledge of the spectral behavior of the aerosol characteristics of the atmosphere;

– the proposed technique is efficient only in the case of isolated absorption lines of sounded atmospheric gases;

– in the case of sounding of OCS and NO at the second harmonic of the CO_2 laser based on the parent isotope, the interfering effect of the water vapor absorption can be eliminated by way of an increase in the pressure of gas mixture;

– sounding at the second harmonic of the lasing line of the CO_2 laser 9R18 with different line widths makes feasible simultaneous determination of the background levels of carbon oxide and water vapor concentration.

On the whole, results of our calculations have shown that the CO_2 lasers with different pressures of gas mixture are promising for gas analysis of the atmosphere by the differential absorption method.

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