The best absorption lines for the detection of carbon monoxide at 2.35 micron with tunable diode lasers

E V Stepanov¹, S N Kotelnikov¹, A Y Stavtsev², S G Kasoev¹

¹ A.M. Prokhorov General Physics Institute of Russian Academy of Science, Moscow, Russia, 119991, Moscow, 38 Vavilova Str.
² K.G. Razumovsky Moscow State University of Technologies and Management (The First Cossack University), 73 Zemlyanoy Val, Moscow, 109004, Russia

eugenestepanov@yandex.ru

Abstract. A modeling of high-resolution absorption spectra of carbon monoxide (CO) and other interfering gases at 2.35 μm was conducted. Several CO absorption lines have been determined as the best for the use in laser based spectral analysis of CO under conditions of high humidity and high concentrations of CO₂ in complex gas mixtures. Measurements of resonance absorption in these lines allow one to obtain maximum sensitivity and selectivity of CO analysis in the near-infrared spectral region.

1. Introduction

High-resolution absorption spectra of CO were simulated to determine the optimal spectral ranges for analytical studies of complex gas mixtures containing gaseous carbon monoxide with tunable diode lasers. The spectra were modeled with spectral resolution of ~0.001 cm⁻¹ in the IR range from 2000 to 70000 cm⁻¹ taking into account various mechanisms of spectral line broadening. The HITRAN2005 high-resolution molecular IR spectra database [1] and specialized software for molecular absorption spectra calculations were used for this modelling.

2. Modeling the absorption spectra of CO

The most intense CO absorption bands in the IR range were determined at the first stage and their intensities were compared. Figure 1 shows the CO bands most intense in their spectral regions. As can be seen, the carbon monoxide molecule in the infrared range has several vibrational-rotational absorption bands that are intense in their regions. Near 1900 cm⁻¹ the fundamental absorption band 0–1 is located, the intensity of individual lines in which reaches 4.5×10⁻¹⁹ cm⁻¹/(mol·cm⁻²). The band of the first overtone 0–2 is located in the region of 4200 cm⁻¹, the line intensity in which is 2.5 orders of magnitude less than in the 0–1 band. Finally, near 6300 cm⁻¹ is a band of the second overtone of the main CO oscillation. The most intense lines of this band are 5 orders of magnitude less intense than the lines from the fundamental absorption band. As follows from Figure 1, the 0–1 and 0–2 bands are promising for the use in the spectral analysis of CO in complex gas mixtures based on the application of tunable diode lasers [2-4]. The first 0–1 band is due to the fact that the most intense lines are located in it, and the second 0–2 band due to the fact that it is located in the near infrared region where tunable diode lasers work at room temperatures more [5-7].

Using the parameters of CO absorption lines given in the HITRAN 2005 high-resolution spectral molecular database the absorption coefficient spectra of CO lines were calculated for both bands 0–1
and 0–2 for conditions that are realized at high humidity and increased CO$_2$ content in the complex gas mixtures analyzed. Such conditions can be realized in the atmosphere of artificial habitat complexes, in greenhouses and in exhaled air. The total pressure was taken as 760 mm Hg, temperature 296 K, the relative CO content in the air $10^{-6}$ (1 ppm) when simulating.

The CO absorption spectra calculated during the simulation are presented in Figure 2. At the top, Figure 2 shows the calculated absorption spectrum of CO in the P- and R-branches of 0-2 band disposed in the range 4150-4350 cm$^{-1}$. As can be seen, in this spectral range, the absorption spectrum of CO is a set of separate non overlapping and almost equidistant lines with a distance between the individual lines of $\sim 4$ cm$^{-1}$. We emphasize that for the most intense lines of the 0–2 CO band under the same conditions, the absorption coefficient at the maximum of the lines is only $\sim 5 \cdot 10^{-7}$ cm$^{-1}$. Thus, in order to realize concentration sensitivity in this spectral range comparable with that in the mid-IR range (0-1 band), the absorption sensitivity of the spectral system should be $\sim 2$ orders of magnitude higher.

![CO absorption spectra](image_url)

Fig. 1  A - location and intensity of vibrational-rotational absorption bands of CO in the infrared range. B - location and intensity of the lines of P- and R-branches of the 0-1 CO absorption band. C - location and intensity of the lines of P- and R-branches absorption 0-2 CO band.

3. Interference of CO spectra with other gases
One of the most serious problems which must be resolved at developing methods and means of a highly sensitive and selective analysis of trace CO in complex gas mixtures is related with possible high CO$_2$ and water vapor content. The content of CO$_2$ compared with atmospheric can be increased by two orders of magnitude (from 330 ppm to 3%), and the content of H$_2$O vapor can be increased by several times. For example, exhaled air is a 100% saturated gas mixture with water vapor. The content of H$_2$O can reach up to 5%. Thus, the concentration of CO in the air at the level of $10^{-6}$ must be analyzed against a background of more than 10000 times higher concentrations of CO$_2$ and H$_2$O.
Moreover, in the case of applying spectral analysis methods to complex gas mixtures, it becomes significant that both of these molecules, CO₂ and H₂O, have a rather complex structure of absorption spectra covering almost the entire IR range.

The use of spectral methods based on the application of laser radiation having a high spectral resolution can nevertheless solve this problem by carefully analyzing the absorption spectra of interfering gases (CO₂, H₂O and other) and choosing the best spectral regions for analysis.

A careful analysis of the absorption spectra of CO₂ and H₂O in the spectral regions promising for the analysis of CO in complex gas mixtures was performed. For these purposes, the absorption spectra of these molecules were simulated. The HITRAN2005 high-resolution molecular IR spectral databases and specialized software were used for the modeling of molecular absorption spectra.

![Absorption coefficient spectra of 0-2 CO band and H₂O vapour in the spectral range of 4150-4350 cm⁻¹](image1)

![The most intense absorption bands of CO, CO₂ and H₂O in the spectral range of 1800-7000 cm⁻¹](image2)

Figure 2 shows the relative arrangement of the main absorption bands of CO₂ and H₂O vapor in the IR range (1800-7000 cm⁻¹). It can be seen that the CO 0-1 and 0-2 bands are located in the region of relative transparency, i.e. where the absorption of CO₂ and H₂O is not too large. Nevertheless, the 0-1 band interferes with both the CO₂ and H₂O bands. In the region of 4500 cm⁻¹, where the 0-2 CO band is located, the main interfering effect will be caused by the absorption of H₂O vapor. The CO₂ absorption is practically absent here. We emphasize that due to the different internal structure of CO and H₂O molecules the intensity of the absorption lines changes differently when passing from low optical frequencies to higher ones. The relative fraction of absorption of the H₂O vapor lines increases compared to CO lines. So the detection of CO in the band 0-1 is preferable, because it will have less sensitivity to the absorption of water vapor which will give a higher selectivity of the analysis. Unfortunately tunable diode lasers operate at cryogenic temperatures at that spectral region and this limits their analytical applications.

For a more careful analysis of the interference problem, the absorption spectra of CO₂ and H₂O were simulated. In Figure 2 the spectra of absorption coefficients of CO and H₂O were presented in the spectral range of 4150-4350 cm⁻¹ where the lines of the P- and R-branches of the 0-2 CO band are
located. As can be seen, in this spectral region the lines of the P-branch of the 0–2 CO band are the most susceptible to interference with the absorption lines of H₂O vapor. For a more accurate selection of the CO analytical lines, an even more carefully studies of the CO and H₂O spectra are required.

Figure 4 shows a more detailed mutual arrangement of H₂O lines near the most intense CO lines in the R-branch of 0-2 band. As follows from Figure 3, the absorption of CO₂ in this spectral range is practically absent and therefore can be excluded from consideration. As can be seen in the R-branch of 0-2 band, very strong interference of CO and H₂O lines is observed. Almost every CO line promising for use for gas analysis is located in close proximity to any H₂O line. Some of them overlap strongly.

In the immediate vicinity of the CO lines of the 0-2 branch that appear most suitable for use in the analysis of CO in complex gas mixtures the transmission spectra were calculated and simulated. The content of the gases in the complex mixture was taken as follows: CO – 1 ppm, CO₂ – 3 %, H₂O – 5 %, the rest is atmospheric air. Temperature is 296K, optical path length is 20 meters.

Figure 5 shows the calculated transmission spectra of the studies gas mixture near four CO lines from the R-branch of 0-2 band. As can be seen, in the R-branch of 0-2 band only the line R(6) is good for use in the analysis when using direct registration of spectra. There are much more intense H₂O absorption lines in the close vicinity of it. The other three lines shown in Figure 5 are located on the slopes of the intense absorption lines of H₂O. As can be seen the value of the resonant absorption of CO at a concentration of 1 ppm and an optical path length of 20 m is about 0.1 %.

To select and compare the optimal spectral regions in situations that are realized in the R-branch of 0–2 band, we used the special approach described earlier in [8-9]. The proposed method for optimizing the conditions for recording spectra consists in increasing the contrast of absorption signals due to hardware or software differentiation of laser transmission spectra.

The approach developed by us to the selection of the best absorption lines and optimal analysis conditions for the case of interference of the absorption lines of the studied gaseous substance and interfering gases was used to analyze the transmission spectra of complex gas mixtures near the location of the R-branch lines of 0-2 CO band shown in Figure 5. For these parts of the spectrum the application of this approach will be most effective, since here, as can be seen from Figure 5, the most significant interference of CO absorption lines with CO₂ and H₂O absorption lines is observed.
Fig. 5. The simulated transmission spectra of the complex gas mixture in the region of the R-branch of the 0-2 CO band (4280-4300 cm\(^{-1}\)) for 4 absorption lines most suitable for laser spectral analysis of the composition of exhaled air with an optical path length of 20 m.

From the point of view of the influence of line interference, the spectral range of 4280-4300 cm\(^{-1}\) much more complex than the range of 2100-2130 cm\(^{-1}\), since the fraction of absorption by H\(_2\)O vapour in this range is significantly higher than in the second. However, this range is attractive from the point of view of its practical application, since lasers and photodetectors in this spectral range operate at room temperatures.

Let us consider in more detail the interference of analytical and interfering lines in the spectral range of 4280-4300 cm\(^{-1}\) for direct recording of transmission spectra, see Figure 5. As can be seen from the figure, the R(5) CO line is located on the wing much whiter than the intense H\(_2\)O absorption line and the determination of the baseline (zero absorption level) can be significantly complicated taking into account the fact that the absorption in the CO line is less than 0.1% of signal power. The R(6) CO line is very well located between the H\(_2\)O lines, comparable in absorption intensity. The position of the baseline and the value of resonant absorption are easily determined for this line even from the direct transmission spectrum. In this sense, it is a pleasant exception to the rule. The R(8) line interferes with one fairly intense and one weak absorption line of H\(_2\)O, which can affect the level of zero absorption in the analytical line. The R(10) line interferes with the H\(_2\)O line, comparable in
intensity. The weak H\textsubscript{2}O absorption line on the wing of the line, which is about 40%, can slightly distort the position of the zero absorption line in the analytical line.

Fig. 7. The second derivatives of the simulated transmittance spectra of the complex gas mixture in the region of the R-branch of the 0-2 CO band (4280-4300 cm\textsuperscript{-1}) for 4 absorption lines most suitable for laser spectral analysis of the composition of exhaled air, with an optical path length of 20 m.

Let us consider how the situation will change if the first and second derivatives of the transmission spectrum shown in Figure 6 and 7 will be used for the spectral analysis. It is seen that the use of the first and especially the second derivative of the transmission spectrum sharply increases the contrast of the recorded resonance features of the spectra. As in the case described above, the zero level is confidently determined in the spectrum of the second derivative, regardless of how strong the intersection of the analytical and interfering lines is. In addition, the position of the interfering lines is clearly defined, up to very small ones, for example, weak side resonances near the lines R(8) and R(10). This allows, if necessary, to take into account their influence when calculating the resonance value of the analytical line.

4. Conclusion
Thus, as a result of the analysis of the absorption spectra of CO and the interfering gases CO\textsubscript{2} and H\textsubscript{2}O in the infrared range, several CO absorption lines were determined that are most convenient for their use in analyzing the content of trace concentrations of CO in a complex gas mixtures. The analysis showed that in this case, the best CO lines for analysis are the lines R(5), R(6), R(8) and R(10), located in the range of 4280-4300 cm\textsuperscript{-1}. They interfere strongly with the absorption lines of H\textsubscript{2}O to the least extent but not with CO\textsubscript{2} lines. The use of the first and second derivatives of the transmission spectrum of the studied gas mixtures can significantly increase the contrast of detecting resonance features in the transmission spectra and thus increase the accuracy, sensitivity and selectivity of the analysis of CO in the case of strong interference with absorption spectra of CO\textsubscript{2} and H\textsubscript{2}O.

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