To the choice of spectral region for laser based analysis of molecular gases at strong interference of absorption spectra

E V Stepanov¹, S G Kasoev¹, G N Yulina², S N Kotelnikov¹

¹ Prokhorov General Physics Institute of Russian Academy of Science (GPI RAS), 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. The interference of the absorption bands of H₂O, CO₂, and several gaseous biomarkers was analyzed in the middle and near-IR spectral region using the HITRAN2006 database. It was demonstrated that the problem of the vibration-rotation band interference for detected and interfering gases is aggravated in the near-IR spectral region. This aggravation is caused not only by the decrease in the absolute band intensity for overtones and combination bands of the molecular vibrations but also by the relative increase in the absorption in H₂O lines and high density of CO₂ lines in the near-IR spectral region

1. Introduction
The problem of interference of the absorption bands of the detected and interfering molecules in the near-IR range requires special consideration. The near-IR range is favorable for applying TDL-based methods of spectral analysis due to the very high operating characteristics of laser diodes based on III–V compounds, whose set covers the spectral range from visible to 3.3 μm. However, it is known that the near-IR range contains mainly bands of overtones and combined vibrations, which arise due to the anharmonicity of vibrations and nonlinearity of the dipole moment of molecules and, as a result, are characterized by much lower absorption intensities [1, 2]. Each subsequent overtone of the fundamental vibration is generally two to four orders of magnitude weaker than the previous one. This rule is on the whole valid for combined vibrations as well. Therefore, the individual lines of the gas molecules detected, which belong to such bands and are used in concentration measurements, have an absorption intensity several orders of magnitude lower than the lines in the fundamental bands in the mid-IR range. The specificity of the choice of the optimal spectral range and the most appropriate analytical line in the near-IR range, related to the interference of molecular absorption bands, is that the regularities of a decrease in the intensity of the absorption lines in the bands of overtones and combined vibrations are distinguished for different molecules and types of vibrations of a particular molecule. The interference of the absorption bands of H₂O, CO₂, and several gaseous biomarkers was analyzed in the middle and near-IR spectral region using the HITRAN2005 database [3, 4].

2. Comparative analysis of molecular absorption bands
The dependences of the intensities of the strongest lines on the position of the band center were constructed using the data of the HITRAN2005 atlas of spectral lines [3, 4]. For comparison, Figs. 1–3 show the intensities of the strongest lines in a band, depending on the position of the band...
center, for the fundamental transitions, overtones, and combined vibrations of H$_2^{16}$O, $^{12}$CO$_2$, and some other molecules of current interest for laser gas analysis.

**Fig. 1.** Dependence of the intensity of the strongest line in a band on the position of the band center in the vibration-rotation absorption spectra of H$_2$O in the IR and visible regions. Overtones of vibrations are denoted by the same symbols. The upper vibrational state is indicated for some part of bands; for these bands, the lower state is 000.

It can be seen in Fig. 1 that the intensity of the overtones of the 010–000 vibrational transition in H$_2$O decreases much faster than, for example, the intensity of the overtones of the 100–000 and 001–000 fundamental transitions, as well as the overtones of 101–000 combined vibrations. Moreover, since the 001–000 band has a relatively high intensity (the maximum absorption in lines exceeds 2 · 10$^{-19}$ cm$^{-1}$/mol cm$^{-2}$) and the frequency of the 100–000 fundamental vibration is relatively high (3652 cm$^{-1}$), the intensity of the resonant absorption in H$_2$O decreases sufficiently slowly with approaching the near-IR range. The individual H$_2$O absorption lines in the 201–000 and 300–000 bands, located near 1 μm, have an intensity of ~10$^{-21}$ cm$^{-1}$/mol cm$^{-2}$.

**Fig. 2.** Dependence of the intensity of the strongest lines in a band on the position of the band center in the vibration-rotation absorption spectra of CO$_2$ in the IR range: (■, □, ○) bands of overtones of the fundamental and combined vibrations of CO$_2$, (♦) other hot CO$_2$ bands, and (*) absorption bands of H$_2$O. For the bands with indicated upper vibrational state, the lower state is 00001.

The CO$_2$ bands are characterized by a faster (in comparison with H$_2$O) decrease in the absorption intensity in lines at the approach to the near-IR range (Fig. 2). Although the strongest lines in the 0001–00001 CO$_2$ band, which is located at 4.3 μm (~2350 cm$^{-1}$), have an intensity of ~4 · 10$^{-18}$ cm$^{-1}$/mol cm$^{-2}$, the intensity of the individual CO$_2$ absorption lines near 1 μm is only
10^{-25} \text{ cm}^{-1}/(\text{mol cm}^{-2}). \) This fact is in part due to the lower frequency of the fundamental transitions in CO$_2$. Another consequence of this factor is that the CO$_2$ absorption bands much more densely fill the spectral range from 4000 to 10000 cm$^{-1}$ in comparison with the H$_2$O band (Fig. 2). In addition, the relatively small rotational constant of the CO$_2$ molecule ($\sim 0.39$ cm$^{-1}$), as well as its linear symmetry and specific (for such a symmetry) selection rules for the vibration-rotation transitions, determine the regular and sufficiently dense position of individual lines in the CO$_2$ absorption bands, including the bands of overtones and combined vibrations. This circumstance additionally complicates the choice of transparency microwindows in the absorption spectrum of CO$_2$ when the concentration of this gas is high in the gas mixtures studied.

Figure 3 shows the data on the absorption bands of some compounds of current interest for gas analysis, as well as H$_2$O (shown by the dotted lines). It can be seen that in most cases the passage to the near-IR range is accompanied by a relative increase in the absorption intensity of water lines. Only for the HF molecule, which has a very high frequency ($\sim 4000$ cm$^{-1}$) and intensity of the fundamental vibration (the intensity of the strongest lines is $\sim 3 \times 10^{-18}$ cm$^{-1}/(\text{mol cm}^{-2})$, a passage to overtone lines is not accompanied by the enhancement of the interference from H$_2$O and other possible admixtures. However, this case is rather an exception confirming the general regularity. For the overtones of the CO, HCl, and NO linear molecules, as well as the overtones of some vibrations of CH$_4$ and NH$_3$, a decrease in the absorption intensity with an increase in frequency has been observed; this decrease is comparable with that observed for the CO$_2$ bands. In view of much slower (in comparison with most other molecules) decrease in the intensity of the absorption lines of the overtones and combined vibrations of H$_2$O, as well as the high density of lines in the CO$_2$ bands, the search for the spectral range appropriate for measurement of low resonant absorption in the gas molecules studied should be performed with consideration of the absorption of isotopic modifications of H$_2$O and CO$_2$. The latter lines are not shown in Figs. 1 and 2 in order not to make the plots cumbersome. First of all, it is necessary to take into account the absorption band of the H$_2^{18}$O and $^{13}$CO$_2$ molecules because the abundances of $^{18}$O and $^{13}$C are $\sim 0.037$ % and $\sim 1.11$ %, respectively. Due to the isotopic shift of the absorption bands, their effect may be dominant at the periphery of the bands of the main isotopic modifications, where the absorption of the latter decreases due to the temperature distribution of the line intensity in the vibration-rotation band.
3. Analysis of relative parameters of molecular absorption bands

Let us consider the main regularities determining the intensities of the absorption lines of the studied and interfering compounds in the near-IR range. Along with the intensity of the fundamental transition involved in the formation of an overtone or a combined vibration, other important factors are the fundamental transition frequency and mechanical and electrical anharmonicities of the vibration under consideration (i.e., deviation of vibrations from harmonicity and nonlinear dependence of the dipole moment of a molecule on the interatomic distance). Both the first and second factors are determined by the symmetry of the molecule and vibration studied and the parameters of the atoms forming the molecule and the interatomic bonds. In addition, the relative close position of the vibration frequencies of the molecule can also be significant. Due to the Fermi resonance, this factor can make some forbidden vibration-rotation transitions allowed and increase the intensity of the combined vibration lines [1, 2].

![Graph showing the dependence of the relative intensity of the strongest lines in a band on the central band frequency normalized to the fundamental vibration frequency for the overtones of the fundamental vibrations of the linear diatomic molecules (▼) CO, (◆) NO, (■) HF, (●) HCl, and (▲) HBr.]

These considerations are illustrated in Figs. 4–7, which show the same data as in Figs. 1–3 but normalized to frequency and intensity. Here, the frequencies and intensities of the lines of overtones and combined vibrations are reduced to the frequencies and intensities of the lines of their fundamental vibrations. The data are classified according to the types of molecules.
Fig. 5. Dependence of the relative intensity of the strongest absorption lines in a band on the central band frequency normalized to the fundamental vibration frequency for the overtones and combined vibrations of the linear triatomic molecules (●) CO\textsubscript{2} and (○) N\textsubscript{2}O. For the bands with indicated upper vibrational state, the lower state is 00001.

Figure 4 shows the relative intensities of the strongest lines in a band, depending on the normalized central vibration frequency for the linear diatomic HF, HCl, HBr, CO, and NO molecules. Each such compound has only one fundamental absorption band and, therefore, overtones of the fundamental vibration. It can be seen that a decrease in the line intensity from overtone to overtone does not significantly change in the range of low overtones: it ranges from one and a half to two orders of magnitude for different molecules. Such coincidence can be explained by the fact that the values of the anharmonicity of the fundamental vibration at low excitations of vibrational levels are similar for molecules of this type. Thus, for linear diatomic molecules, the most significant factor determining the absorption intensity in the near-IR range is the fundamental vibration frequency. For example, as was noted above, for the HF molecule with a fundamental vibration frequency of \(\sim 4000\ \text{cm}^{-1}\), the absorption lines near 1.25 \(\mu\text{m}\) (\(\sim 8000\ \text{cm}^{-1}\)) will belong to the first overtone, i.e., will be weaker than the lines from fundamental band only by one and a half orders of magnitude. At the same time, the neighboring (near 1.2 \(\mu\text{m}\)) CO absorption lines will belong to the second overtone of the fundamental vibration of this molecule, with a frequency of \(\sim 2150\ \text{cm}^{-1}\); therefore, they will be weaker than the initial ones by five to six orders of magnitude. Figures 5 and 6 show the normalized data for the absorption bands of triatomic molecules: linear molecules CO\textsubscript{2} and N\textsubscript{2}O and asymmetric tops H\textsubscript{2}O and O\textsubscript{3}.
Fig. 6. Dependence of the relative intensity of the strongest absorption lines in a band on the central band frequency normalized to the fundamental vibration frequency for overtones of the fundamental vibrations of the linear asymmetric tops (●) H₂O and (○) O₃. For the bands with indicated upper vibrational state, the lower state is 000.

It can be seen that different types of vibrations in these molecules have different anharmonicities, which determine the intensity of their overtones and the combined vibration bands formed by them. In particular, for CO₂, the least anharmonic vibration that forms the fundamental 01001–00001 band decreases the absorption intensity by three and a half orders of magnitude per overtone, while the least harmonic vibration (10001–00001 band) determines a decrease in the intensity of the subsequent overtones and combined vibrations by only one and a half orders of magnitude (Fig. 5). However, it is important that the 10001–00001 transition frequency is only ~ 1300 cm⁻¹; hence, only the second and third overtones of this transition are present in the combined vibration in the near-IR range. The data for the absorption band of another triatomic molecule, N₂O, reported here, show that the anharmonicity of vibrations of this linear but asymmetric molecule is stronger than that for CO₂. This circumstance leads to a decrease in the absorption intensity only by an order of magnitude per overtone.

It is well known that the water molecule vibrations are also characterized by strong anharmonicity, which is primarily related to the nonrigidity of this molecule (due to the presence of hydrogen atoms). It can be seen in Fig. 6 that the most anharmonic vibration (the 100–000 band) gives on average only one order of magnitude for a decrease in the overtone intensity, whereas the most harmonic vibration of H₂O (the 010–000 band) gives three orders of magnitude. In this case, it is important that the central frequency of the 100–000 band is ~ 3650 cm⁻¹, whereas that of the 010–000 band is only ~ 1600 cm⁻¹, i.e., the effect of the overtones of the less harmonic vibration, which are characterized by slowly decaying intensity, is most significant in the near-IR range and can be extended to the visible range.
Since the H$_2$O molecule is the most important interfering component in gas analysis and its absorption should be taken into account first of all, two dot-dashed lines in Figs. 4–7 indicate the range of possible variations in the relative absorption intensity in overtones and combined bands for H$_2$O. For convenience of data comparison, such ranges are also indicated in Figs. 4, 5, and 7. Figure 7 shows the normalized data on some absorption bands of a series of molecules that are of current interest for gas spectral analysis: triatomic asymmetric tops SO$_2$, NO$_2$, and H$_2$S and polyatomic symmetric tops NH$_3$ and CH$_4$. In particular, it can be seen that the anharmonicity of vibrations of NO$_2$ and H$_2$S molecules is comparable with the H$_2$O anharmonicity, as a result of which only one order of magnitude of the absorption intensity can be lost in each overtone. However, the central frequencies of the absorption bands of these molecules are lower than those of the 100–000 and 001–000 bands of H$_2$O; therefore, at the transition to the near-IR range, the intensity of their absorption lines decreases faster than for the lines of overtones and combined vibrations of water. As can be seen in Fig. 7, the anharmonicity of the fundamental vibrations of other molecules is much lower than that of water; therefore, from two to four orders of line intensity can be lost at each overtone.

4. Discussion

Thus, the above analysis of the spectral data suggests that, at a transition from the mid- to near-IR range, the effect of interference of the absorption bands of the detected and interfering compounds increases. In view of the specificity of the CO$_2$ and H$_2$O molecules and their absorption spectra, as well as their high contents in gas mixtures of biological origin (up to 3–5 %), the choice of the transparency microwindows in the CO$_2$ and H$_2$O absorption bands, which could be used for highly sensitive spectral analysis of molecular gases, should be even more careful than in the mid-IR range. Consideration of the intensities of the absorption lines of the molecular compounds under study in the bands of overtones and combined vibrations in the near-IR range must be performed taking into account the relative intensities and frequencies of the fundamental transitions; the symmetry of the molecules and the rigidity of their interatomic bonds; and the characteristics of the molecular dipole moment, which determine the mechanical and electrical anharmonicity of the molecules and, therefore, the strength of overtones and combined vibrations and their position in the spectrum. Application of the algorithm described in [5] to the choice of analytical lines at interference of vibration-rotation bands is even more urgent for this spectral range [6-13].
Conclusion

Highly sensitive spectral analysis of trace molecular gases, based on measurement of resonant absorption in their vibration-rotation spectra, requires careful choice of the analytical line because, on the one hand, the concentrations of the compounds studied could be very low and, on the other hand, their vibration-rotation spectra interfere in the IR range with the spectra of the dominant components (water and carbon dioxide) of gaseous mixtures studied. The use of the near-IR range for highly sensitive analysis of gaseous biomarkers leads not only to a decrease in the absolute intensity of the absorption lines in overtones and combined bands for most molecules studied but also to a relative increase in the absorption in the H$_2$O lines, which is due to the high anharmonicity of vibrations of water molecules and high density of CO$_2$ lines in this spectral range. At higher (up to 3–5 %) concentrations of these compounds in a gas mixture studied, the problem of interference of vibration-rotation bands of the detected and interfering compounds in this spectral range becomes even more severe, as a result of which one has carefully choose the transparency microwindows in the transmission spectrum of the gaseous medium analyzed and the absorption lines of the detected compound are the most appropriate for analysis.

Acknowledgments

The work supported by project "Physical methods in agriculture and ecology" and grant of Russian Foundation for Basic Research 18-02-00705.

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