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**SPECTROSCOPIC DETECTION  
OF SULFUR OXIDES IN  
THE AIRCRAFT WAKE**

MOSCOW 2004

## SPECTROSCOPIC DETECTION OF SULFUR OXIDES IN THE AIRCRAFT WAKE

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### Abstract

Absorption/emission spectral regions of SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O and HSO are analyzed for the range from UV ( $\lambda \geq 0.2 \mu\text{m}$ ) to IR ( $\lambda < 30 \mu\text{m}$ ) and are compared with atmospheric transmission spectrum. It is shown that many vibrational bands of considered compounds fall into atmospheric transmission windows. For vibrational bands of SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O and HSO molecules there are some gases which hinder the absorption diagnostics of indicated compounds. These interfering gases are natural components of atmospheric air as well as specific gases of aircraft engine exhaust. It is found that the least influence of the interference takes place in 2400-2700 cm<sup>-1</sup> IR region. Spectroscopic techniques applied for the detection of aircraft engine exhaust compounds are briefly reviewed attending much consideration to SO<sub>2</sub>. IR absorption spectra of SO<sub>2</sub> and other gases are calculated for the conditions of aircraft engine nozzle exit. Narrow spectral intervals suitable for SO<sub>2</sub> detection in a hot flow are determined. The analysis is made for the detection capabilities of CO<sub>2</sub> lasers (including isotope CO<sub>2</sub> lasers) and CO lasers (both fundamental band and first-overtone ones) as applied for SO<sub>2</sub> detection in aircraft engine exhaust.

### СПЕКТРОСКОПИЧЕСКОЕ ДЕТЕКТИРОВАНИЕ ОКИСЛОВ СЕРЫ В САМОЛЕТНОМ СЛЕДЕ

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Проанализированы спектры поглощения/излучения молекул SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O и HSO в области от УФ ( $\lambda \geq 0.2 \mu\text{м}$ ) до ИК ( $\lambda < 30 \mu\text{м}$ ) и проведено их сравнение со спектрами атмосферного пропускания. Показано, что многие колебательные полосы рассмотренных соединений попадают в атмосферные окна прозрачности. Для колебательных полос молекул SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O и HSO определены газы, мешающие диагностике их поглощения. Эти газы являются как естественными компонентами атмосферного воздуха, так и специфическими газами выхлопа авиационного двигателя. Обнаружено, что наименьшее влияние этих газов имеет место в ИК диапазоне частот 2400-2700 см<sup>-1</sup>. Кратко рассмотрены спектроскопические методы детектирования веществ в выхлопе авиационного двигателя, при этом наибольшее внимание уделено SO<sub>2</sub>. Рассчитаны ИК спектры поглощения SO<sub>2</sub> и других газов для условий на срезе сопла двигателя самолета. Определены узкие спектральные интервалы, пригодные для обнаружения SO<sub>2</sub> в горячей струе. Проанализированы возможности CO<sub>2</sub> лазеров (включая лазеры на изотопах CO<sub>2</sub>) и CO лазеров (действующих на фундаментальных колебательных переходах и на переходах первого колебательного обертона) применительно к обнаружению SO<sub>2</sub> в выхлопах авиационного двигателя.

## Contents

|   |           |
|---|-----------|
| 1. Introduction   | 4         |
| 2. Spectroscopic properties of some sulfur oxides   | 5         |
| 3. Absorption bands of sulfur oxides and atmospheric transmission spectra   | 7         |
| 4. Brief review of spectroscopic techniques for SO <sub>x</sub> detection in a hot flow   | 12        |
| <i>Spectroscopic detection of gases in aircraft wake</i>  | 12        |
| 5. Calculation of SO <sub>2</sub> IR absorption spectrum for aircraft exhaust flow  | 16        |
| 6. Analysis of diagnostic possibilities of CO <sub>2</sub> and CO lasers for SO <sub>2</sub><br>detection in aircraft exhaust jet | 20        |
| 7. Conclusions  | 23        |
| <b>8. Acknowledgment</b>  | <b>25</b> |
| 9. References   | 25        |
| Tables  | 28        |

## 1. Introduction

Sulfur compounds (mainly SO, SO<sub>2</sub> and SO<sub>3</sub>) play a key role in chemical reactions taking place in aircraft vortex wake [1]. Concentrations of these compounds at the exit of engine nozzle and in the near wake region govern essentially the further evolution of reactions in other wake areas. The absence of reliable and detailed information on the amount of sulfur compounds in different sections of wake restrains the solution of a number of practical problems related to the ecological impact of aviation on the Earth atmosphere. It is clear that the measurement of concentrations in the immediate vicinity of an aircraft engine is possible only remotely, i.e. by spectroscopic methods.

Spectroscopic methods are of growing interest today due to recent development of powerful lasers that are tunable over large wavelength ranges, which permits the detection of numerous species at low concentrations. In contrast to non-spectroscopic schemes (gas chromatography, etc.) these methods exhibit some unique advantages. They allow non-intrusive, continuous and simultaneous detection of many gases. In some cases they allow three-dimensional space mapping of pollutant concentrations.

Determination of concentrations of sulfur compounds in aircraft wake by spectroscopic methods is, as a matter of fact, the problem of multicomponent mixture analysis. The measurements are rather complicated because of low concentrations of detected gases. To solve such a problem it is necessary to know the absorption (or Raman scattering) cross-sections of all the components of gas mixture at given frequency. The accuracy of concentrations determination depends on the precision of this information, as well as on the choice of sounding frequencies. Sounding frequencies must: 1) coincide with strong lines of detected gas minimizing the overlap with lines of other substances; 2) fall into transmission windows (or microwindows) of the atmosphere.

Detailed absorption spectra of substances are usually measured directly or calculated by means of special computer codes (e.g., FASCODE, LOWTRAN, MODTRAN) using spectroscopic databases (e.g., HITRAN, GEISA). In the calculations the positions and intensities of multiple lines (electronic and vibrational-rotational) are taken into account as well as their spectral contours, which depend on temperature and pressure. Despite great amount of researches on sulfur compounds, it is not enough detailed spectroscopic information for these molecules. For example, HITRAN database contains the information only on some bands of SO<sub>2</sub> and H<sub>2</sub>S.

We consider here the following sulfur compounds: SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O and HSO. The main spectroscopic properties of indicated compounds are reviewed below. Spectral regions of radiation absorption/emission are analyzed for each substance, and interfering gases of atmospheric air and aircraft wake are identified. Also, the spectroscopic schemes applied to detection of aircraft engine exhaust gases are briefly reviewed. The much consideration is given to SO<sub>2</sub> detection. IR spectra of SO<sub>2</sub> and other exhaust gases are calculated for the engine nozzle exit conditions of Boeing 707 aircraft. The analysis is made for detection capabilities of CO<sub>2</sub> and CO lasers as applied for SO<sub>2</sub> detection in aircraft exhaust flow.

## 2. Spectroscopic properties of some sulfur oxides

SO (sulfur monoxide). Ground electronic state of this radical is X<sup>3</sup>Σ<sup>-</sup>. S-O bond energy is D<sub>0</sub>(S-O)= 5.34±0.02 eV. The electronic transitions B<sup>3</sup>Σ<sup>-</sup> – X<sup>3</sup>Σ<sup>-</sup> and A<sup>3</sup>Π – X<sup>3</sup>Σ<sup>-</sup> were observed in the UV regions 1900-2600 and 2400-2600 Å respectively. SO(X<sup>3</sup>Σ<sup>-</sup>) radical is formed as a primary product in SO<sub>2</sub> photolysis in the wavelength region below 2190 Å [2]. In the ground electronic state of <sup>32</sup>S<sup>16</sup>O, its fundamental band is centered at  $\nu_{01} = \omega_e - 2\omega_e x_e = 1137.96 \text{ cm}^{-1}$ . Herewith  $\omega_e = 1149.22 \text{ cm}^{-1}$ ,  $\omega_e x_e = 5.63 \text{ cm}^{-1}$  [3]. More detailed information on electronic and vibrational-rotational spectra of SO is contained, e.g., in [4-10].

SO<sub>2</sub> (sulfur dioxide). Ground electronic state is  $\tilde{X}^1A_1$ , the angle between O-S-O bonds is 119.5°. SO<sub>2</sub> is bent triatomic molecule with C<sub>2v</sub> symmetry, showing slightly asymmetric top rotational spectrum properties [2, 11]. Bond energy D<sub>0</sub>(OS-O) is 5.65±0.01 eV. Sulfur dioxide has complex absorption spectra in near and vacuum UV regions. There exist three main regions of absorption in UV: very weak absorption in the range of 3400-3900 Å, weak absorption in 2600-3400 Å, strong absorption in 1800-2350 Å [2]. SO<sub>2</sub> dissociation to SO+O begins under the action of light with  $\lambda < 2190$  Å. At the wavelengths longer than 2190 Å the light causes strong fluorescence and phosphorescence of SO<sub>2</sub>. Detailed structure of SO<sub>2</sub> electronic bands and relevant absorption cross sections were studied in [12]. SO<sub>2</sub> molecule has intense vibrational and rotational spectra, which are currently sufficiently well studied. Information on high-resolution spectra of many SO<sub>2</sub> bands is contained in HITRAN database [13] (see Table 2).

SO<sub>3</sub> (sulfur trioxide). Ground electronic state of SO<sub>3</sub> has a plane structure with D<sub>3h</sub> symmetry; O-SO<sub>2</sub> bond energy is D<sub>0</sub>(O-SO<sub>2</sub>)=3.55±0.01 eV. Absorption spectrum of sulfur trioxide begins near 3100 Å and consists of weak diffuse bands, superimposing the continuum [2]. In [14, 15] SO<sub>3</sub> UV absorption spectrum was studied in detail with the indication of cross sections. In the Table 4 the positions of main vibrational bands of SO<sub>3</sub> are presented. Rotational Raman spectrum of SO<sub>3</sub> was obtained in [18]. It is possible to use Raman band at 1068 cm<sup>-1</sup> for SO<sub>3</sub> determination in SO<sub>2</sub> by measurement of intensity of this band relative to SO<sub>2</sub> band at 1151 cm<sup>-1</sup> [2].

S<sub>2</sub>O (disulfur oxide). Disulfur oxide is bent triatomic molecule having C<sub>s</sub> symmetry (S=S=O) and, consequently, three nondegenerate vibrational modes are expected:  $\nu_1$ (S-O stretch)= 1166.45 cm<sup>-1</sup>,  $\nu_2$ (bending)= 382 cm<sup>-1</sup>,  $\nu_3$ (S-S stretch)= 679.14 cm<sup>-1</sup>. There is some overlap of  $\nu_1$  band of S<sub>2</sub>O near 1166 cm<sup>-1</sup> and  $\nu_1$  band of SO<sub>2</sub> band near 1152 cm<sup>-1</sup>. In the ground electronic state  $\tilde{X}^1A'$  structural parameters are  $r_{SO} =$

1.4594 Å,  $r_{SS} = 1.8845$  Å,  $\angle SSO = 118.08^\circ$ . Intense richly structured absorption and emission spectra in  $\sim 3400\text{-}2500$  Å are studied and assigned as  $\tilde{C}^1A' - \tilde{X}^1A'$  ( $\pi^* - \pi$ ) electronic transition [19]. High-resolution spectra of  $S_2O$  bands were studied, e.g., in [20, 21].

HSO. Ground electronic state of HSO radical is  $\tilde{X}^2A''$ , the angle between H-S-N bonds is  $102^\circ$ ; bond energies are  $D_0(\text{H-SO}) \approx 1.6$  eV and  $D_0(\text{HS-O}) = 3.4$  eV [2]. Chemiluminescence observed in the region of  $5200\text{-}9600$  Å in the flow containing  $O\text{-H}_2\text{S-O}_3$  mixture, was referred in [22] to  ${}^2A' - {}^2A''$  transition of HSO radical. Excited electronic state  ${}^2A'$ , probably, is formed in the reaction  $\text{SH} + \text{O}_3 \rightarrow \text{HSO}({}^2A') + \text{O}_2$ . Fundamental vibrational frequencies of HSO molecule in electronic states  ${}^2A''$  and  ${}^2A'$  are presented in Table 3.

### 3. Absorption bands of sulfur oxides and atmospheric transmission spectra

Fig. 1 shows transmission spectra of standard atmosphere in a wide wavelength range (from IR to UV). Spectra are calculated using MODTRAN code. It is seen from this figure that abrupt transmission decrease at the beginning of UV region is caused by strong absorption of radiation by ozone (Hartley bands), oxygen (Schumann-Runge system) and by Rayleigh (molecular) scattering of radiation. In Fig. 2 the transmission in IR bands of main atmospheric gases is plotted. In Fig. 3 the wavelength regions of electronic absorption bands of  $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{S}_2\text{O}$  and HSO are shown. Fig. 5 shows the positions of IR absorption bands centers of these molecules. Fig. 4 contains more detailed information on absorption cross-sections of  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{COS}$  and  $\text{CS}_2$  in UV region. From all these figures it is possible to conclude that UV absorption diagnostics of considered sulfur compounds is possible only at small distances. On the other hand, in visible, IR and microwave ranges there is a number of transmission windows (as well as microwindows) where the attenuation of radiation in the atmosphere is low and, hence, diagnostics is possible using large distances. From the standpoints of sulfur compounds detection the

following windows are interesting:  $500\text{-}600\text{ cm}^{-1}$  (for  $\text{SO}_2$ ,  $\text{SO}_3$ ),  $1150\text{-}1200\text{ cm}^{-1}$  (for  $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{S}_2\text{O}$ ),  $2450\text{-}2800\text{ cm}^{-1}$  (for  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HSO}$ ).

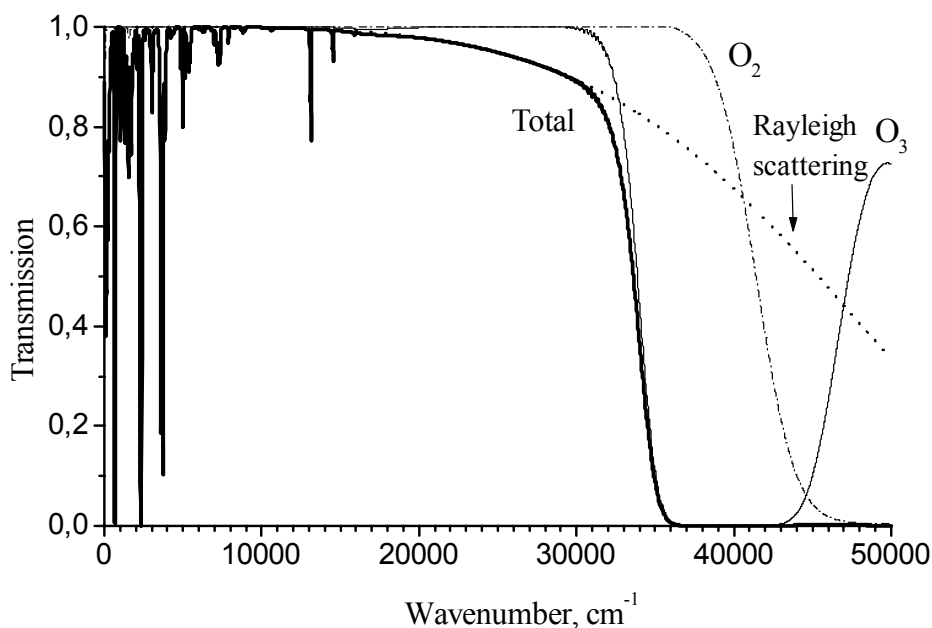


Fig.1. Transmission spectra of standard 1976 US atmosphere from far IR to UV. MODTRAN calculations. Horizontal path  $L=5\text{ km}$  at altitude  $H=12.2\text{ km}$ . No aerosols included. Spectral resolution is  $25\text{ cm}^{-1}$ .

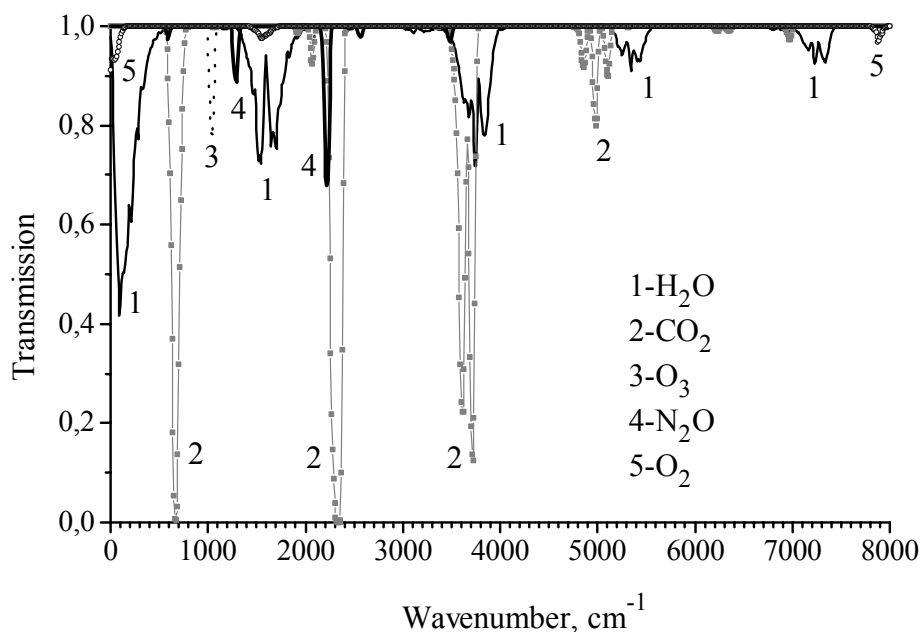


Fig.2. Infrared transmission spectra of standard 1976 US atmosphere. MODTRAN calculations. Horizontal path  $L=5\text{ km}$  at altitude  $H=12.2\text{ km}$ . No aerosols included. Spectral resolution is  $25\text{ cm}^{-1}$ .



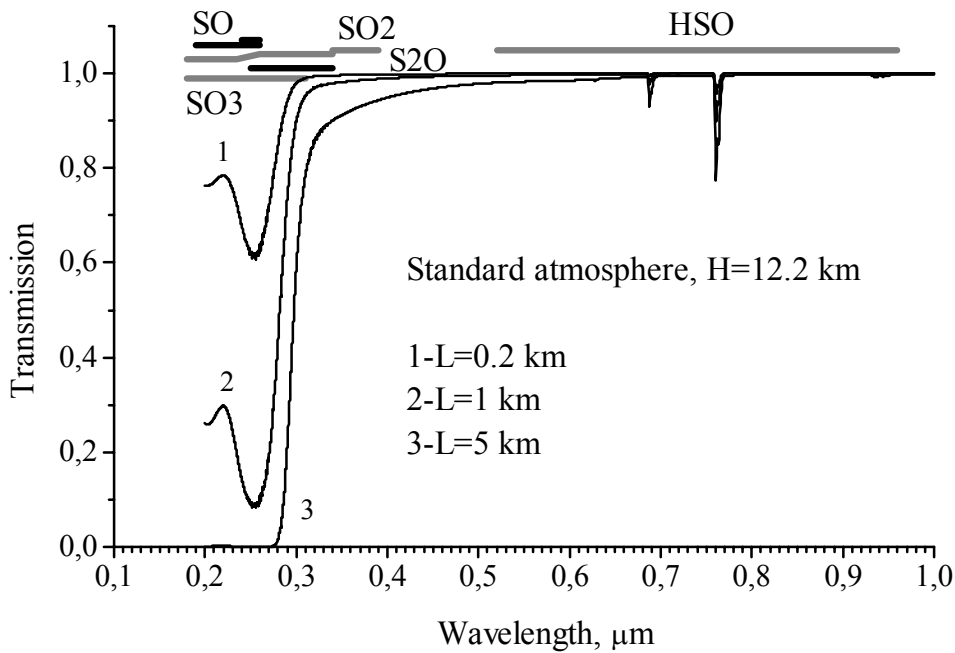


Fig.3. Regions of electronic absorption bands of SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O and HSO (see the text). Transmission spectrum of standard aerosolless atmosphere is shown (MODTRAN calculations). Horizontal path L (indicated near the curves) at altitude H=12.2 km.

Let define the gases, which can hinder absorption diagnostics of sulfur compounds in aircraft wake. Amongst the atmospheric gases we consider molecules contained in HITRAN-96 spectroscopic database: H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, CO, CH<sub>4</sub>, O<sub>2</sub>, NO, SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, HNO<sub>3</sub>, OH, HF, HCl, HBr, HI, ClO, OCS, H<sub>2</sub>CO, HOCl, N<sub>2</sub>, HCN, CH<sub>3</sub>Cl, H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, PH<sub>3</sub>, COF<sub>2</sub>, SF<sub>6</sub>, H<sub>2</sub>S, HCOOH. Many of these gases are presented in significant amount (above atmospheric) in exhausts of aircraft engines (e.g., H<sub>2</sub>O, CO<sub>2</sub>, CO, NO, NO<sub>2</sub>, HNO<sub>3</sub>, OH, H<sub>2</sub>CO, H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>). Among volatile organic compounds the following gases are additionally present in the exhausts: ethene (C<sub>2</sub>H<sub>4</sub>), propene (C<sub>3</sub>H<sub>6</sub>), acetaldehyde (C<sub>2</sub>H<sub>4</sub>O), acrolein (C<sub>3</sub>H<sub>4</sub>O), benzene (C<sub>6</sub>H<sub>6</sub>), toluene (C<sub>7</sub>H<sub>8</sub>), etc. Table 5 shows the information on interfering gases, which hinder detection of sulfur oxides in IR region within indicated spectral intervals ( $\pm 100 \text{ cm}^{-1}$  offset is taken around each central frequency). Fig. 6 shows IR absorption spectra of some organic substances related to aircraft engine exhausts as well as the positions of IR bands of SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O, HSO. From Table 5 and Fig.

6 it follows that minimum influence of interfering gases is observed in the IR region of  $2400\text{-}2700\text{ cm}^{-1}$ . It should be pointed out that this spectral region overlaps with lasing range of first-overtone CO laser [52].

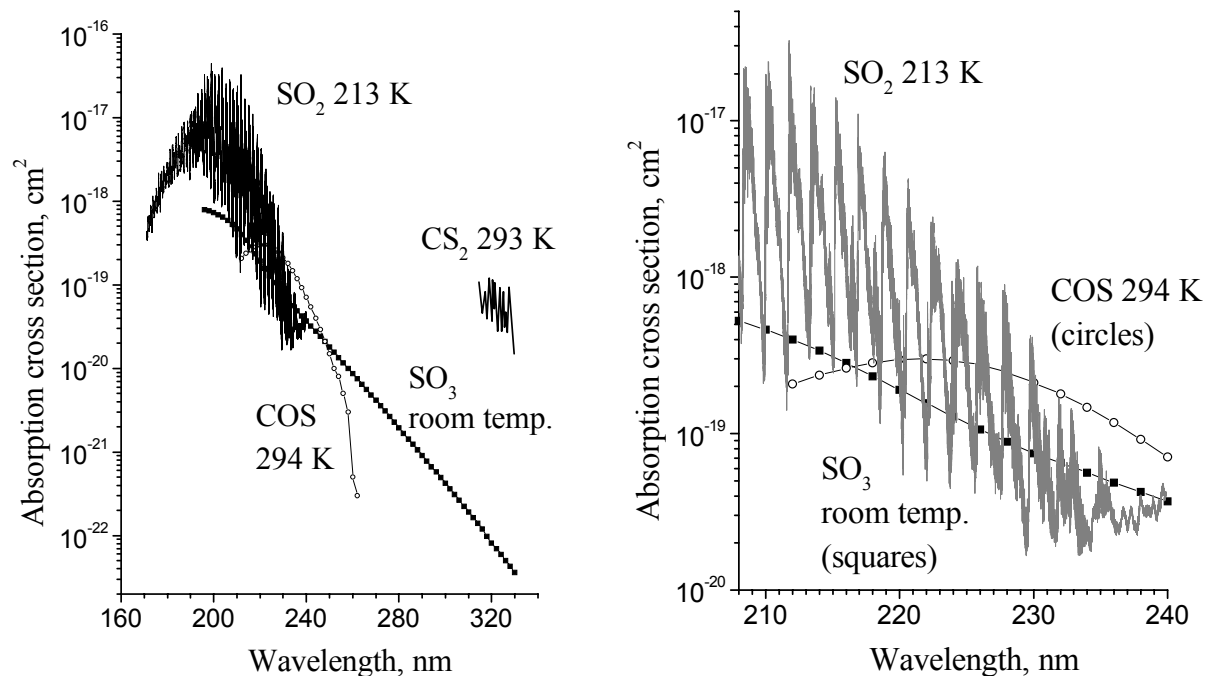


Fig.4. Absorption cross-sections of  $\text{SO}_2$  [12],  $\text{SO}_3$  [15], COS and  $\text{CS}_2$  [14] in UV region. Right figure shows in detail the spectrum in the region of 208-240 nm.

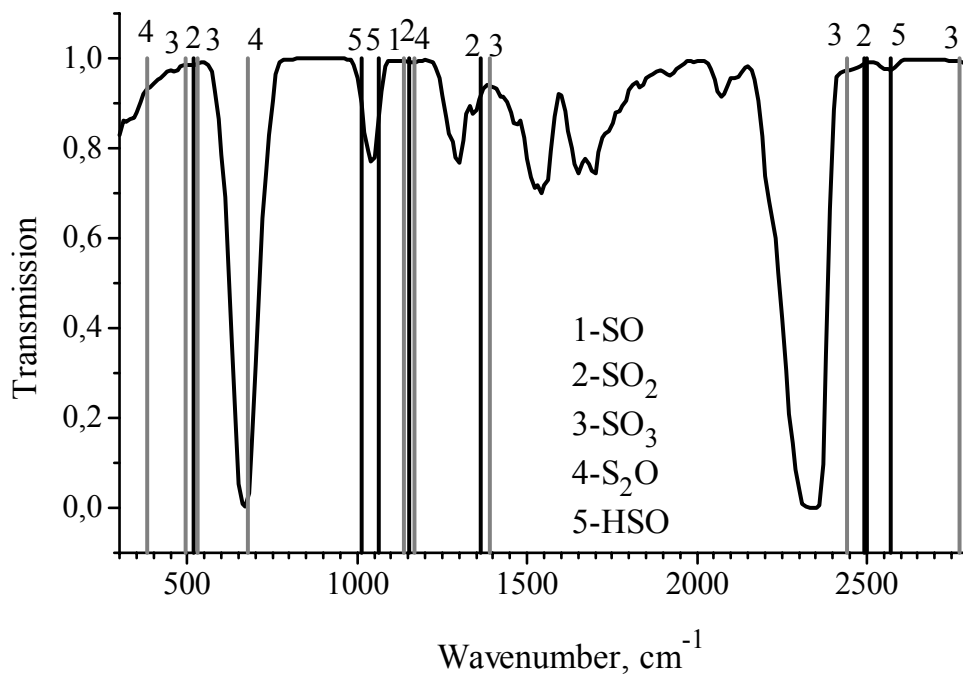


Fig.5. Position of IR bands for SO,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{S}_2\text{O}$  and HSO. Transmission spectrum of standard US 1976 atmosphere is shown. No aerosols included.  $H=12.2\text{ km}$ , horizontal path  $L=5\text{ km}$ .

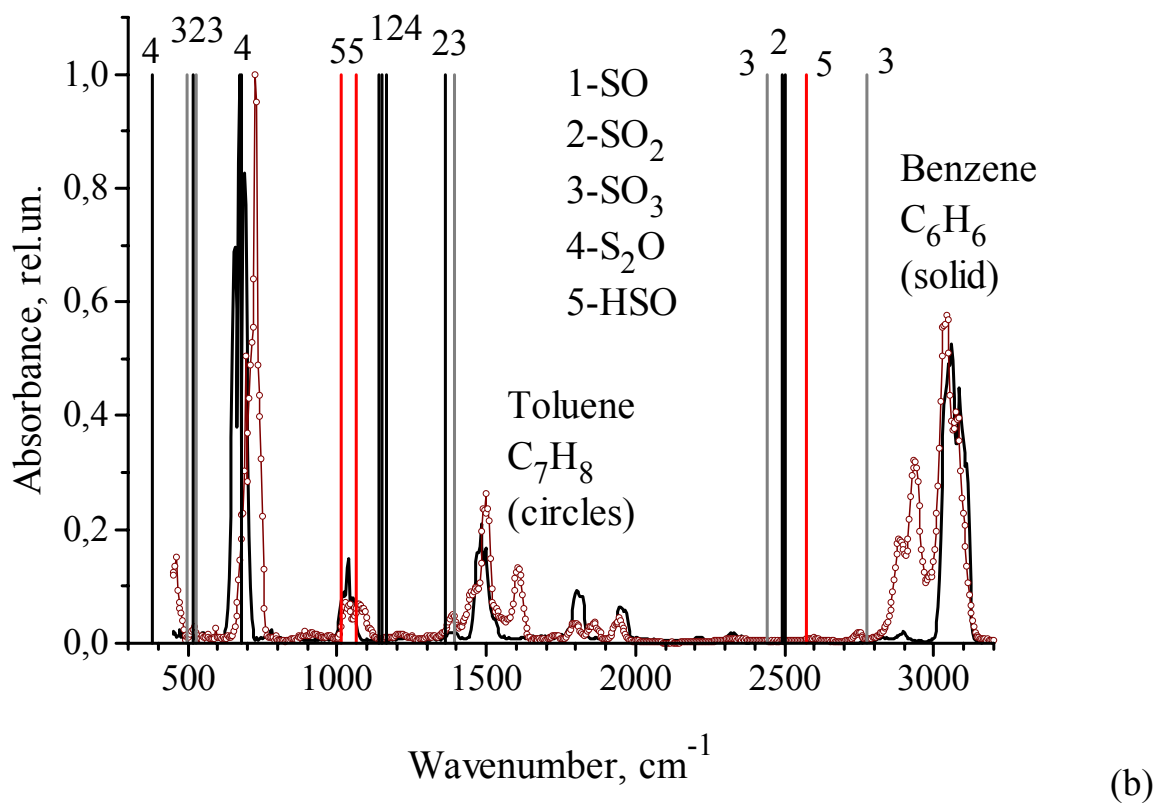
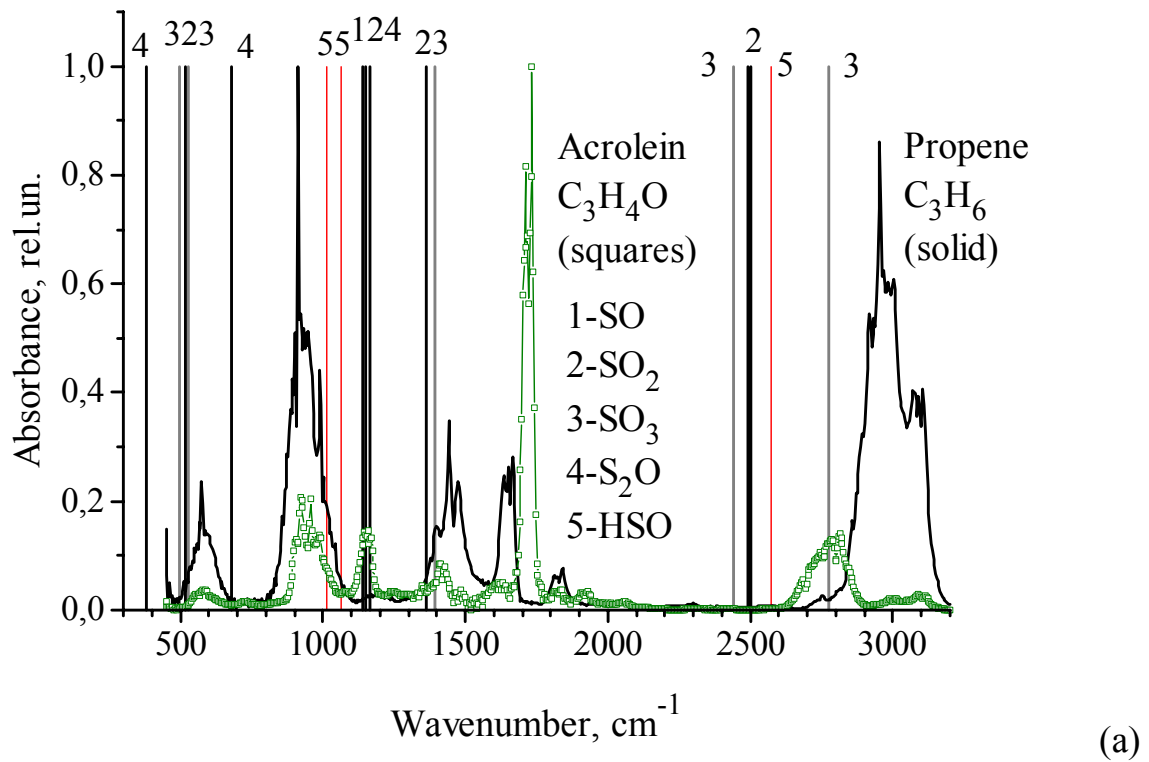


Fig.6. Infrared absorption spectra of some organic compounds related to aircraft engine exhaust. Each spectrum is normalized to its maximum. Position of IR bands of SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O and HSO are indicated.

#### 4. Brief review of spectroscopic techniques for SO<sub>x</sub> detection in a hot flow

Air pollution monitoring by spectroscopic techniques has been reviewed in many monographs and articles, e.g., [23-31]. The physical phenomena used in spectroscopic detection are as follows:

- a) Raman scattering. Advantages: laser emission at a single wavelength is sufficient for detection of many gases. Shortcomings: small scattering cross-sections; possible interference with fluorescence; use of a high-frequency laser is desirable (UV, visible).
- b) Laser-induced fluorescence (LIF). Advantages: especially suitable for detecting of atoms and radicals; somewhat larger scattering cross-sections compared to those for Raman scattering. Shortcomings: multi-line emission quenched by collisions.
- c) Absorption processes. Advantages: very large cross-sections (they are from six to eight orders of magnitude larger than those for Raman scattering).

Today the most widely used spectroscopic detection schemes for air pollution monitoring are based on absorption processes having the largest cross sections. The most informative in the sense of spectroscopic absorption is IR range of spectrum, which contains fundamental absorption bands, their overtones and combination vibration-rotational bands of numerous gases of natural and anthropogenic origin. This spectral region has an ensemble of very intensive and narrow lines of absorbing components. Besides this, in IR a number of laser sources are successfully produced, having discrete as well as continuous tuning of radiation frequency.

#### *Spectroscopic detection of gases in aircraft wake*

Presently, the monitoring of gas flows is conducted by different spectroscopic methods. It is necessary, however, to notice that the words "diagnostics" or "sounding" of the object are often treated in different manner. It is, for instance, visualization, determination of vortex structure, temperature, concentrations of gases and aerosols. The results of sounding can be qualitative as well as quantitative, range-resolved as well as averaged over path length.

The following methods are presently used for the diagnostics of concentrations of gases in exhaust flows:

- laser long-path absorption spectroscopy in visible and UV [32];
- IR tunable diode laser spectroscopy [33, 34];
- Fourier transform IR (FTIR) spectroscopy [35-37];
- laser heterodyne spectroscopy [24];
- laser-induced fluorescence [38];
- resonance holographic interferometry [39]
- Raman spectroscopy [24].

Emphasize that none of these methods is absolutely universal and free from the shortcomings. Further we consider only some of these methods.

Fourier transform spectrometers allow to get the spectra from the interferograms and then, by using the method of least square fitting of measured spectra to calculated ones, extract the concentrations of gases in the mixture considered. The "weak spot" of Fourier spectrometers is their strong sensitivity to different mechanical influences and relatively large time required for the writing of interferograms. However, recently the advanced Fourier IR spectrometer MIROR (Michelson Interferometer with Rotating Retroreflector) was designed [36]. MIROR possesses the increased stability; it is specially intended for the in-flight measurements of aircraft engine emission indexes. However, its spectral resolution ( $\sim 0.12 \text{ cm}^{-1}$ ) is not high, and, as a consequence, the sensitivity of measurements is low and the variety of detecting molecules is limited by the gases which concentrations in the flow is great ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ). Ground-based laboratory measurements of flow temperature and the concentrations of main exhaust gases of aircraft engine ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{CO}$ ) were made using Fourier transform IR spectrometer of greater, than MIROR, spectral resolution equal to  $0.06 \text{ cm}^{-1}$  [35, 37]. The evaluated accuracy of the system was 30%. Even in this case of high-resolution instrument, not all the gases could be measured (see Table

6). For example, it was impossible to detect the gases if their detection limits are greater than the amount in the medium. These are such molecules as  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_4$ . The authors [35,37] fairly noted the interfering role of spectral lines of many gases of a mixture in determination of given gas concentration. Note that this problem is well known in spectroscopic gas analysis.

Diagnostics of  $\text{SO}_2$  by means of diode lasers. Several lines of  $\nu_1$   $\text{SO}_2$  band were registered in [40] by means of the  $\text{Pb}_{1-x}\text{Sn}_x$  ( $x=0.07$ ) diode laser operating in the vicinity of  $\lambda=8.8 \mu\text{m}$  using the method of first derivative. The measurements were conducted in the sample of air containing 670 ppmV  $\text{SO}_2$  sealed to the pressure of 5 Torr (path length was 7.3 m). The selectivity of measurements was extremely high because of low pressure of the sample. Note that in experiment there the lines of moderate intensity of  $\nu_1$  band of  $\text{SO}_2$  were used. If one select the other stronger lines, it is possible to enhance the signal approximately by the factor of 20. In the book of Hinkley [24] the example is also cited related to  $\text{SO}_2$  measurements *in situ* by means of IR diode laser spectroscopy. The  $\lambda=8.8 \mu\text{m}$  radiation of the  $\text{Pb}_{1-x}\text{Sn}_x$  ( $x=0.08$ ) diode laser was directed across the pipe of the 5 m diameter to the receiver. The transmission was only 10% because of burned coal particles. However, they succeeded in defining real-time  $\text{SO}_2$  concentration under the acceptable signal-to-noise ratio. In [34] mid-IR led-salt diode laser and multipass cell were used to measure a few ppmV  $\text{SO}_2$  concentrations in aircraft engine exhaust in an altitude test chamber. Also, the possibility was demonstrated of similar sensitivity for  $\text{SO}_3$ .

$\text{SO}_2$  detection by the heterodyne method [24]. In the Hinkley's laboratory  $\text{SO}_2$  detection was made by the heterodyne method using the commercial  $\text{CO}_2$  laser with  $^{12}\text{C}^{18}\text{O}_2$  rare isotope active medium. The laser operating on this rare isotope radiates shorter wavelengths than  $^{12}\text{C}^{16}\text{O}_2$  laser. The lines 9R(40) ( $\nu=1107.9499 \text{ cm}^{-1}$ ) and 9R(42) ( $\nu=1108.9246 \text{ cm}^{-1}$ ) were used. It was noted that the sensitivity of heterodyne method in  $\text{SO}_2$  detection in the vicinity of  $\lambda \sim 9 \mu\text{m}$  turns out to be higher at high temperatures than at 300 K. For example, at 400 K the sensitivity was

2.5 times higher than at 300 K. It was noted also that it is quite possible to reach the limiting sensitivity of 10 ppmV at 400 K using the path length of 1 m. The contribution of water vapor into absorption of radiation at each frequency must be determined in separate measurements on additional wavelengths.

SO<sub>2</sub> detection by means of spontaneous Raman scattering. Diagnostic methods based on Raman scattering (RS) possess some unique advantages as compared to absorption spectroscopy. The methods of laser remote sensing based on RS are very promising since they provide the possibility of atmosphere sensing from one point. The effect of RS itself does not depend on wavelength as well as on quenching collisions being instant. The important advantage of RS based scheme is that it does not require the selective excitation of different gases by separate frequencies because the backscattered signal contains the spectra of all RS active air components with the intensities of lines being proportional to concentrations. At the same time the cross-sections of spontaneous RS are typically less than those of Rayleigh scattering by approximately three orders of magnitude. For example, SO<sub>2</sub> differential section  $d\sigma/d\Omega$  is approximately equal to  $10^{-29}$  cm<sup>2</sup>/sr (nonresonant RS) and  $10^{-26}$  cm<sup>2</sup>/sr (resonant RS). As a result of careful measurements of RS differential cross section

$\left(\frac{d\sigma}{d\Omega}\right)_{Q,N_2}$  of Q-branch of nitrogen there was obtained the following weighted

average value  $\left(\frac{d\sigma}{d\Omega}\right)_{Q,N_2} = (5.05 \pm 0.1) \cdot 10^{-48} \cdot (v_0 - 2331)^4$ , cm<sup>6</sup>/sr, where  $v_0$  is a

wavenumber of exciting radiation (cm<sup>-1</sup>). Differential cross-sections of other gases can be calculated using the following expression

$\frac{d\sigma_j}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_{Q,N_2} \cdot \frac{(v_0 - v_j)^4}{(v_0 - 2331)^4} \cdot \Sigma_j$ , where  $v_j$  is RS band center of the component

$j$ ;  $\Sigma_j$  is relative (as compared to N<sub>2</sub>) normalized total (i.e., for the whole band) differential cross section of RS for the component  $j$  (see Table 7).

In [41] by means of mobile installation the diagnostics of H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub> and kerosene vapor was made with the spatial resolution of ~10 m at the day time. The estimates of the contents of SO<sub>2</sub> (300 ppmV) and kerosene (17 ppmV) molecules prove the service ability of RS method for the remote monitoring of the air pollution sources even at a day time. In [42] the results of field experiments on the remote determination of composition and temperature of combustion products of aircraft gas turbine engine were described. Nitrogen laser ( $\lambda=337.1$  nm) was used at the pulse repetition rate of 500 Hz. The analysis of H. Inaba for typical RS LIDAR systems made in the book [24] shows that carefully developed RS LIDAR scheme will have the sensitivity allowing to detect the atmospheric pollution having the concentrations of several ppmV at distances of several hundred meters. Such sensitivity being, certainly, insufficient for the measurement of pollution in usual air, is completely suitable for monitoring the content of different chemical substances in stationary sources: injections of smoke-stacks, exhausts of car and aircraft engines.

## **5. Calculation of SO<sub>2</sub> IR absorption spectrum for aircraft exhaust flow**

In order to study the possibilities of SO<sub>2</sub> detection by means of IR absorption we calculated IR spectrum of jet exhaust gases of Boeing 707 aircraft as well as of surrounding atmosphere at the cruising altitude of H=12.2 km. The calculations were made for typical conditions of the US standard atmosphere and the engine exit plane (see Table 8). The results of calculations are presented in Fig. 7 and 8. The absorption lines of hot SO<sub>2</sub> in IR are overlapped mainly by H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> gases (the order of gases reflects the degree of their interference). In Fig. 7 the absorption spectrum of hot SO<sub>2</sub> and total spectrum of all the other exhaust gases are shown. Also, the absorption spectrum of ambient (cold) atmosphere is shown (the same gases as in exhaust plus ozone; certainly, with mole fractions in ambient air). Atmospheric mole fractions are taken from [43].



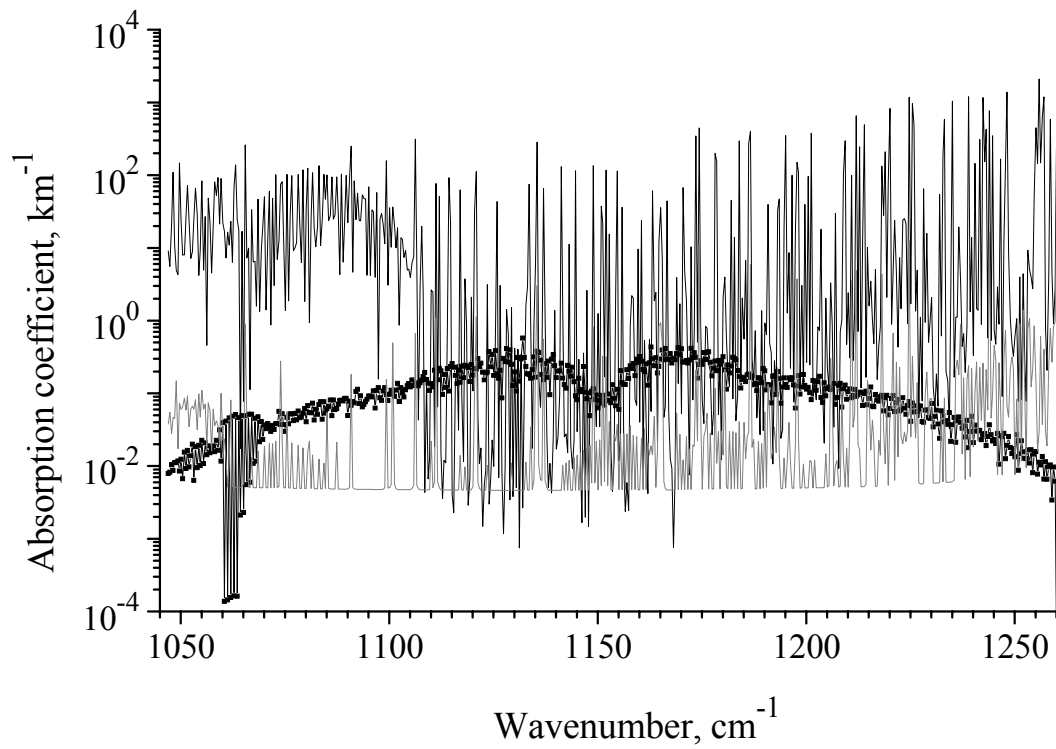
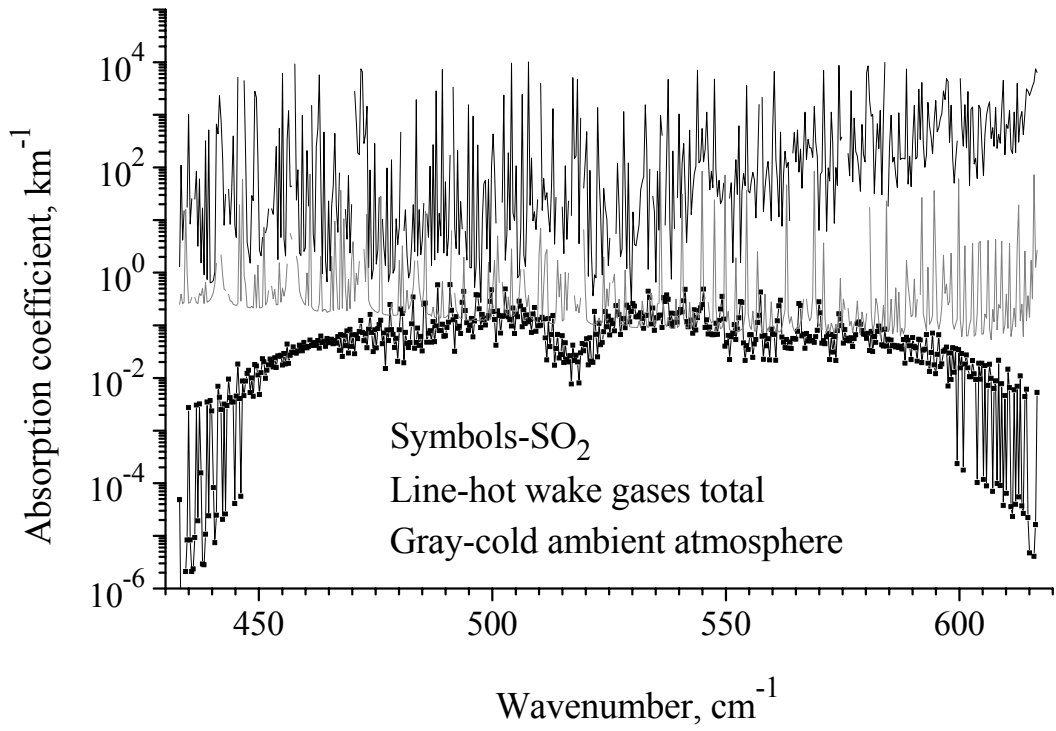


Fig.7. Absorption spectra of hot SO<sub>2</sub> and total hot wake gases in B707 near wake. Ambient total absorption is also shown (the same gases+ozone). Altitude H=12.2 km, P=0.1715 atm. Nozzle exit plane conditions. T=604.7 K. Mole fractions are taken from [1] and [43].

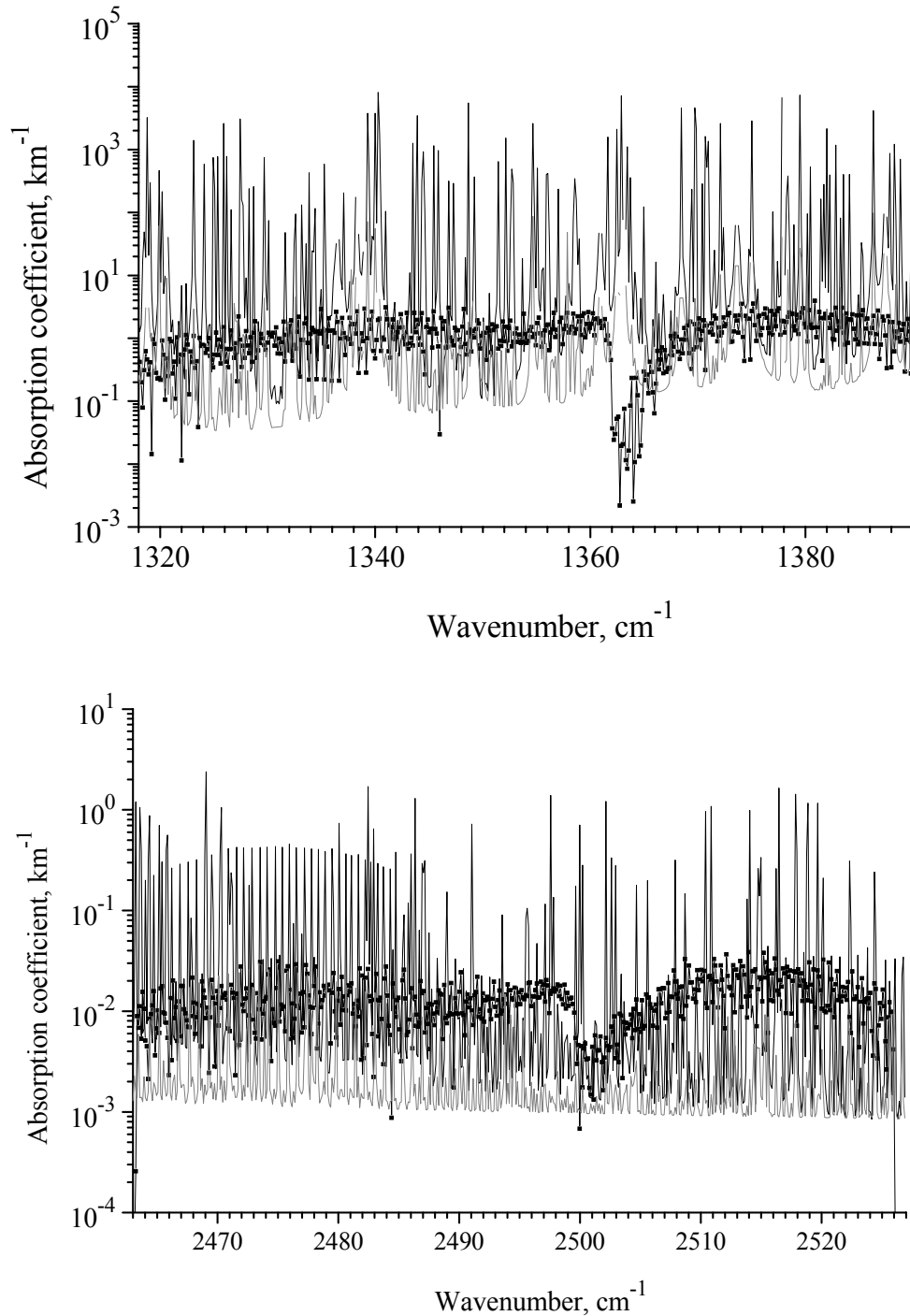


Fig.7 (continued). Absorption spectra of hot  $\text{SO}_2$  and total hot wake gases in B707 near wake. Ambient total absorption is also shown (the same gases+ozone). Altitude  $H=12.2$  km,  $P=0.1715$  atm. Nozzle exit plane conditions.  $T=604.7$  K. Mole fractions are taken from [1] and [43].

The difference of absorption spectra of  $\text{SO}_2$  and all other (background) gases of hot jet is presented in Fig. 8. These data allow us to select the spectral intervals, which are suitable for  $\text{SO}_2$  diagnostics in a hot exhaust of aircraft.

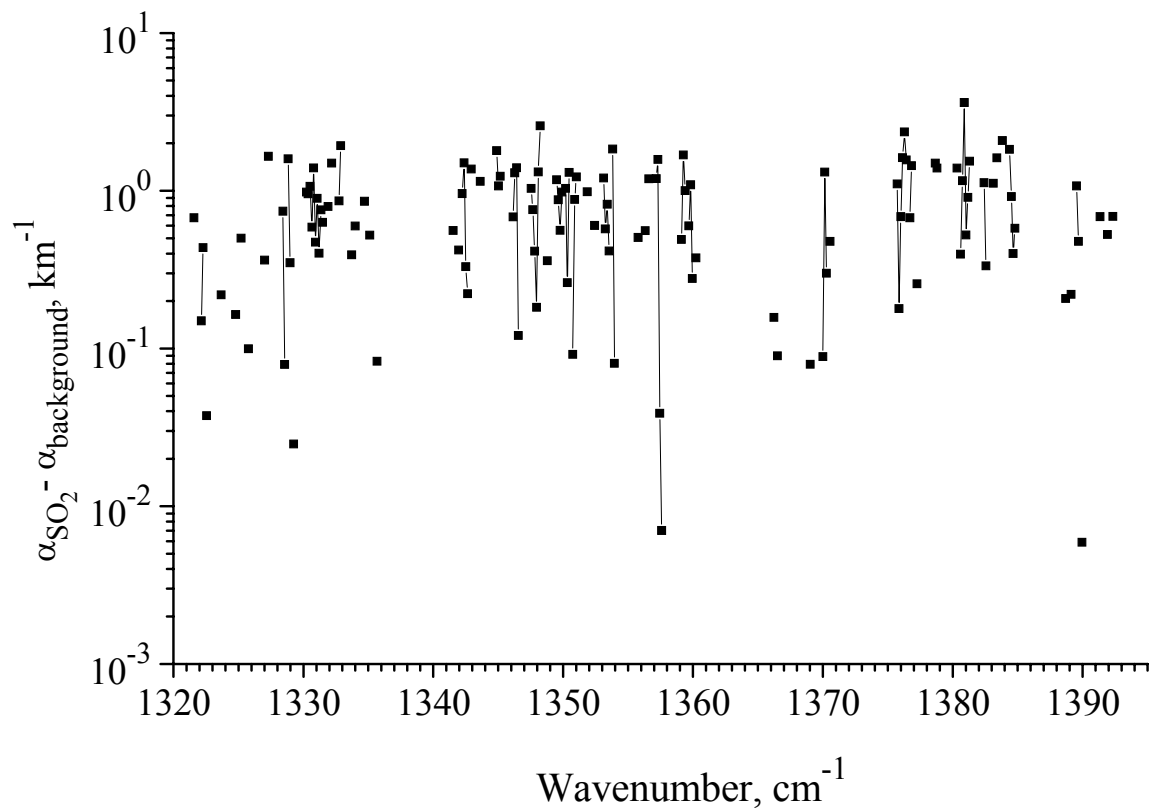
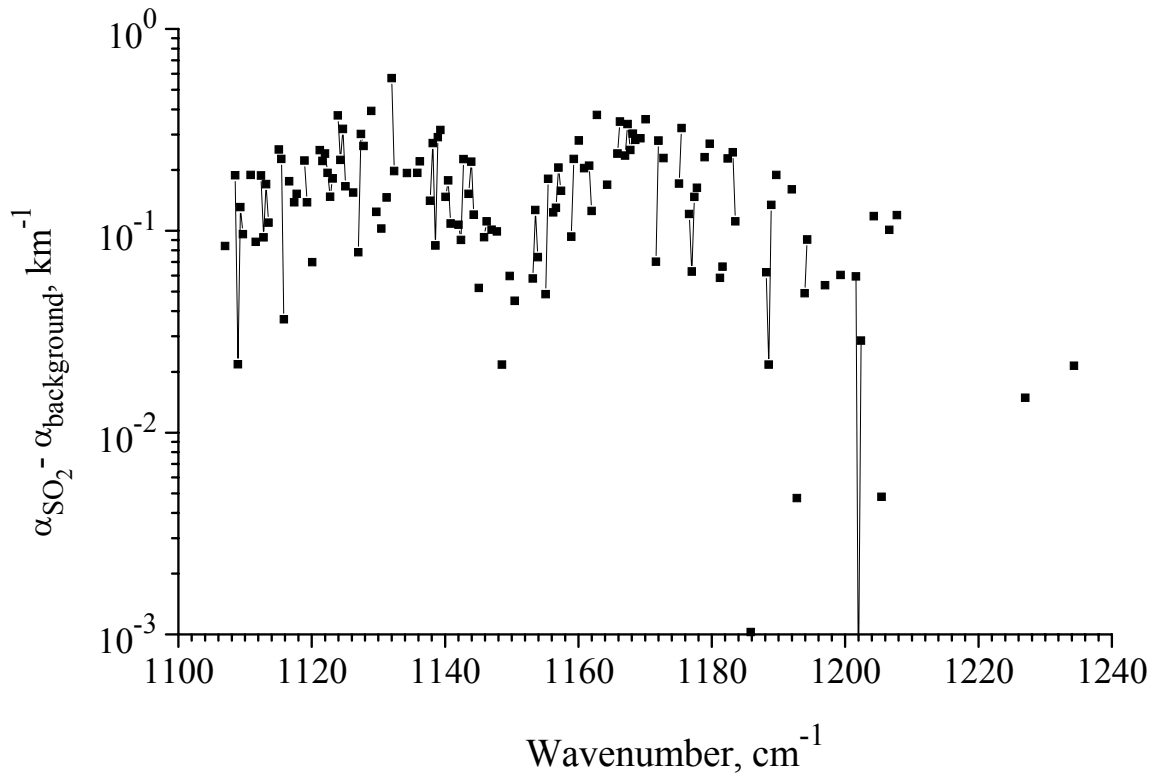


Fig. 8 (see also below).

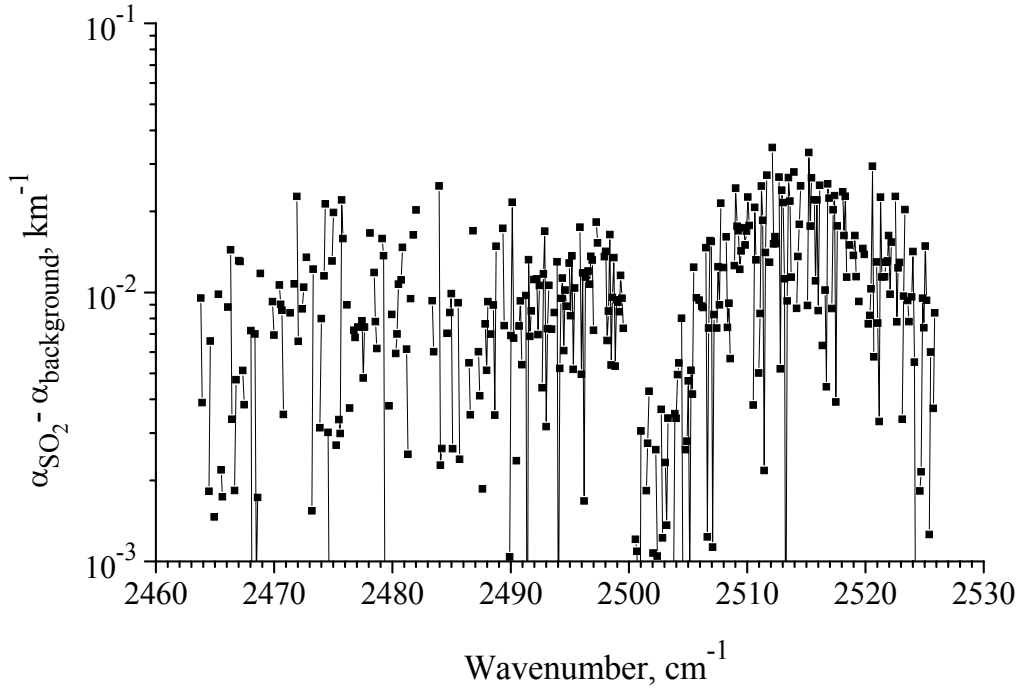


Fig.8.(continued). Difference of absorption spectra of hot SO<sub>2</sub> and total hot wake gases in B707 aircraft near wake. Altitude H=12.2 km, P=0.1715 atm. Nozzle exit plane conditions [1]. T=604.7 K.

The most contrast of SO<sub>2</sub> with respect to absorption of other gases is observed on the following frequencies: 1380.88 cm<sup>-1</sup> ( $\Delta\alpha=3.62$  km<sup>-1</sup>), 1348.23 cm<sup>-1</sup> ( $\Delta\alpha=2.58$  km<sup>-1</sup>), 1376.28 cm<sup>-1</sup> ( $\Delta\alpha=2.36$  km<sup>-1</sup>), 1383.82 cm<sup>-1</sup> ( $\Delta\alpha=2.08$  km<sup>-1</sup>), 1332.88 cm<sup>-1</sup> ( $\Delta\alpha=1.93$  km<sup>-1</sup>). Note that at frequency 1380.88 cm<sup>-1</sup> absorption coefficient of SO<sub>2</sub> reaches its maximum equal to  $\alpha_{\text{SO}_2}=3.945$  km<sup>-1</sup>.

## 6. Analysis of diagnostic possibilities of CO<sub>2</sub> and CO lasers for SO<sub>2</sub> detection in aircraft exhaust jet

CO<sub>2</sub> and CO lasers [44, 45] being now one of the most powerful IR lasers are widely used in spectroscopic diagnostics of various media. CO laser operating in fundamental and first-overtone bands looks like an attractive device for remote spectroscopic gas analysis [46-50]. Our goal was to evaluate the diagnostic possibilities of indicated lasers for SO<sub>2</sub> detection for the conditions of aircraft exhaust jet. The calculations were performed using the code ANLINES [51] and

HITRAN-96 database [13]. The following extended sets of emission frequencies of lasers were used. CO<sub>2</sub> laser: main isotope 626 (i.e. <sup>16</sup>O<sup>12</sup>C<sup>16</sup>O) and isotope modifications 627, 628, 636, 828; total 713 transitions from 857.94 to 1116.05 cm<sup>-1</sup>. The positions of CO<sub>2</sub> laser lines were taken from the book of Witteman [44]. Fundamental band CO laser (main isotope <sup>12</sup>C<sup>16</sup>O; 726 transitions from 1162.42 to 2022.72 cm<sup>-1</sup>). First-overtone CO laser (main isotope <sup>12</sup>C<sup>16</sup>O, 726 transitions from 2364.93 to 4034.06 cm<sup>-1</sup>). The positions of 726 transitions V=4-36, J=4-25 of fundamental band CO laser and first-overtone CO laser [52] were calculated using spectroscopic constants of <sup>12</sup>C<sup>16</sup>O molecule [53].

The analyzed gas mixture consisted of nine IR active gases: H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O, CO, CH<sub>4</sub>, NO, SO<sub>2</sub>, NO<sub>2</sub>, OH. The pressure-induced absorption of N<sub>2</sub> and O<sub>2</sub> was considered as a continuum. Besides this, N<sub>2</sub> and O<sub>2</sub> gases served as broadening gases. Analytical lines were selected using the following criterion: 1) nearly the exact resonance with of laser frequency with molecular absorption line (within 2 halfwidths); 2) the contribution of given molecular line into absorption cross-section of the gas considered must be greater than 10<sup>-22</sup> cm<sup>2</sup>. Using this criterion there were selected 82 lines of CO<sub>2</sub> laser, 366 lines of fundamental band CO laser and 244 lines of first-overtone CO laser. These three sets of analytical frequencies were then examined for sensitivity and selectivity in determination of concentrations of gases of the mixture. Minimum detectable concentrations  $c_j^{\min}$  were calculated assuming moderate value of minimum detectable absorption coefficient  $\alpha^{\min} = 10^{-6}$  cm<sup>-1</sup>. Note that typical  $\alpha^{\min}$  value for CO<sub>2</sub> laser photoacoustic spectroscopy [8] is less than 10<sup>-7</sup> cm<sup>-1</sup>.

The detection sensitivity of a substance  $j$  is related with the strength of its absorption and usually is defined by minimum detectable concentration  $c_j^{\min}$ :

$c_j^{\min} = (1/N) \cdot \min_i(\alpha^{\min} / \sigma_{ij})$ , where  $\alpha^{\min}$  is the minimum detectable absorption

coefficient defined by the method of measurement and apparatus,  $\sigma_{ij}$  is the absorption cross-section of substance  $j$  at laser transition  $i$ ,  $N$  is total concentration of molecules in mixture. Note that  $c_j^{\min}$  is the exact measure of minimum detectable concentration only for interference-free conditions, i.e., when spectra of other substances of the mixture do not overlap the spectrum of gas  $j$  at laser frequency  $i$  (this is exactly the case when the gas  $j$  is a single absorber in the mixture).

For the determination of the concentration of substance  $j$  on corresponding laser frequency  $j$  the possible influence of substance  $k$  is described by means of cross sensitivity  $Q_{jk} = \sigma_{jk} / \sigma_{jj}$ . The uncertainty  $\Delta c_k$  of determination of concentration  $c_k$  of the substance  $k$  increases the uncertainty  $\Delta c_j$  of measured concentration  $c_j$  of the substance  $j$  as follows:  $\Delta c_j \geq Q_{jk} \Delta c_k$ . It is clear from this relation that to enhance the accuracy of gas analysis of multicomponent mixture it is necessary to select those laser frequencies at which the values of cross sensitivities  $Q_{jk}$  ( $j \neq k$ ) are small (or reduce  $\Delta c_k$ , that is not always possible).

The results of the calculation of cross sensitivity  $Q_{jk}$  for selected analytical frequencies of CO<sub>2</sub> laser, fundamental band CO and first-overtone CO lasers are presented in Tables 9, 11, 13. Minimum detectable concentrations  $c_j^{\min}$ , the estimate of total interference of other gases  $\sum_{j \neq k} Q_{jk}$  and absorption coefficients for analytical frequencies of CO<sub>2</sub>, fundamental band CO and first-overtone CO lasers are given in Tables 10, 12, 14.

It follows from the listed data that:

1) minimum detectable concentrations of SO<sub>2</sub> which can be measured by means of CO<sub>2</sub> lasers, fundamental band CO laser and first-overtone CO laser are respectively 16.7, 0.38 and 23.8 ppmV, i.e. the best sensitivity of detection can be reached with using fundamental band CO laser;

- 2) when using the II 828 R(54) transition of CO<sub>2</sub> laser for SO<sub>2</sub> diagnostics the noticeable interference of N<sub>2</sub>O spectrum occurs. In this case  $Q_{jk}=0.28$ . Note that this laser frequency falls into solely "clear" spectral interval (absorption coefficient is only 0.07 km<sup>-1</sup>);
- 3) when detecting SO<sub>2</sub> using 28-27 P(23) line of fundamental band CO laser the spectral interference of other gases (amongst considered) is negligible. At the same time the total absorption is noticeable ( $\alpha=4.4$  km<sup>-1</sup>). It is mainly caused by water vapor which concentration in aircraft wake is great;
- 4) when detecting SO<sub>2</sub> with using 35-33 P(22) line of first-overtone CO laser the spectral interference of other gases (amongst considered) is also low (low influence results only from N<sub>2</sub>O,  $Q_{jk}=0.04$ ). The total absorption at this frequency is low ( $\alpha=0.03$  km<sup>-1</sup>) being less than that for CO<sub>2</sub> laser.

## 7. Conclusions

1. Spectral regions of absorption/emission of sulfur oxide molecules (SO, SO<sub>2</sub>, SO<sub>3</sub>, S<sub>2</sub>O and HSO) are analyzed in a wide wavelength range from UV ( $\lambda \geq 0.2$   $\mu\text{m}$ ) to IR ( $\lambda < 30$   $\mu\text{m}$  ). In the IR range these regions correspond to vibrational transitions, while in visible and UV ranges to electronic transitions of indicated molecules.
2. Atmospheric transmission spectra are calculated and analyzed in a wide wavelength range (from IR to UV). It is shown that absorption diagnostics of sulfur oxides in the UV range is possible only at small distances because of strong absorption of radiation by ozone, oxygen and Rayleigh scattering. On the other hand, in visible, IR and microwave regions there are some transmission windows (as well as microwindows), where attenuation of radiation is low, and so long-path diagnostics is possible. This is particularly important for the external diagnostics of aircraft wake (from the board of another air vehicle). It is found also that many vibrational bands of sulfur compounds considered just fall into transmission

windows: 500-600  $\text{cm}^{-1}$  ( $\text{SO}_2$ ,  $\text{SO}_3$ ), 1150-1200  $\text{cm}^{-1}$  ( $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{S}_2\text{O}$ ), 2450-2800  $\text{cm}^{-1}$  ( $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HSO}$ ).

3. For vibrational bands of  $\text{SO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{S}_2\text{O}$  and  $\text{HSO}$  the gases are determined which can hinder IR absorption diagnostics of indicated molecules. These interfering gases are natural components of atmospheric air as well as specific gases of engine exhaust. It is found that the least influence of interfering gases takes place in 2400-2700  $\text{cm}^{-1}$  region overlapping with lasing range of a first-overtone CO laser.

4. The analysis of traditional spectroscopic methods with reference to detection of aircraft exhaust gases demonstrates that the measurement of  $\text{SO}_2$  concentration in the near wake of aircraft ( $\text{SO}_2$  mole fraction is about 1-10 ppmV) is quite real to be realized by various methods. These can be, e.g., long-path laser IR absorption spectroscopy (including CO and  $\text{CO}_2$  lasers, diode spectroscopy, heterodyne spectroscopy, etc.), as well as Raman scattering LIDAR method. LIDAR scheme based on RS can have the sensitivity, allowing to detect the atmospheric pollution having the concentrations of several ppmV at a distance of several hundred meters. For the time being, Fourier transform spectroscopy does not seem to be able to ensure acceptable sensitivity of  $\text{SO}_2$  detection in aircraft exhaust.

5. The spectral intervals suitable for  $\text{SO}_2$  IR absorption detection in engine exhaust hot flow are determined. If very sensitive detection of  $\text{SO}_2$  is important, 1330-1390  $\text{cm}^{-1}$  interval is preferable for measurements. The most contrast of  $\text{SO}_2$  absorption with respect to absorption of other gases is observed on the following frequencies: 1380.88  $\text{cm}^{-1}$  ( $\Delta\alpha=3.62 \text{ km}^{-1}$ ), 1348.23  $\text{cm}^{-1}$  ( $\Delta\alpha=2.58 \text{ km}^{-1}$ ), 1376.28  $\text{cm}^{-1}$  ( $\Delta\alpha=2.36 \text{ km}^{-1}$ ), 1383.82  $\text{cm}^{-1}$  ( $\Delta\alpha=2.08 \text{ km}^{-1}$ ), 1332.88  $\text{cm}^{-1}$  ( $\Delta\alpha=1.93 \text{ km}^{-1}$ ). In the case of  $\text{SO}_2$  detection with enhanced selectivity the spectral region of 2400-2700  $\text{cm}^{-1}$  is preferable.

6. The analysis is made for the detection capabilities of  $\text{CO}_2$  lasers (including isotope  $\text{CO}_2$  lasers) and CO lasers (fundamental band and first-overtone ones) as



applied for SO<sub>2</sub> detection in aircraft exhaust flow. Calculated minimum detectable concentrations of SO<sub>2</sub> were found to be 16.7, 0.38 and 23.8 ppmV for CO<sub>2</sub> lasers, fundamental band CO laser and first-overtone CO laser respectively. These estimates were obtained in the suggestion that minimum detectable absorption coefficient of apparatus is 10<sup>-6</sup> cm<sup>-1</sup>. Thereby, the sensitivity of SO<sub>2</sub> detection is the best in the case of application of fundamental band CO laser. The spectral interference of other gases (amongst considered) was found as a totally negligible for determination of SO<sub>2</sub> concentration with using selected analytical lines of considered lasers.

## 8. Acknowledgment

This research was supported by the ISTC Projects 2249 and 2415P.

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**Table 1.** Electronic transitions of SO radical [2].

| Electronic state | Energy $E_0$ , eV | System (emission region)           | Lifetime, ns |
|------------------|-------------------|------------------------------------|--------------|
| $X^3\Sigma^-$    | 0                 |                                    |              |
| $a^1\Delta$      | 0.79              |                                    |              |
| $b^1\Sigma^+$    | 1.303             | $b \rightarrow X$ , (9500-10900 Å) |              |
| $A^3\Pi_0$       | 4.748             | $A \rightarrow X$ (2400-2600 Å)    |              |
| $B^3\Sigma^-$    | 5.161             | $B \rightarrow X$ (1900-2600 Å)    | $17 \pm 3$   |

**Table 2.** The most significant absorption bands of  $^{32}\text{S}^{16}\text{O}_2$  in microwave and IR ([13]).

| Band $V'-V''$ | $\lambda_0$ , $\mu\text{m}$ | $\nu_0$ , $\text{cm}^{-1}$ | $\nu_{\text{min}}-\nu_{\text{max}}$ , $\text{cm}^{-1}$ | Number of lines | Integral intensity, $\text{cm}/\text{molec.}$ |
|---------------|-----------------------------|----------------------------|--|-----------------|---|
| (000)-(000)   |                             |                            | 0-257  | 1883            | $3.954 \cdot 10^{-19}$                        |
| (010)-(000)   | 19.31                       | 517.75                     | 433-617  | 3326            | $3.899 \cdot 10^{-18}$                        |
| (100)-(000)   | 8.68                        | 1151.7135                  | 1047-1262  | 5812            | $3.519 \cdot 10^{-18}$                        |
| (001)-(000)   | 7.34                        | 1362.0295                  | 1316-1394  | 2075            | $3.080 \cdot 10^{-17}$                        |
| (111)-(010)   | 4.01                        | 2492.4438                  | 2463-2516  | 654             | $2.110 \cdot 10^{-20}$                        |
| (101)-(000)   | 4.00                        | 2499.8701                  | 2463-2527  | 1883            | $3.954 \cdot 10^{-19}$                        |

**Table 3.** Fundamental vibrational frequencies of HSO molecule,  $\text{cm}^{-1}$  [22].

| Band    | Electronic state $X^2A''$ | Electronic state $^2A'$ |
|---------|---------------------------|-------------------------|
| $\nu_1$ | 2570                      | 2769                    |
| $\nu_2$ | 1063                      | 828                     |
| $\nu_3$ | $1013 \pm 5$              | $702 \pm 5$             |

**Table 4.** Vibrational bands of SO<sub>3</sub> [16, 17].

| Band              | Band center, cm <sup>-1</sup> | Note              |
|-------------------|-------------------------------|-------------------|
| $\nu_1(a_1')$     | 1068                          | Only Raman active |
| $\nu_2(a_2'')$    | 495                           |                   |
| $\nu_3(e')$       | 1391.5205                     |                   |
| $\nu_4(e')$       | 529                           |                   |
| $\nu_1+\nu_3(e')$ | 2443                          |                   |
| $2\nu_3(e')$      | 2773                          |                   |

**Table 5.** Interfering gases which hinder absorption diagnostics of sulfur oxides in IR region.

| Sulfur oxide    | Band                            | Range, cm <sup>-1</sup> | Interfering gases of atmospheric air and engine exhaust (by HITRAN-92)  | Other interfering organics contained in engine exhaust |
|-----------------|---------------------------------|-------------------------|---|--|
| SO              | 0-1                             | 1137.96<br>±100         | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , HOCl, H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , PH <sub>3</sub> , COF <sub>2</sub> , H <sub>2</sub> S                               | Acrolein, benzene, toluene, ethene                     |
| SO <sub>2</sub> | $\nu_2$                         | 517.75<br>±100          | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , NO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , HF, HCl, HCN  | Acrolein, propene, toluene                             |
|                 | $\nu_1$                         | 1151.7135<br>±100       | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , HOCl, H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , PH <sub>3</sub> , COF <sub>2</sub> , H <sub>2</sub> S   | Acrolein, benzene, toluene, ethene                     |
|                 | $\nu_3$                         | 1362.0295<br>±100       | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , O <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , OH, HOCl, HCN, H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , PH <sub>3</sub> , COF <sub>2</sub> , H <sub>2</sub> S                       | Acrolein, benzene, propene, toluene, ethene            |
|                 | $\nu_1+\nu_2$<br>$+\nu_3-\nu_2$ | 2492.4438<br>±100       | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , OH, HCl, HBr, HI, N <sub>2</sub>   |  |
| HSO             | $\nu_1$                         | 2499.87<br>±100         | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , OH, HCl, HBr, HI, N <sub>2</sub>   |  |
|                 | $\nu_2$                         | 1063<br>±100            | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , H <sub>2</sub> O <sub>2</sub> , PH <sub>3</sub> , COF <sub>2</sub> , H <sub>2</sub> S   | Acrolein, benzene, propene, toluene, ethene            |
|                 | $\nu_3$                         | 1013<br>±100            | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , PH <sub>3</sub> , COF <sub>2</sub> , SF <sub>6</sub> , H <sub>2</sub> S | Acrolein, benzene, propene, toluene, ethene            |
| SO <sub>3</sub> | $\nu_2$                         | 495<br>±100             | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , HF, HCl, HCN  | Acrolein, propene, toluene                             |
|                 | $\nu_3$                         | 1391.5205<br>±100       | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , O <sub>2</sub> , NO, SO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , OH, HCN, H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , PH <sub>3</sub> , H <sub>2</sub> S                          | Acrolein, benzene, propene, toluene, ethene            |
|                 | $\nu_4$                         | 529<br>±100             | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NO <sub>2</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , HF, HCl, HCN  | Acrolein, propene, toluene                             |
|                 | $\nu_1+\nu_3$                   | 2443                    | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , OH,  |  |

|                  |                 |                     |   |                               |
|------------------|-----------------|---------------------|---|-------------------------------|
|                  |                 | $\pm 100$           | HCl, HBr, HI, N <sub>2</sub>  |                               |
|                  | 2v <sub>3</sub> | 2773<br>$\pm 100$   | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , NO <sub>2</sub> , OH,<br>HCl, HBr, H <sub>2</sub> CO   | Acrolein, propene,<br>toluene |
| S <sub>2</sub> O | v <sub>1</sub>  | 1166.5<br>$\pm 100$ | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NH <sub>3</sub> ,<br>HNO <sub>3</sub> , HOCl, H <sub>2</sub> O <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> , PH <sub>3</sub> ,<br>COF <sub>2</sub> , H <sub>2</sub> S                           | Acrolein, ethene              |
|                  | v <sub>2</sub>  | 382<br>$\pm 100$    | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , CH <sub>4</sub> , SO <sub>2</sub> , NH <sub>3</sub> ,<br>HNO <sub>3</sub> , OH, HF, HCl, HBr, HI,<br>HOCl  | Acrolein, propene,<br>toluene |
|                  | v <sub>3</sub>  | 679<br>$\pm 100$    | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , NO <sub>2</sub> ,<br>NH <sub>3</sub> , HNO <sub>3</sub> , OH, HF, HCl, HI, ClO,<br>HOCl, HCN, C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , PH <sub>3</sub> , COF <sub>2</sub> | Benzene, toluene              |
| HSO              | v <sub>1</sub>  | 2570 $\pm 100$      | H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , SO <sub>2</sub> , OH,<br>HCl, HBr,   | Toluene                       |

**Table 6.** Gas components of aircraft jet measured by FTIR emission spectroscopy in ground-based experiments [15]. Jet diameter is 50 cm, temperature is 380°C.

| Gas               | Spectral interval, cm <sup>-1</sup> | Interfering gases                        | Concentration, ppmV | Detection limit, ppmV |
|-------------------|-------------------------------------|--|---------------------|-----------------------|
| CO <sub>2</sub>   | 2380-2400                           | -  | 1-4·10 <sup>4</sup> | 60                    |
| H <sub>2</sub> O  | 1965-1985                           | (CO)                                     | 2-6·10 <sup>4</sup> | 7000                  |
| CO                | 2160-2180                           | H <sub>2</sub> O, (CO <sub>2</sub> )     | 10-3000             | 20                    |
| NO                | 1890-1910                           | H <sub>2</sub> O, (CO, CO <sub>2</sub> ) | 10-200              | 90(>60)               |
| NO <sub>2</sub>   | 1620-1640                           | H <sub>2</sub> O                         | 10-100              | 60                    |
| N <sub>2</sub> O  | 2180-2200                           | CO, H <sub>2</sub> O, CO <sub>2</sub>    | ≤7                  | 10                    |
| SO <sub>2</sub>   | 1350-1370                           | H <sub>2</sub> O, CO, (HC)               | ≤10                 | 340                   |
| H <sub>2</sub> CO | 2805-2825                           | H <sub>2</sub> O, (CH <sub>4</sub> +...) | <15                 | 50                    |
| CH <sub>4</sub>   | 3055-3075                           | H <sub>2</sub> O                         | <10                 | 150(>100)             |

**Table 7.** The values of  $\nu_j$  and  $\Sigma_j$  for spontaneous Raman scattering of different molecules.

| Molecule                         | $\nu_j, \text{cm}^{-1}$ | $\Sigma_j$ | Molecule                      | $\nu_j, \text{cm}^{-1}$ | $\Sigma_j$ |
|----------------------------------|-------------------------|------------|-------------------------------|-------------------------|------------|
| Cl <sub>2</sub>                  | 550                     | 2.2        | CO                            | 2143                    | 0.9        |
| CHCl <sub>3</sub>                | 671                     | 2.6        | N <sub>2</sub> O              | 2224                    | 0.5        |
| F <sub>2</sub>                   | 893                     | 0.3        | N <sub>2</sub>                | 2331                    | 1.1        |
| C <sub>6</sub> H <sub>6</sub>    | 992                     | 11.0       | H <sub>2</sub> S              | 2611                    | 6.8        |
| SO <sub>2</sub>                  | 1151                    | 4.4        | HCl                           | 2886                    | 3.1        |
| CO <sub>2</sub>                  | 1285                    | 0.7        | CH <sub>4</sub>               | 2914                    | 8.3        |
| N <sub>2</sub> O                 | 1285                    | 2.0        | C <sub>2</sub> H <sub>4</sub> | 3019                    | 6.4        |
| C <sub>2</sub> H <sub>4</sub>    | 1342                    | 2.8        | C <sub>6</sub> H <sub>6</sub> | 3070                    | 14.5       |
| CO <sub>2</sub>                  | 1388                    | 1.1        | NH <sub>3</sub>               | 3334                    | 5.8        |
| O <sub>2</sub>                   | 1555                    | 1.0        | H <sub>2</sub> O              | 3652                    | 4.5        |
| C <sub>2</sub> H <sub>4</sub>    | 1623                    | 1.6        | HF                            | 3962                    | 1.3        |
| C <sub>2</sub> H <sub>3</sub> Cl | 1632                    | 1.6        | H <sub>2</sub>                | 4156                    | 3.8        |

|    |      |     |  |  |  |
|----|------|-----|--|--|--|
| NO | 1877 | 0.3 |  |  |  |
|----|------|-----|--|--|--|

**Table 8.** Typical concentrations of gases in the standard atmosphere at different altitudes  $H$  [43] and in Boeing 707 wake [1].  $L$  is the distance downstream the engine exit plane. *Note:* 1) HO<sub>2</sub> concentration in the atmosphere was taken from [1]; 2) pressure and temperature for ambient atmosphere at  $H=12.2$  km were taken from [1]. (\*) - fixed to ambient atmosphere value; (\*\*) - rough estimate as an average of the exit plane and ambient atmosphere values; (\*\*\*) – corresponds to 5% relative humidity - rough estimate for the plume axis with using [1] data.

| Gas                           | Mole fraction                         |   |   |   |
|-------------------------------|---------------------------------------|---|---|---|
|                               | Atmosphere                            |   | B707 wake at $H=12.2$ km  |   |
|                               | $H=0$ km<br>$P=1$ atm,<br>$T=288.2$ K | $H=12.2$ km<br>$P=0.1715$ atm,<br>$T=217.3$ K | Engine exit plane<br>( $L=0$ m)<br>$P=0.1715$ atm,<br>$T=604.7$ K | $L=30.5$ m,<br>$P=0.1715$ atm,<br>$T=338.9$ K |
| N <sub>2</sub>                | 0.781                                 | 0.781   | 0.789   | 0.785 (**)                                    |
| O <sub>2</sub>                | 0.209                                 | 0.209   | 0.159   | 0.184 (**)                                    |
| H <sub>2</sub> O              | $7.75 \cdot 10^{-3}$                  | $1.91 \cdot 10^{-5}$                          | $3.4 \cdot 10^{-2}$   | $7.52 \cdot 10^{-2}$ (***)                    |
| CO <sub>2</sub>               | $3.3 \cdot 10^{-4}$                   | $3.3 \cdot 10^{-4}$                           | $3.0 \cdot 10^{-2}$   | $1.52 \cdot 10^{-2}$ (**)                     |
| N <sub>2</sub> O              | $3.2 \cdot 10^{-7}$                   | $3.1 \cdot 10^{-7}$                           | $3.1 \cdot 10^{-7}$ (*)   | $3.1 \cdot 10^{-7}$ (*)                       |
| CH <sub>4</sub>               | $1.7 \cdot 10^{-6}$                   | $1.66 \cdot 10^{-6}$                          | $1.66 \cdot 10^{-6}$ (*)  | $1.66 \cdot 10^{-6}$ (*)                      |
| CO                            | $1.5 \cdot 10^{-7}$                   | $7.81 \cdot 10^{-8}$                          | $2.5 \cdot 10^{-5}$   | $1.25 \cdot 10^{-5}$ (**)                     |
| O <sub>3</sub>                | $2.66 \cdot 10^{-8}$                  | $3.1 \cdot 10^{-7}$                           | $3.1 \cdot 10^{-7}$ (*)   | $3.1 \cdot 10^{-7}$ (*)                       |
| H <sub>2</sub> CO             | $2.4 \cdot 10^{-9}$                   | $3.39 \cdot 10^{-11}$                         | $3.39 \cdot 10^{-11}$ (*)   | $3.39 \cdot 10^{-11}$ (*)                     |
| HCl                           | $10^{-9}$                             | $4.36 \cdot 10^{-11}$                         | $4.36 \cdot 10^{-11}$ (*)   | $4.36 \cdot 10^{-11}$ (*)                     |
| NH <sub>3</sub>               | $5 \cdot 10^{-10}$                    | $6.3 \cdot 10^{-12}$                          | $6.3 \cdot 10^{-12}$ (*)  | $6.3 \cdot 10^{-12}$ (*)                      |
| NO                            | $3 \cdot 10^{-10}$                    | $3 \cdot 10^{-10}$                            | $8.3 \cdot 10^{-5}$   | $2.15 \cdot 10^{-5}$                          |
| SO <sub>2</sub>               | $3 \cdot 10^{-10}$                    | $5.6 \cdot 10^{-11}$                          | $6.6 \cdot 10^{-6}$   | $1.79 \cdot 10^{-6}$                          |
| H <sub>2</sub> O <sub>2</sub> | $2 \cdot 10^{-10}$                    | $1.95 \cdot 10^{-11}$                         | $3.5 \cdot 10^{-9}$   | $2.66 \cdot 10^{-8}$                          |
| HCN                           | $1.7 \cdot 10^{-10}$                  | $1.6 \cdot 10^{-10}$                          | $1.6 \cdot 10^{-10}$ (*)  | $1.6 \cdot 10^{-10}$ (*)                      |
| HNO <sub>3</sub>              | $5 \cdot 10^{-11}$                    | $2.41 \cdot 10^{-10}$                         | $6.2 \cdot 10^{-12}$  | $1.4 \cdot 10^{-7}$                           |
| NO <sub>2</sub>               | $2.3 \cdot 10^{-11}$                  | $3.15 \cdot 10^{-11}$                         | $9.1 \cdot 10^{-6}$   | $2.51 \cdot 10^{-6}$                          |
| HOCl                          | $7.7 \cdot 10^{-12}$                  | $5.01 \cdot 10^{-12}$                         | $5.01 \cdot 10^{-12}$ (*)   | $5.01 \cdot 10^{-12}$ (*)                     |
| HI                            | $3 \cdot 10^{-12}$                    | $3 \cdot 10^{-12}$                            | $3 \cdot 10^{-12}$ (*)  | $3 \cdot 10^{-12}$ (*)                        |
| HBr                           | $1.7 \cdot 10^{-12}$                  | $1.7 \cdot 10^{-12}$                          | $1.7 \cdot 10^{-12}$ (*)  | $1.7 \cdot 10^{-12}$ (*)                      |
| HO <sub>2</sub>               |                                       | $3.6 \cdot 10^{-13}$                          | $2.2 \cdot 10^{-8}$   | $2.84 \cdot 10^{-14}$                         |
| OH                            | $4.4 \cdot 10^{-14}$                  | $4.94 \cdot 10^{-14}$                         | $5 \cdot 10^{-6}$   | $5.26 \cdot 10^{-12}$                         |
| ClO                           | $10^{-14}$                            | $3.18 \cdot 10^{-14}$                         | $3.18 \cdot 10^{-14}$ (*)   | $3.18 \cdot 10^{-14}$ (*)                     |

**Table 9.** Cross sensitivities  $Q_{jk}$  for analytical frequencies of CO<sub>2</sub> lasers selected for detection of SO<sub>2</sub> gas in hot aircraft wake. Among the analytical frequencies (i.e., which satisfy the selection criterion, see text) only the frequencies for SO<sub>2</sub> detection were found. The frequencies (not analytical) for detection of H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were chosen from all analytical ones for the reason of maximum absorption cross section of given gas. The frequencies for detection of CO, NO, NO<sub>2</sub> and OH were not considered because of very small cross sections. The conditions of calculations see in Table. 8.

| CO <sub>2</sub> laser line<br>$\nu$ , cm <sup>-1</sup> | Gas "j"<br>to be<br>detected | Interfering gas "k"  |                      |                      |                      |                 |
|--|------------------------------|----------------------|----------------------|----------------------|----------------------|-----------------|
|  |                              | H <sub>2</sub> O     | CO <sub>2</sub>      | N <sub>2</sub> O     | CH <sub>4</sub>      | SO <sub>2</sub> |
| II626 R(62)<br>1099.6873                               | H <sub>2</sub> O             | 1                    | 0.569                | $7.72 \cdot 10^{-5}$ | $6.14 \cdot 10^{-4}$ | 0.902           |
| II626 R(30)<br>1084.6352                               | CO <sub>2</sub>              | $1.44 \cdot 10^{-5}$ | 1                    | $1.87 \cdot 10^{-3}$ | $9.62 \cdot 10^{-6}$ | 0.200           |
| II828 R(54)<br>1114.3783                               | N <sub>2</sub> O             | $5.16 \cdot 10^{-4}$ | $5.12 \cdot 10^{-6}$ | 1                    | $1.69 \cdot 10^{-2}$ | 3.54            |
| II628 R(47)<br>1101.3977                               | CH <sub>4</sub>              | $4.34 \cdot 10^{-2}$ | 0.732                | $2.44 \cdot 10^{-4}$ | 1                    | 9.91            |
| II828 R(54)<br>1114.3783                               | SO <sub>2</sub>              | $1.46 \cdot 10^{-4}$ | $1.45 \cdot 10^{-6}$ | 0.282                | $4.77 \cdot 10^{-3}$ | 1               |

**Table 10.** Minimum detectable concentrations  $c_j^{\min}$ , the estimate of total interference of other gases  $\sum_{j \neq k} Q_{jk}$  and absorption coefficients  $\alpha$  at analytical frequencies of CO<sub>2</sub> lasers in hot aircraft wake (see also the heading in Table 9).

| CO <sub>2</sub> laser line<br>$\nu$ , cm <sup>-1</sup> | Detected<br>gas  | $c_j^{\min}$ , ppmV | $\sum_{j \neq k} Q_{jk}$ | $\alpha$ , km <sup>-1</sup> |
|--|------------------|---------------------|--------------------------|-----------------------------|
| II626 R(62)<br>1099.6873                               | H <sub>2</sub> O | 50.287              | 1.4708                   | $1.0155 \cdot 10^2$         |
| II626 R(30)<br>1084.6352                               | CO <sub>2</sub>  | 20.349              | 0.20232                  | $1.4773 \cdot 10^2$         |
| II828 R(54)<br>1114.3783                               | N <sub>2</sub> O | 59.289              | 3.5606                   | $6.9845 \cdot 10^{-2}$      |
| II628 R(47)<br>1101.3977                               | CH <sub>4</sub>  | 218.29              | 10.685                   | 10.747                      |
| II828 R(54)<br>1114.3783                               | SO <sub>2</sub>  | 16.733              | 0.28715                  | $6.9845 \cdot 10^{-2}$      |



**Table 11.** Cross sensitivities  $Q_{jk}$  for "optimum" analytical frequencies (at which  $c_j^{\min}$  are reached) of fundamental band CO laser selected for detection of different gases in hot aircraft wake. Among the analytical frequencies (i.e., which satisfy the selection criterion, see text) the frequencies for detection of H<sub>2</sub>O, N<sub>2</sub>O, CH<sub>4</sub>, NO, SO<sub>2</sub> and NO<sub>2</sub> were found. The lines for detection of CO<sub>2</sub> and CO (not analytical) were chosen from all analytical ones for the reason of maximum absorption cross section of given gas. The frequencies for detection of OH were not considered because of very small cross section. The conditions of calculations see in Table. 8.

| CO laser line<br>$\nu, \text{cm}^{-1}$ | Gas "j"          | Interfering gas "k" |                   |                   |                   |                   |                    |                   |                   |                    |
|--|------------------|---------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-------------------|-------------------|--------------------|
|  |                  | H <sub>2</sub> O    | CO <sub>2</sub>   | N <sub>2</sub> O  | CO                | CH <sub>4</sub>   | NO                 | SO <sub>2</sub>   | NO <sub>2</sub>   | OH                 |
| 16-15 P(19)<br>1684.8358               | H <sub>2</sub> O | 1                   | 0                 | $2 \cdot 10^{-9}$ | 0                 | $2 \cdot 10^{-6}$ | $3 \cdot 10^{-7}$  | 0                 | $5 \cdot 10^{-5}$ | $2 \cdot 10^{-29}$ |
| 10-9 P(9)<br>1874.4519                 | CO <sub>2</sub>  | 0.08                | 1                 | $9 \cdot 10^{-2}$ | $10^{-5}$         | $4 \cdot 10^{-3}$ | 40                 | 0                 | $3 \cdot 10^{-6}$ | $2 \cdot 10^{-22}$ |
| 34-33 P(13)<br>1271.9622               | N <sub>2</sub> O | $10^{-4}$           | $2 \cdot 10^{-7}$ | 1                 | 0                 | $9 \cdot 10^{-4}$ | 0                  | $10^{-7}$         | $7 \cdot 10^{-5}$ | $3 \cdot 10^{-38}$ |
| 7- 6 P(15)<br>1927.2960                | CO               | 0.6                 | 1                 | $9 \cdot 10^{-3}$ | 1                 | $3 \cdot 10^{-2}$ | $5 \cdot 10^3$     | 0                 | 0                 | $6 \cdot 10^{-19}$ |
| 32-31 P(19)<br>1299.6728               | CH <sub>4</sub>  | $2 \cdot 10^{-5}$   | $4 \cdot 10^{-8}$ | 0.3               | 0                 | 1                 | 0                  | $4 \cdot 10^{-5}$ | $5 \cdot 10^{-5}$ | $2 \cdot 10^{-36}$ |
| 8-7 P(11)<br>1917.8613                 | NO               | $10^{-3}$           | $1 \cdot 10^{-5}$ | $2 \cdot 10^{-6}$ | $4 \cdot 10^{-8}$ | $3 \cdot 10^{-8}$ | 1                  | 0                 | 0                 | $9 \cdot 10^{-25}$ |
| 28-27 P(23)<br>1379.9170               | SO <sub>2</sub>  | $3 \cdot 10^{-4}$   | $5 \cdot 10^{-7}$ | $3 \cdot 10^{-6}$ | 0                 | $3 \cdot 10^{-4}$ | 0                  | 1                 | $2 \cdot 10^{-5}$ | $7 \cdot 10^{-38}$ |
| 20-19 P(6)<br>1633.3132                | NO <sub>2</sub>  | $4 \cdot 10^{-5}$   | 0                 | $2 \cdot 10^{-3}$ | 0                 | $10^{-4}$         | $4 \cdot 10^{-10}$ | 0                 | 1                 | $4 \cdot 10^{-32}$ |
| 6-5 P(20)<br>1931.6931                 | OH               | $2 \cdot 10^{15}$   | $4 \cdot 10^{13}$ | $2 \cdot 10^{13}$ | $3 \cdot 10^{13}$ | $4 \cdot 10^{14}$ | $9 \cdot 10^{18}$  | 0                 | 0                 | 1                  |

**Table 12.** Minimum detectable concentrations  $c_j^{\min}$ , the estimate of total interference of other gases  $\sum_{j \neq k} Q_{jk}$  and absorption coefficients  $\alpha$  at analytical frequencies of fundamental band CO laser in hot aircraft wake (see also the heading in Table 8).

| CO laser line | $\nu, \text{cm}^{-1}$ | Detected gas     | $c_j^{\min}, \text{ppmV}$ | $\sum_{j \neq k} Q_{jk}$ | $\alpha, \text{km}^{-1}$ |
|---------------|-----------------------|------------------|---------------------------|--------------------------|--------------------------|
| 16-15 P(19)   | 1684.8358             | H <sub>2</sub> O | 0.133                     | $5.014 \cdot 10^{-5}$    | $2.56 \cdot 10^4$        |
| 10-9 P(9)     | 1874.4519             | CO <sub>2</sub>  | $2.183 \cdot 10^3$        | 38.63                    | 1.641                    |
| 34-33 P(13)   | 1271.9622             | N <sub>2</sub> O | 0.1728                    | $1.137 \cdot 10^{-3}$    | 3.034                    |
| 7- 6 P(15)    | 1927.2960             | CO               | $1.235 \cdot 10^4$        | $5.169 \cdot 10^3$       | 3.920                    |
| 32-31 P(19)   | 1299.6728             | CH <sub>4</sub>  | 1.0578                    | 0.3437                   | 0.2411                   |
| 8-7 P(11)     | 1917.8613             | NO               | 0.1921                    | $1.3526 \cdot 10^{-3}$   | 67.15                    |
| 28-27 P(23)   | 1379.9170             | SO <sub>2</sub>  | 0.3842                    | $6.7897 \cdot 10^{-4}$   | 4.4187                   |
| 20-19 P(6)    | 1633.3132             | NO <sub>2</sub>  | 0.1404                    | $2.1129 \cdot 10^{-3}$   | 7.4747                   |
| 6-5 P(20)     | 1931.6931             | OH               | $4.85 \cdot 10^{19}$      | $8.85 \cdot 10^{18}$     | 1.6712                   |

**Table 13.** Cross sensitivities  $Q_{jk}$  for "optimum" analytical frequencies (at which  $c_j^{\min}$  are reached) of first -overtone CO laser selected for detection of different gases in hot aircraft wake. Among the analytical frequencies (i.e., which satisfy the selection criterion, see text) the frequencies for detection of H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, NO, SO<sub>2</sub>, NO<sub>2</sub> and OH were found. The frequencies for CO detection were not considered because of very small cross section. The conditions of calculations see in Table. 8.

| CO laser line<br>v, cm <sup>-1</sup> | Gas<br>"j"       | Interfering gas "k" |                    |                    |                    |                     |                     |                 |                     |
|--------------------------------------|------------------|---------------------|--------------------|--------------------|--------------------|---------------------|---------------------|-----------------|---------------------|
|                                      |                  | H <sub>2</sub> O    | CO <sub>2</sub>    | N <sub>2</sub> O   | CH <sub>4</sub>    | NO                  | SO <sub>2</sub>     | NO <sub>2</sub> | OH                  |
| 8- 6 P(21)<br>3853.9633              | H <sub>2</sub> O | 1                   | 9·10 <sup>-8</sup> | 6·10 <sup>-5</sup> | 10 <sup>-5</sup>   | 4·10 <sup>-10</sup> | 0                   | 0               | 8·10 <sup>-6</sup>  |
| 38-36 P(25)<br>2364.9292             | CO <sub>2</sub>  | 10 <sup>-7</sup>    | 1                  | 8·10 <sup>-7</sup> | 10 <sup>-6</sup>   | 0                   | 0                   | 0               | 7·10 <sup>-15</sup> |
| 35-33 P( 6)<br>2577.9590             | N <sub>2</sub> O | 2·10 <sup>-7</sup>  | 2·10 <sup>-7</sup> | 1                  | 10 <sup>-4</sup>   | 0                   | 2·10 <sup>-11</sup> | 0               | 8·10 <sup>-14</sup> |
| 22-20 P(25)<br>3131.7294             | CH <sub>4</sub>  | 2·10 <sup>-6</sup>  | 10 <sup>-8</sup>   | 2·10 <sup>-8</sup> | 1                  | 0                   | 0                   | 0               | 10 <sup>-7</sup>    |
| 12-10 P( 8)<br>3707.6209             | NO               | 0.1                 | 0.5                | 8·10 <sup>-4</sup> | 7·10 <sup>-8</sup> | 1                   | 0                   | 0               | 4·10 <sup>-3</sup>  |
| 35-33 P(22)<br>2519.9057             | SO <sub>2</sub>  | 9·10 <sup>-6</sup>  | 7·10 <sup>-7</sup> | 4·10 <sup>-2</sup> | 5·10 <sup>-3</sup> | 0                   | 1                   | 0               | 10 <sup>-11</sup>   |
| 27-25 P(25)<br>2888.9574             | NO <sub>2</sub>  | 10 <sup>-6</sup>    | 0                  | 0                  | 5·10 <sup>-2</sup> | 0                   | 0                   | 1               | 3·10 <sup>-7</sup>  |
| 15-13 P( 8)<br>3554.7194             | OH               | 0.3                 | 0.2                | 0                  | 0                  | 2·10 <sup>-7</sup>  | 0                   | 0               | 1                   |

**Table 14.** Minimum detectable concentrations  $c_j^{\min}$ , the estimate of total interference of other gases  $\sum_{j \neq k} Q_{jk}$  and absorption coefficients  $\alpha$  at analytical frequencies of first-overtone CO laser in hot aircraft wake (see also the heading in Table 13).

| CO laser line | v, cm <sup>-1</sup> | Detected gas     | $c_j^{\min}$ , ppmV  | $\sum_{j \neq k} Q_{jk}$ | $\alpha$ , km <sup>-1</sup> |
|---------------|---------------------|------------------|----------------------|--------------------------|-----------------------------|
| 8-6 P(21)     | 3853.9633           | H <sub>2</sub> O | 0.312                | 7.633·10 <sup>-5</sup>   | 10 <sup>4</sup>             |
| 38-36 P(25)   | 2364.9292           | CO <sub>2</sub>  | 5.1·10 <sup>-2</sup> | 2.031·10 <sup>-6</sup>   | 5.88·10 <sup>4</sup>        |
| 35-33 P( 6)   | 2577.9590           | N <sub>2</sub> O | 1.109                | 1.471·10 <sup>-4</sup>   | 2.92·10 <sup>-2</sup>       |
| 22-20 P(25)   | 3131.7294           | CH <sub>4</sub>  | 0.196                | 1.907·10 <sup>-6</sup>   | 0.88                        |
| 12-10 P( 8)   | 3707.6209           | NO               | 25.01                | 0.183                    | 23.8                        |
| 35-33 P(22)   | 2519.9057           | SO <sub>2</sub>  | 23.77                | 4.96·10 <sup>-2</sup>    | 2.92·10 <sup>-2</sup>       |
| 27-25 P(25)   | 2888.9574           | NO <sub>2</sub>  | 2.234                | 1.95·10 <sup>-2</sup>    | 0.41                        |
| 15-13 P( 8)   | 3554.7194           | OH               | 4.807                | 5.26·10 <sup>-2</sup>    | 35.75                       |