Absorption of the CO laser sum frequency radiation obtained in a nonlinear crystal AgGaSe$_2$ by molecular gases

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Abstract. The broadband laser system based on multi-line Q-switched CO laser was experimentally studied in a nonlinear crystal AgGaSe$_2$. The internal efficiency of sum frequency generation reached 1%. Test experiments on measurement of the absorption of the CO-laser sum frequency radiation by such gaseous substances as nitrous oxide and carbon dioxide were realized. A comparison of the experimental data with the theoretically calculated absorption spectrum of radiation was obtained.

1. Introduction
Because of increasing atmospheric pollution, rapid monitoring of the concentration of gas impurities has become more important, and such monitoring can be done using laser remote sensing of the atmosphere. Maximum information in remote sensing of the atmospheric composition with high spatial and temporal resolution can be obtained only by the optical method using laser, i.e., lidar. Spectral range of broadband CO laser is very attractive for laser remote gas analysis, because, firstly, it is within the window of atmosphere transparency in the wavelength range from 3 to 5 $\mu$m, and secondly, coincides with the absorption bands of a number of pollutant and natural component of the atmosphere. Thirdly, the sensitivity of sensors based on InSb has record values in this spectral range [1]. CO-laser, therefore, is a promising device for various applications in remote laser sensing, spectroscopic gas analysis, medicine etc., where it is able to compete with well-known chemical HF/DF lasers [2-3], the converted frequency CO$_2$ lasers [4-5] and tunable difference frequency generators [6]. Frequency selective mode of generation of a pulsed CO laser is currently implemented by more than 1000 vibrational-rotational transitions in the fundamental [7] and first-overtone vibrational bands [8]. Opportunities of overtone CO laser (2.5-4.2 $\mu$m) for remote gas analysis by differential absorption method were demonstrated in works [9-10]. In addition, it was demonstrated the possibility of using overtone CO laser to determine of the isotopic composition of methane ($^{12}$CH$_4$, $^{13}$CH$_4$) in natural air samples with a cavity ring-down technique. A CO overtone sideband laser was utilized to excite a high-finesse cavity, which provides an effective optical absorption path length of 3.6 km [11].

All of the above suggests that the current state of spectroscopic gas analysis requires the search and introduction of new laser IR sources with the possibility of lasing on a large number of narrow spectral lines, in the widest possible frequency range and with a small step of frequency tuning. Emission spectrum of the CO laser can be significantly enriched and expanded from near-to far-IR by frequency
conversion in nonlinear crystals. The frequency conversion includes second-harmonic generation (SHG), sum-frequency generation (SFG), and difference frequency generation (DFG).

It was experimentally demonstrated a broadband two-stage frequency conversion of laser radiation by CO laser in a ZnGeP$_2$ crystal with simultaneous generation of several hundred lines in the wavelength range from 2.45 to 6.3 µm [12] and from 2.5 to 8.3 µm [13]. The broadband two-stage frequency conversion of the CO laser radiation was realized in nonlinear AgGaSe$_2$ (AGSe) crystal too [14]. In the experiment ~70 spectral lines of CO laser within range from 4.9 to 6.3 µm and from 2.5 to 8.3 µm were converted into ~70 spectral lines of sum frequencies radiation within range from 2.45 to 2.85 µm. The spectrum of DFG consisted of 70 spectral lines within spectral range from 4.3 to 4.9 µm.

In this paper we study absorption of the sum frequencies radiation in nonlinear crystal AGSe by such gaseous substances as nitrous oxide (N$_2$O) and carbon dioxide (CO$_2$).

2. Optical scheme

In our experiment we used the AGSe crystal with length of 12 mm. The same multi-line low-pressure Q-switched CO laser as in [12, 13] was used. The optical scheme of our experiment is presented in figure 1. Low-pressure cryogenic cooling CO laser tube 1 was pumped by DC glow discharge. The peak radiation power was about ~1 kW at pulse duration ~1 µs. Laser cavity was formed by a spherical mirror 2 (radius of curvature 9.0 m) and partially reflective mirror 3 (reflectance ≥90% in the wavelength range from ~5.0 to 6.5 mm). The laser operated in Q-switch mode by a rotating mirror 4. The aperture diaphragm 5 (diameter 10 mm) installed near a partially reflecting mirror 3. To measure parameters of CO laser radiation, part of the laser beam was split off by flat CaF$_2$ plates 6 onto spherical mirror 7 (radius of curvature 0.25 m). From the spherical mirror, the radiation is directed to measuring average power meter 8 (Ophir-10A), mounted 15 cm in from of spherical mirror 7. Part of the radiation through the plate 9 of CaF$_2$ was directed to a photodetector 10 (PEM-L-3) installed in the focal plane of the spherical mirror 7. Using the power meter we controlled the average power of CO laser radiation.

Multi-line laser radiation was focused by CaF$_2$ lens 11 with focal length of 60 mm onto AGSe crystal 12. For optimal focusing of the radiation on the crystal, the crystal holder had 3 translational degrees of freedom and 1 rotational degree of freedom for finding the direction of phase synchronism. To collimate the diverging after the crystal radiation the lens 13 (CaF$_2$, focal length ~60 mm) was used.

By flat turning mirrors 15 and 17, and spherical (radius of curvature 0.25 m) 16 mirror, the converted radiation was directed into a spectrometer 18 (IKS-31). Then the radiation passed through the gas cell 20 (length of 10 cm) and using a spherical mirror 21, it was directed to the photodetector 22 (PDA20H-EC, ThorLabs). In this case, the radiation after leaving the IKS (but before gas cell) was

Figure 1. Optical scheme. 1 – CO laser tube; 2 – spherical mirror; 3 – partially reflective mirror; 4 – rotating mirror; 5 – diaphragm; 6,9 – CaF$_2$ flat plates; 7, 16, 21, 23 – spherical mirrors; 8 – power meters; 10, 22, 24 – photodetectors; 11,13 – lens made of CaF$_2$; 12 – AGSe crystal; 15, 17 – turning mirrors, 18 – spectrometer IKS-31, 19 – ZnSe flat plate, 20 – gas cell (10 cm)
given to the flat plate 19 (ZnSe) on a spherical mirror 23, from which the radiation was directed to the photodetector 24 (FSG-22-3A1). Shape and amplitude of the CO laser pulse was recorded by using the photodetector 10 on the oscillograph (Tektronix TDS 2014). The signals from the photodetectors 22 and 24 were registered by oscilloscope Tektronix TDS 5052B. The method to record the SFG spectra was a simultaneous startup of the oscilloscope and the rotation of the diffraction grating (150 grooves/mm) in the IKS-31 from the known initial value of the wavelength. Time dependence, obtained from the photodetectors 22 and 24, were recalculated to the wavelength dependence.

3. SFG spectra

![Figure 2. SFG efficiency versus incidence angle of pump radiation on the crystal AGSe.](image)

The internal efficiency of SFG, which considering optical losses on Fresnel reflection from the uncoated faces of the crystal, reaching 1% at the incidence angle of CO laser radiation on crystal $\alpha=42^\circ$ (Figure 2). When we change the incidence angle on the crystal of $\pm 3^\circ$, the efficiency decrease by 2 times, and spectrum of SFG radiation depends on the incidence angle on the crystal and can be changed. It must be note that frequency conversion efficiency in nonlinear crystal can be increased with increasing input laser intensity. For example, when using a Q-switched and mode-locked regime of the electron-beam sustained discharge CO laser with a short (total pulse duration of about 1 $\mu$s) train of nanosecond pulses, the internal efficiency of SHG was increased up to 37% [15].

To measure the absorption of radiation in N$_2$O, AGSe crystal was mounted so that the incidence angle $\alpha$ of the CO laser radiation on the input facet of the crystal was equal $40.3^\circ$. SFG spectra of radiation before gas cell with N$_2$O (gray) and after gas cell (black) are presented in Figure 3. The average power of CO laser generation was 45.6 mW. The gas pressure in the gas cell was 1 atm at a length of 10 cm, which corresponds to the atmospheric path 1 km at the concentration of N$_2$O at the level of MAC (maximum allowable concentration).

![Figure 3. SFG spectra before gas cell (gray) and after cell (black) with 1 atm N$_2$O](image)

To measure the absorption of radiation in CO$_2$, crystal was mounted so that the incidence angle $\alpha$ of the CO laser radiation on the input facet of the crystal was equal 42.5$^\circ$. SFG spectra of radiation before gas cell with CO$_2$ (gray) and after gas cell (black) are presented in Figure 4. In this experiment, the radiation passed through the cell with gas mixture: 0.3 atm CO$_2$ and 0.7 atm N$_2$. The average power of CO laser generation was 47.5 mW.
Spectra are normalized to the equaled value of the power in arbitrary units at wavelengths that should not be absorbed in the cell. The Figure 4 shows that the radiation up to 2.67 μm and higher 2.71 μm is not practically absorbed, while in the interval from 2.67 to 2.71 μm power of the transmitted radiation decreases significantly. For example, the maximum radiation power at ~ 2.7 μm drops by 2.5 times (from 1 to 0.4).

4. Absorption of SFG

For the calculation of absorption based on experimental data for comparison with absorption, theoretically calculated for our experimental conditions we applied following methodology. Characteristic waveform of a single spike from the spectrum presented in Figure 3, shown in Figure 5.

The gray line corresponds to radiation on the input of the gas cell and black is after passing the gas cell with CO\textsubscript{2} (were multiplied by -20, for visual comparison). Since the shape of the spikes are not the same (different photodetectors are used), it is possible to calculate the absorption we took the integral value of pulses. It should be noted that this pulse shape does not correspond to the real temporal shape of the total pulse of SFG ~1 μs. Then absorption \( a \) was calculated by formula:

\[
    a = \ln \left( \frac{s_2}{s_1} \right) - A
\]

where \( s_1 \) and \( s_2 \) are energies of incident and transmitted radiation in each spike, respectively, \( A \) is average experimental value of the absorption in the band, which is not absorbed by molecules. Figure 6 shows the values of the absorption for the gas cell with CO\textsubscript{2}.
resolution of the spectrometer was ~ 0.001 μm. It can not allow sufficiently to distinguish complex SFG spectrum and to detect narrow CO$_2$ absorption lines.

Figure 6. Spectra of incident and transmitted radiation in the range from 2.699 to 2.704 μm, theoretical and experimental absorption

The SFG spectra on the input of the gas cell and after gas cell with CO$_2$ and N$_2$O respectively, and also theoretical and experimental graphs of the radiation absorption in the gas cell are presented in Figures 7 and 8.

Figure 7. Spectra of incident and transmitted SFG radiation (gray and black graphs respectively; the last graph multiplied by 10) and theoretically calculated absorption spectrum in gas cell with CO$_2$ (black line, pending negative of ordinate axis). Experimental values of absorption (black dots) were calibrated on the lines, which are not absorbed by CO$_2$ molecules (λ~2.63 – 2.66 μm)
Figure 8. Spectra of incident and transmitted SFG radiation (gray and black graphs respectively; the last graph multiplied by 5) and theoretically calculated absorption spectrum in gas cell with N$_2$O (black line, pending negative of ordinate axis). Experimental values of absorption (black dots) were calibrated on the lines, which are not absorbed by N$_2$O molecules ($\lambda \sim 2.56–2.58 \mu$m).

From the absorption measurement data, we see that the experimental and calculated agree satisfactorily over the entire spectral range in which the measurements were made. We also need to take into account the uncertainty in measurement of the radiation energy by the OPHIR calorimeter, which is no greater than 5%. Some discrepancies between the calculation and the measurements can be explained by not sufficiently high spectral resolution of the spectrometer. It is not allowed complex SFG spectrum of the multi-line CO laser detects narrow absorption lines of the investigated gases.

5. Conclusions
As a result of experiments it was obtained SFG spectra of CO laser radiation. Absorption of SFG radiation in gas cell with a length of 10 cm, containing gaseous nitrous oxide N$_2$O and carbon dioxide CO$_2$ at different partial pressures with the addition buffer gas (nitrogen) of up to atmospheric pressure were measured. Analysis of experimental data shows that in those spectral intervals where the absorption of radiation is small, the experimental values of the absorption vary around zero. In other intervals, the measured absorption coefficients, on average, take the values close to the calculated values, but the spectral resolution of the spectrometer was not sufficiently high to allow complex SFG spectrum of the multi-line CO laser and detect narrow absorption lines of the investigated gases.

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