Lidar monitoring of nitrogen and sulphur oxides molecules in ship power installation emissions. Computer simulation

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Abstract. The Raman lidar equation computer simulation for measurement of the nitrogen and sulphur oxides molecules at the low permissible concentration (LPC) level and above (in the range from 2.6 \texttimes 10^{-18} to 1.1 \texttimes 10^{-20} m\textsuperscript{-3}) in the atmosphere at the ranging distance up to 500 m in the synchronous photon counting mode and the choice of the optimal parameters of such a lidar variant have been fulfilled. It is shown that it is possible to register this concentration level for sulfur dioxide with the time duration of 616 s at the ranging distance of 500 m, for nitrogen dioxide - with 50 s and for nitrogen oxide only during measurement time up to 5000 s by the Raman lidar sensing of all studied molecules in atmosphere at the 532 nm laser radiation wavelength.

Keywords: Monitoring; Raman lidar; Molecule; Concentration, Ranging distance; Laser radiation wavelength

1. Introduction
Nowadays IMO requirements regarding to the reduction of the various toxic substances emissions as a part of the fulfilled gases of ship power installations have become stricter. Most ecologically dangerous of them - emissions of the nitrogen and sulphur oxides with the fulfilled gases of diesel engines and boilers of sea-crafts - are regulated by the Appendix VI «Prevention of pollution of atmosphere from ships» to the International convention MARPOL 73/78, came into force since May, 19th, 2005. Generally, the pollution of atmosphere by nitrogen and sulphur oxides molecules represents the large problem because of their great volumes as well in emissions of various modern manufactures [1]. Working out of new laser methods and systems for the measurement of oxides molecules with LPC concentration level [1,2] and above in atmosphere demands a choice of the optical scheme and optimal parameters of this lidar variant for monitoring of such molecules. Earlier, as a result of the analysis of lidar sensing methods for the gaseous molecules in atmosphere in [1,3-6] it has been received that Raman lidar can be used for remote measurement of the molecules concentration at the level of tens and hundreds LPC concentration level. And the Raman lidar equation variant decision for gaseous molecules in atmosphere in [4,7,8] for optimization of the laser monitoring system has been offered.

Therefore, the present work purpose is the lidar monitoring system computer simulation for the oxides molecules concentration at the LPC concentration level and above in atmosphere at the ranging...
distance up to 500 m in the synchronous photon counting mode and the choice of the optimal parameters for such a lidar system.

2. Raman Lidar
The Raman lidar optical biaxial layout was used in the presented monitoring system as in [1,3,4] which shown in the figure 1.

![Figure 1. The lidar monitoring system optical layout: 1 – laser, 2 – photodetector, 3 – interference filter, 4 – mirror, 5 – glass plate, 6 – fiber input, 7 – micro spectrometer, 8 – lens objective, 9 – spherical mirror of receiving telescope.](image)

As probing radiation the YAG- Nd- laser radiation of third and second harmonics with the semiconductor laser pumping at the 355 and 532 nm wavelengths and the semi-conductor laser at the 650 nm wavelength with pulse time duration of 10 ns and pulse energy of 10 μJ at the repetition rate f up to 100 kHz [9,10] were used. The laser l radiation beam was directed in parallel to the receiving telescope axis at the distance of 250 mm, as well as in [1,10] and the back scattering Raman radiation by the oxides molecules in atmosphere was gathered by the Newton type receiving telescope with a spherical mirror 9 with diameter of 400 mm and was focused by the lens objective 8 in fiber input 6 of the FSD-8 type micro spectrometer 7 controlled by the personal computer PC.

Part of laser radiation was directed by the glass plate 5 and the mirror 4 through interference filter 3 to the photo detector 3 voltage \( U_0 \) from which was registered by the data gathering board in the personal computer, for the control of the laser pulse energy and formation of a zero reference mark of for the measurement time.

3. Raman lidar equation
We will use the photons number \( n_0 \) in the laser radiation pulse of time duration \( \tau_0 \) sent to atmosphere and we will consider the lasing spectral line as the Gauss function with the maximum frequency \( v_0 \) and half-width of \( \Gamma_0 \) to characterize the lidar laser.

Then photons number \( n(v,z) \) of the Raman radiation by studied oxides molecules with the concentration \( N(z) \) at the photo detector of lidar will be possible to receive from the lidar equation in the photon counting mode in a view of [4, 7] as the integral in the range from \( (v_0 - \Gamma_0) \) to \( (v_R - \Gamma_R) \) [7]:
\[
n(v, z) = n_0c^2 \int_{z_0}^{z} T_0(v_0, z) \cdot T(v_R, z) \cdot \Phi(v) A(v) dv \quad 2z^2 \quad (1)
\]

where \( n(v, z) \) is the photons number registered by the lidar photo detector at the Raman frequency \( v_R \) from the ranging distance \( z \); \( n_0 \) – photon number at the laser radiation frequency \( v_0 \). Besides, \( S_0 \) is the receiving telescope aperture cross section; \( G(z) \) – lidar geometrical function \([1,7,10]\) are designated. This function is defined by the lidar optical scheme parameters \([10]\) and located within \( 0 < G(z) < 1 \).

The following quantities: \( N(z) \) - studied molecules concentration; \( t \) – time of measurement or Raman signal accumulation and \( (d\sigma/d\Omega) \) – Raman differential cross section of these molecules. And two factors – atmospheric transmission – as well as in \([1,10]\) are equal accordingly:

\[
T_0(v_0, z) = \exp\left[ -\int_0^z \alpha(v_0, r) dr \right] \quad T(v_R, z) = \exp\left[ -\int_0^z \alpha(v_R, r) dr \right],
\]

where \( \alpha(v_0, r) \) and \( \alpha(v_R, r) \) are the extinction coefficients at the laser radiation frequencies and Raman frequencies for the oxides molecules. Considering these expressions and \( \Phi(v) \) as the photons distribution function in the laser radiation line \([7-9]\) in our case is the Gauss function. Besides that we will consider, that apparatus function or spectral transmission coefficient of the lidar receive system \( A(v) \) \([1,8,10]\) has the Gauss form too and was adjusted precisely at the Raman line frequency \( v_R \) for oxides molecules with the half-width \( \Gamma_s \) which is more than \( \Gamma_R \) and \( \Gamma_0 \). \( K_i \) is the lidar constant at the \( v_0 \) laser radiation frequency, measured experimentally in \([11]\), and \( \xi (v_0) \) – relative spectral sensitivity of the photo detector at the Raman frequency \( v_R \). Then we will rewrite the equation (1) in form:

\[
n(v, z) = \frac{B}{2} N(z) tI(v, z)
\]

the constant \( B \) is designated in this expression as:

\[
B = \frac{c \tau_1}{2} S_0 f
\]

and some function \( I(v, z) \), using the errors integral \([7, 8]\), can be presented in a view:

\[
I(v, z) = G(z)n_0(d\sigma / d\Omega) \cdot 0.34K_i \xi(v)T_0(v_0, z) \cdot T(v_R, z)
\]

suggested that \( \Phi(v)=1 \), when the lasing line half-width is much less, than half-width of the lidar apparatus function. Also we consider that the Raman differential cross section can be considered as the constant in the integration frequency interval, as well as, the extinction coefficients at the laser radiation and Raman emission by the oxides molecules frequencies \([12]\).

\[
t = \frac{n(v, z)z^2}{BI(v, z)N(z)}
\]

Let us consider further one scattering Raman emission and homogeneous atmosphere \([1,10,12]\). The values of the Raman NO and SO stretching lines maximum for oxides molecules are collected from \([1,10,11,13,14]\) in Table 1 and the values of Raman differential cross section for these lines of all
molecules at the 337.1 nm laser radiation wavelength were taken from [12,13]. The Raman differential cross section values \( \frac{d\sigma}{d\Omega} \) for all molecules and the chosen wavelengths of laser radiation 355, 532 and 650 nm have been defined from table 1 taking into account the dependence \( 1/\lambda^4 \) for wavelengths interesting us [7]. All these values are collected in table 2.

### Table 1. Nitrogen and sulphur oxide molecules parameters

| Pollutant               | LPC, mg/m³ | LPC, m³ | Raman frequency of molecules, \( \bar{\nu} \), cm⁻¹ | Raman differential cross section of molecules, \( d\sigma/d\Omega \times 10^{18} \) cm² *** |
|------------------------|------------|---------|-----------------------------------------------|------------------------------------------------------------------------------------------------|
| Nitrogen oxide (NO)    | 0.4        | 8·10¹⁸  | 1877                                          | 1.5                                                                                               |
| Nitrogen dioxide (NO₂) | 0.2        | 2.6·10¹⁸ | 1320                                          | 51                                                                                                |
| Sulphur dioxide (SO₂)  | 0.5        | 4.7·10¹⁸ | 1151.5                                        | 17.0                                                                                              |

* LPC values were taken from [2];
** Values of the Raman frequency of molecules were taken from [1,10];
*** Values of the Raman differential cross sections of these molecules lines were taken from [10, 13].

### Table 2. The laser radiation and oxides molecules Raman lines wavelength and frequency values, Raman differential cross sections for these lines, the extinction coefficient in atmosphere at these wavelengths and relative spectral sensitivity of the photo detector

| Wave-length, \( \lambda \), nm | Frequency, \( \nu \), GHz | Raman differential cross sections \( d\sigma/d\Omega \), \( 10^{30} \) cm² | Extinction coefficient \( a(\nu_0, \rho) \), km⁻¹ | Extinction coefficient \( a(\nu_\rho, \rho) \), km⁻¹ | Relative spectral sensitivity of photo detector \( \xi(\nu) \) |
|--------------------------------|---------------------------|-------------------------------------------------|---------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Nitrogen oxide (NO)            | \( \nu = 1877 \) cm⁻¹     | LPC = 0.4 mg/m³ \( (8·10^{18} \) m⁻³)          | 0.29                                        | 0.3                                             |
| 355                            | 845.1                     | 1.2                                             | 0.16                                        | 0.025                                           | 0.83                                            |
| 370.6                          | 809.5                     | 0.3                                             | 0.14                                        | 0.24                                           | 0.83                                            |
| 532                            | 563.9                     | 0.1                                             | 0.14                                        | 0.13                                           | 0.76                                            |
| 567.9                          | 528.3                     | 1.5                                             |                                             |                                                 |                                                 |
| 650                            | 461.5                     |                                                 |                                             |                                                 |                                                 |
| 704.3                          | 426.0                     |                                                 |                                             |                                                 |                                                 |
| 337                            | 890.2                     |                                                 |                                             |                                                 |                                                 |
| Nitrogen dioxide (NO₂)         | \( \nu = 1320 \) cm⁻¹     | LPC = 0.2 mg/m³ \( (2.6·10^{18} \) m⁻³)        | 0.28                                        | 0.35                                            |
| 355                            | 845.1                     | 41.5                                            | 0.16                                        | 0.005                                           | 0.96                                            |
| 372.5                          | 805.4                     | 10.1                                            |                                             |                                                 |                                                 |
| 532                            | 563.9                     | 1.6                                             |                                             |                                                 |                                                 |
| 572.2                          | 524.3                     | 3.7                                             | 0.14                                        | 0.13                                           | 0.76                                            |
| 650                            | 461.5                     | 0.14                                            |                                             |                                                 |                                                 |
| 711.0                          | 421.9                     | 1.0                                             |                                             |                                                 |                                                 |
| 337                            | 890.2                     | 51.0                                            |                                             |                                                 |                                                 |
| Sulphur dioxide (SO₂)          | \( \nu = 1151.5 \) cm⁻¹   | LPC = 0.5 mg/m³ \( (4.7·10^{18} \) m⁻³)        | 0.28                                        | 0.3                                             |
| 355                            | 845.1                     | 13.8                                            | 0.16                                        | 0.028                                           | 0.3                                             |
| 370.1                          | 819.6                     | 3.8                                             | 0.16                                        | 0.15                                           | 0.85                                            |
| 532                            | 563.9                     | 2.7                                             |                                             |                                                 |                                                 |
| 566.7                          | 529.4                     | 1.8                                             |                                             |                                                 |                                                 |
| 650                            | 461.5                     | 1.2                                             | 0.14                                        | 0.13                                           | 0.83                                            |
| 702.6                          | 427.0                     | 1.8                                             |                                             |                                                 |                                                 |
| 337                            | 890.2                     | 17.0                                            |                                             |                                                 |                                                 |
The values of the extinction coefficient for these frequencies $\alpha (\nu_0, z)$ and $\alpha (\nu, z)$ from [15] also are collected in table 2. The lidar receiving telescope aperture cross section was 0.12 m$^2$. And a step on distance $– 7.5$ m for the time of one measurement of 50 ns for which 200 photons can be registered [9].

4. Lidar equation computer simulation results

The computer simulation of the lidar equation (5) was fulfilled assuming that $G(z)$ in our case is 1 and concentration of studied molecules is equal $N(z) = 10^{18}$ m$^{-3}$.

For such a case we will execute the simulation of the equation (5) for three values 355, 532 and 650 nm of laser radiation wavelengths with the laser pulse repetition rate of 100 kHz, pulse energy of 1 mJ and a ranging distance values from 50 to 500 m. The equation (5) simulation results for this case are presented in figure 2 as the dependence of measurement time $t$ on ranging distance $z$ for our experimental situation. On the plot shown in Fig. 2 the increasing in the measurement time $t$ among the wavelengths of laser radiation are 532 – 355 – 650 nm from the spectral dependence of the values included in the equation (5), thus the value of the measurement time sharply growth at the first 200 m approximately in 10 times.

![Figure 2](image_url)

Figure 2. The plot of the measurement time $t$ (in logarithmic scale, in s) dependence on the ranging distance $z$ (in m) calculated by the equation (5) for nitrogen dioxide molecules, as an example, with concentration $N(z) = 10^{18}$ m$^{-3}$ in the atmosphere and 532 (1), 355 (2) and 650 (3) nm laser radiation wavelengths at the Raman remote sensing of these molecules.

Further we will consider the equation (5) simulation for a range of nitrogen dioxide molecules concentration of $N(z)$ from $10^{16}$ m$^{-3}$ to $10^{20}$ m$^{-3}$ as an example. For this purpose we will execute the equation (5) simulation at the 532 nm laser radiation wavelength as the best variant according to figure 2. The equation (5) computer simulation results are presented in figure 3.
Figure 3. The plot of the measurement time $t$ (in logarithmic scale, in s) dependence on the ranging distance $z$ (in m) calculated by the equation (5) in the range of the nitrogen dioxide molecules concentration $N(z)$ from $10^{16}\text{m}^{-3}$ (1), $10^{18}\text{m}^{-3}$ (2) and to $10^{20}\text{m}^{-3}$ (3) in the atmosphere and 532 nm laser radiation wavelengths at the same experimental condition.

The dependence of measurement time $t$ for our experimental situation on the nitrogen dioxide molecules concentration $N(z)$ appears the inverse proportionality to the concentration values as well as follows from the equation (5) and grows approximately 10 times with increasing in the ranging distance $z$. We will collect the equation (5) simulation results for three molecules of oxides in figure 4.

Now we will estimate measurement time $t$ for all oxide molecules according to figure 4. For concentration level of $N(z) = 10^{16}\text{m}^{-3}$ measurement time $t$ will be equal for NO$_2$ – 3.6 s, SO$_2$ – 5.4 s and NO – 43.7 s at the ranging distance of 50 m, and for the ranging distance of 200 m these times will be for NO$_2$ – 60.4 s, SO$_2$ – 89.8 s and NO – 732.5 s or about 12 min. This is connected with the spectral dependence of the Raman differential cross section for these molecules lines, the extinction coefficients in atmosphere at these wavelengths and relative spectral sensitivity of the photo detector. It is obviously that the further reduction of the studied molecules concentration level can probably decrease with the measurement time $t$, laser pulses repetition rate $f$ or their energy $E_0$ increasing.
Figure 4. The plot of the measurement time $t$ (in logarithmic scale, in s) dependence on the ranging distance $z$ (in m) calculated by the equation (5) for all oxides molecules with concentration $N(z) = 10^{18} \text{m}^{-3}$ in the atmosphere and 532 nm laser radiation wavelengths: NO$_2$(1), SO$_2$(2) and NO(3).

5. Conclusion

The effective application of lidar monitoring for the remote sensing of the nitrogen and sulphur oxides molecules demands an estimation of the lidar potential possibilities, a range of their using in the remote control of the specific gaseous components taking into account the service conditions influence on the lidar operating mode. The main target is a correct choice of apparatus realization of the optimal method of the parameters measurement for a gas mixture in the each specific task. For this purpose the lidar signals detail studies are required. It is possible to reduce the molecules concentration measurements error and to raise their reliability in this case.

Thus, these results allow to choose the Raman lidar and laser optimal parameters for the oxides molecules remote sensing in atmosphere at the ranging distances up to 500 m. And the nitrogen dioxide molecules with concentration of an order of LPC level can be probed in all range of distances at measurement time of 6.8 min (409 s), but nitrogen oxide molecules only in measurement time of 83.7 min (5024 s).

References

[1] Turkin V A, Turkin A V, Ivanchenko A A 2018 Application of laser technologies for estimation of toxicity of worked gases of ship energy installations Marine intellectual technologies 1-1 111-116: https://www.elibrary.ru/item.asp?id=32717346

[2] RF Hygienic standards GN 2.1.6.3492-17 (dat May, 31, 2018)

[3] Privalov V E, Shemanin V G 2018 Hydrogen Sulfide Molecules Lidar Sensing in the Atmosphere Optical Memory & Neural Networks (Information Optics) 27-2 120-131

DOI: 10.3103/S1060992X18020091
[4] Privalov V E, Shemanin V G 2020 Accuracy of lidar measurements of the concentration of hydrofluoride molecules in the atmospheric boundary layer *Measurement Techniques* **63**-7 543-548 DOI:10.1007/s11018-020-01821-0

[5] Samokhvalov I V, Kopytin Yu D, Ippplitov I I et al 1987 Laser remote sensing of troposphere and underlying surface (*Novosibirsk, Nauka*) 262

[6] Zuev V E, Zuev V V 1992 Optical remote sensing of atmosphere (*SPb, Hydrometeoizdat*) 231

[7] Privalov V E, Shemanin V G 2015 A Lidar Equation with Allowance for the Finite Width of the Lasing Line *Bulletin of the Russian Academy of Sciences. Physics* **79**-2 149-159

[8] Chaikovsky AP, Grudo Ya O, Karol Ya A et al 2015 Regularizing algorithm and processing software for raman lidar-sensing data *J. Appl. Spectroscopy* **82**-5 779-787

[9] Glazov G N 1987 Statistics problems of atmospheric lidar sensing (*Novosibirsk, Nauka*) 308

[10] Measures R 1987 Laser Remote sensing (*Moscow: Mir*) 550

[11] Fouche D G, Chang R K 1972 Relative Raman cross-section for O$_2$, CH$_4$, C$_2$H$_6$, NO, NO$_2$ and H$_2$ *Appl. Phys. Lett.* **20**-2 256-257

[12] Donchenko V A, Kabanov M V, Kaul B V, Samokhvalov I V 2010 Atmospheric electro optics (*Tomsk: NTL Publ.*) 220

[13] Laser monitoring of the atmosphere 1979 Hinkley E D Ed. (*Moscow: Mir*) 416

[14] Sverdlov A M, Kovner M A, Krainov E P 1970 Vibrational Spectra of the many atomic molecules (*Moscow: Nauka*) 560

[15] Laser Handbook 1978 Prokhorov A M Ed (*Moscow: Sov. Radio*) **1** 591

[16] Dyachenko V V, Chartiy P V, Shemanin V G 2019 Laser Systems for the Pollutants Control in the Oil and Gas Industry *IOP Conf. Series: Earth and Environmental Science* **272**-**032003** 1-6 DOI:10.1088/1755-1315/272/3/032003