

ON THE POSSIBILITY OF USING THE LIDARS IN THE STUDY OF THE NITROGEN CYCLE IN A PHOTOCHEMICAL SMOG

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A minimum set of components, namely, NO, NO₂, NO₃, and O₃ describing the day cycle of nitrogen oxides in the polluted troposphere is determined. The possibility of the range-resolved lidar measurements of NO₃ mass concentrations is demonstrated. The DIAL parameters needed for the simultaneous measurements of NO, NO₂, NO₃, and O₃ mass concentrations and relative distribution of an aerosol are determined with the purpose of studying the mechanism for the formation of the photochemical smog.

The chemical cycle of nitrogen oxides is decisive for the formation of the photochemical smog, but the detailed mechanism of smog formation is currently not clear.¹ In the slightly polluted air there occur the processes which are typical of the developed photochemical smog.² Until recently the main attention has been paid to nitrogen oxide and nitrogen dioxide and ozone in studying the nitrogen cycle in the low troposphere. But the last researches in the area of night chemistry of nitrogen oxides has shown the importance of determining NO₃ and N₂O₅ contents in the troposphere.^{3,4} The analyses of the experimental works,^{3,4,5} in which the optical methods of determining NO, NO₂, and NO₃ mass concentrations along the paths were implemented, has shown the inapplicability of these methods in the urban atmosphere because of inhomogeneity in the distribution of the components along with the inhomogeneity of reactions in the regions of emissions into the atmosphere. In addition, in studying the chemical cycle of nitrogen oxides, we must measure simultaneously the mass concentrations of several components during several minutes corresponding to the time of a chemically frozen atmosphere. Using the lidars seems to be most promising for solving this problem.

In this paper the possibility of using the DIAL for the measurement of NO, NO₂, NO₃, and O₃ mass concentrations is considered aimed at studying the daily cycle of nitrogen oxides in the urban smog.

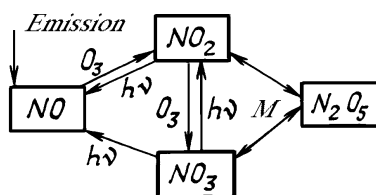


FIG. 1. Basic reactions of the chemical cycle of nitrogen oxides in the troposphere.

The main anthropogeneous source of nitrogen oxides in the atmosphere is the reactions of combustion in which the oxidation of atmospheric nitrogen forms nitrogen oxide, whose subsequent oxidation in the troposphere results in forming others oxides. Figure 1 shows the basic reactions of the chemical cycle of nitrogen oxides selected with an account of the rate constants for reactions and actual mass concentrations of the components in the low troposphere.

Ozone which is involved in oxidation of NO to N₂O and NO₂ to NO₃ is also one of the most toxic components of the smog. Arrows with superscription $h\nu$ designate the photolysis by the solar light. In the reactions of formation and dissociation of N₂O₅



the molecule M (which is typically either nitrogen or oxygen) is involved. This molecule is chemically stable.

During the day the photolysis of NO₃ proceeds with higher rate than the reactions of forming NO₃ (Ref. 6) and a state of pseudoequilibrium between the mass concentrations of NO, NO₂, and O₃ is set up in photolysis of NO₂ and oxidation of NO by ozone,¹ therefore, it is necessary to measure the mass concentrations of NO, NO₂, and O₃ during the day. At night when the photolysis is terminated the main components are NO₂, NO₃, N₂O₅, and O₃. Since the equilibrium between the mass concentrations of nitrogen oxides is set up in reaction (1), we must measure the variations in O₃, NO₂, and NO₃ or N₂O₅ concentrations for understanding the night chemistry.

The chain of reactions and main components are identical for a given time of a day (during the day or at night) and the variations in the mass concentration of the components are directly related with their previous behavior. In studying the urban pollution this relation is of great significance. This fact can be explained by the cyclicity of the anthropogeneous emissions into the atmosphere.

Thus, the complete information about the chemical conversion of nitrogen oxides can be available only after studying their daily cycle.

The daily behavior of the mass concentrations of components is mainly repeated but there exist substantial differences that cannot be explained in the framework of the model of interconversion of nitrogen oxides shown in Fig. 1.

This difference is caused not only by the difference in the power of anthropogeneous sources and meteorological conditions but also the existence of sinks and channels of conversion of nitrogen oxides owing to the reactions with other components among which CO, SO₂, organic compounds, water vapor, and droplets are principal.⁴⁻⁶ Studying the daily cycle of nitrogen oxides enables one to determine the basic channels. Taking account of the

influence of the temperature and humidity is the simplest problem because we may restrict ourselves with local measurements of these parameters.^{3,5}

The operation of the differential absorption lidar (DIAL) is based on the strong dependence of the absorption cross section of the gas under study on the wavelength near the line or band of absorption. The minimum measurable mass concentrations of the components N_{\min} can be estimated by the formula⁷

$$N_{\min} = \frac{1}{2\Delta\sigma\Delta R} \ln\left(1 + \frac{\Delta E}{E}\right), \quad (2)$$

where $\Delta\sigma$ is the differential absorption cross section of the component under study at the sensing wavelengths, ΔR is the length of the sensing strobe, $\Delta E/E$ is the relative error in the signal determination. The DIAL method can be used easily in the visible and near-ultraviolet ranges. To study the daily cycle of nitrogen oxides, we propose to measure the mass concentrations of O_3 , NO, NO_2 , and NO_3 , which have the strong absorption bands in this wavelength region, and to reconstruct the concentration of N_2O_5 on the basis of NO_2 and NO_3 since the absorption spectrum of N_2O_5 does not contain the lines suitable for the measurement by this method. Let us consider the possibility of using the DIAL for sensing the selected components in detail.

NO_3 radical has the absorption line whose maximum is centered at a wavelength of 662 nm with the half-width about 3 nm. For the resonant wavelength $\lambda_0 = 662$ nm and the wavelength $\lambda_\omega = 660$ nm centered at the wing of the absorption line, the differential cross section of absorption due to NO_3 is $\Delta\sigma = 1.47 \cdot 10^{-17}$ cm² (Ref. 8). The only competitive absorbent in this spectral region is water vapor, but its absorption at the selected wavelengths is weak and can be easily taken into account.³ In estimating the minimum measurable NO_3 concentration according to formula (2), the error $\Delta E/E$ of the signal determination was assumed to be equal to 0.002, that is achievable for the present-day installations⁹ with the use of the optimal methods for mathematical processing of the lidar signal. The minimum measurable NO_3 mass concentration for $\Delta R = 300$ m is equal to 90 ppt (parts per 10^{12}). The peak NO_3 mass concentrations at night in the polluted atmosphere reach the values greater than 400 ppt (Ref. 10) which enables one to expect the spatially resolved measurements of NO_3 mass concentrations. In this case the sensing range can reach several kilometers.¹¹

The measurements of O_3 mass concentrations with the DIAL are usually performed in the near-UV spectral region. In so doing an account of the large number of competitive absorbents as well as of the large variance of the aerosol correction factor for the difference between the sensing wavelengths of about 15 nm (Ref. 12) is difficult. When measuring the photochemical smog, the account of these two factors is of great significance.

The competitive absorbents for ozone in the photochemical smog are the following components: N_2O_5 , NO_2 , SO_2 , H_2O , HO_2 , CH_2O , H_2O_2 , HNO_3 , N_2O , H_2S , HNO_2 , NH_3 , and PAN (Refs. 20, 21, and 22). The main of the above-mentioned components are SO_2 , N_2O_5 , NO_2 , and H_2O with the typical mass concentrations of 100, 20, 100 ppb and 2000 ppm, respectively.³⁻⁶ For the typical O_3 concentration of 100 ppb, the total contribution of the rest of the competitive absorbents does not exceed 0.1% of the value

of ozone absorption. Since in this paper NO_2 and H_2O mass concentrations will be directly measured and the profile of N_2O_5 concentration will be reconstructed from NO_2 and NO_3 measurements, the contribution of these absorbents can be taken into account. Thus the only ignored absorbent is SO_2 . The absorption cross section of O_3 in the wavelength range 260–290 nm decreases virtually linearly with increases of the wavelength,¹³ therefore, to increase the sensing range it is expedient to select the wavelengths near 290 nm.

Figure 2 shows the behavior of absorption due to O_3 and SO_2 in the wavelength range 260–310 nm (Refs. 13 and 14). The wavelengths $\lambda_0 = 288.3$ nm and $\lambda_\omega = 289.2$ nm were selected for ozone in such a way that the differential cross section of absorption due to SO_2 was practically equal to zero and the differential cross section of absorption due to O_3 $\Delta\sigma$ was equal to $1.7 \cdot 10^{-19}$ cm². This way of selection of the wavelengths with the difference $\lambda_\omega - \lambda_0 = 0.9$ nm makes it possible to neglect the aerosol correction factor for sufficiently large differential cross section of absorption due to ozone. For $\Delta R = 300$ m and $(\Delta E/E) = 0.002$ the estimate of the minimum measurable O_3 concentration according to formula (2) is equal to 8 ppb. The spatial-resolved O_3 sensing in this wavelength range is possible for the distances of several kilometers.

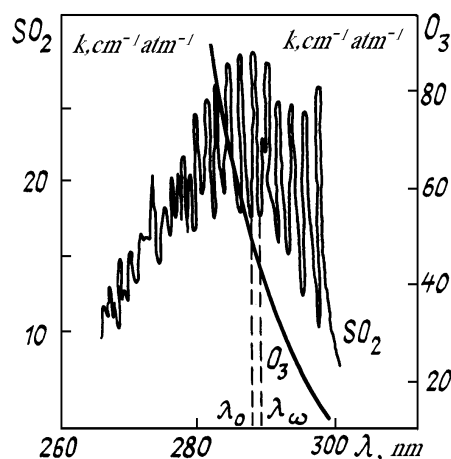


FIG. 2. Spectral behavior of the coefficient of absorption due to SO_2 (Ref. 14) and O_3 (Ref. 13) in the wavelength range 260–310 nm.

To measure NO and NO_2 concentrations the procedure analogous to that described in Ref. 9 is proposed. The behavior of absorption due to NO_2 near 450 nm and absorption due to NO near 226 nm are shown in Fig. 3. For NO_2 sensing the radiation of a dye laser at the wavelengths $\lambda_0 = 448.1$ nm and $\lambda_\omega = 453.6$ nm was used in Ref. 9. Frequency doubling of radiation of this laser with the BBO crystal (Ref. 15) yields the radiation with the wavelengths $\lambda_\omega = 224.05$ nm and $\lambda_0 = 226.8$ nm for NO sensing. However, such selection of the wavelengths does not allow one to measure NO in the real atmosphere because of competitive absorbents. The competitive absorbents for NO are O_3 , SO_2 , and NH_3 near 226 nm. The absorption spectrum due to SO_2 near 226 nm (Ref. 16) is also shown in Fig. 3. The differential absorption coefficients Δk due to these components were equal to $1.0 \cdot 10^{-6}$ cm⁻¹ and $3.15 \cdot 10^{-6}$ cm⁻¹ for the wavelengths used

in Ref. 9 under conditions of typical concentrations of SO₂ (100 ppb) and NO (30 ppb) in the smog. To measure the NO concentrations for such a selection of the wavelengths, we must measure simultaneously the SO₂ concentrations. In this paper we propose the radiation with the wavelengths λ₀ = 226.2 nm and λ_ω = 224.05 nm be used for NO sensing. In so doing, the differential coefficient of absorption due to SO₂ decreases to 0.4·10⁻⁶ cm⁻¹ and the differential coefficient of absorption due to NO increases to 3.5·10⁻⁶ cm⁻¹, i.e., the contribution of absorption due to SO₂ to the measured absorption due to NO will be about 10%. This enables one not to measure directly SO₂ when determining the NO concentration. Ozone has continuous spectrum of absorption near 225 nm. The differential coefficient of absorption due to ozone is about 1.5·10⁻⁶ cm⁻¹ at these wavelengths under conditions of typical ozone concentration 100 ppb (Ref. 13). The absorption due to O₃ comprises about 50% of the value of absorption due to NO, i.e., when measuring the NO concentrations, we must take the absorption by ozone into account. In this paper we propose a direct measurement of ozone concentrations taking ozone contribution to the radiation absorption into account. The differential coefficient of absorption due to NH₃ with its typical concentration 10 ppb is equal to 2·10⁻¹⁹ cm⁻¹ (Ref. 17) for these wavelengths. This makes it possible to ignore the existence of NH₃ in the volume being sensed.

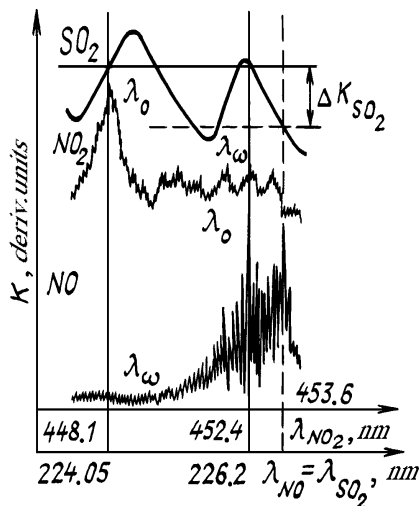


FIG. 3. The behavior of the coefficient of absorption due to SO₂ (Ref. 16) and NO (Ref. 9) near 226 nm and NO₂ (Ref. 9) near 450 nm.

For the minimum measurable NO concentration which is equal to the correction factor for the absorption due to SO₂ (3 ppb) and Δσ = 4.6·10⁻¹⁸ cm² we shall determine the value ΔE/E ≈ 0.02 based on formula (2). The maximum sensing range in this wavelength interval is determined by the absorption due to the molecular oxygen and by the strong Rayleigh scattering. This value is estimated about 1 km that agrees with the experimental results of Ref. 9. The differential cross section of absorption due to NO₂ at the wavelengths λ₀ = 448.1 nm and λ_ω = 452.4 nm is equal to Δσ = 2.4·10⁻¹⁹ cm⁻² (Ref. 18). The large variance of aerosol correction factor caused by the large difference (4.3 nm) between the sensing wavelengths is the main difficulty in NO₂ sensing. The estimate of the aerosol

correction factor for NO₂ under conditions of a polluted urban atmosphere at the above-given wavelengths following the procedure proposed in Ref. 12 gives approximately 10 ppb. For the minimum measurable NO₂ concentration which is equal to the aerosol correction factor, namely, 10 ppb we obtain ΔE/E ≈ 0.003 according to formula (2). The range of NO₂ sensing can reach several kilometers¹¹ near 450 nm.

For simultaneous measurements of O₃, NO, NO₂, and NO₃ concentrations, the following configuration of the differential absorption lidar is proposed. The lidar source consists of two symmetrical blocks which operate synchronously. Either block is used for obtaining the radiation at one of the wavelengths of the selected pair for every investigated component. A block diagram of one of the units is shown in Fig. 4.

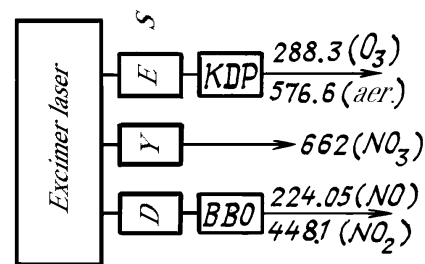


FIG. 4. Block diagram of the DIAL emitting system intended for sensing of NO, NO₂, NO₃, O₃, and aerosol.

For NO₃ sensing, the radiation of the dye laser at a wavelength of 662 nm (660 nm for another block) is used. For O₃ sensing at a wavelength of 288.3 nm (289.2 nm), the radiation of the dye laser is used with subsequent frequency doubling with the KDP crystal. The radiation of the dye laser at a wavelength of 448.1 nm (452.4 nm) is used for NO₂ sensing and frequency doubling with the BBO crystal provides the radiation at a wavelength of 224.05 nm (226.2 nm) for NO sensing. The dye lasers in each block are pumped by the XeCl excimer laser. The proposed configuration makes it possible to obtain the laser pulses at λ₀ and λ_ω for a certain component within a time of the frozen atmosphere, namely, after a time of 1 ms (Ref. 11). Successive switching of the excimer pumping laser on the different types of dyes makes it possible to measure simultaneously the mass concentrations of the four components within the characteristic time of the chemically frozen atmosphere of the order of several minutes.

An analysis of the backscattered signal at the nonresonant wavelengths λ_ω = 452.4 nm for NO₂, λ_ω = 660 nm for NO₃, and doubled wavelengths 578.4 nm and 576.6 nm for ozone sensing makes it possible to reconstruct the relative distribution of aerosol on the path from each measurement.⁷ The regions with an enhanced content of an aerosol can be regarded as probable regions of the increased inhomogeneity of reactions.¹⁹

In measuring simultaneously the above-mentioned four components, the maximum sensing range L will be limited by the NO sensing range which is about 1 km. For L = 1 km the lidar specifications needed for obtaining the above-mentioned values of N_{min} of the components under study were estimated. The laser sensing equation¹¹ was used for estimating. When the active receiving area is equal to 0.1 m² and the pulse repetition rate is about 20 Hz in

sensing of NO and O₃ the output radiation energies are 5 mJ and 30 mJ for NO₂ and 10 mJ per pulse for NO₃. Output energy of the excimer laser must be about 100 mJ per pulse. With the above-mentioned specifications, the time needed for measuring the content of the four components on 1 km path with 50 m range resolution will be about 10 minutes, that is comparable with the time of the chemically frozen atmosphere. Thus, the proposed configuration of the lidar system with the above-indicated parameters makes it possible to measure the mass concentration of NO, NO₂, NO₃, O₃, and aerosol in order to investigate the daily cycle of nitrogen oxides in photochemical smog.

REFERENCES

1. P. Brimblekumb, *Composition and Chemistry of the Atmosphere* (Mir, Moscow, 1988), 351pp.
2. M.T. Dmitriev, in: *Meteorological Aspects of the Atmospheric Pollution* (Gidrometeoizdat, Moscow, 1981), Vol. III, pp. 96–102.
3. U. Platt, D. Perner, T. Schroeder, et. al., *J. Geoph. Res.* **86**, No. C12, 11–965 (1981).
4. U. Platt and D. Perner, *Geoph. Res. Lett.* **7**, No. 1, 89 (1980).
5. U.F. Platt, A.M. Winer, H.W. Biermann, et. all., *Envir. Sci. Technol.* **18**, No. 5, 365 (1984).
6. M. McIven and L. Phillips, *Atmospheric Chemistry* [Russian translation] (Mir, Moscow, 1978), 375 pp.
7. P. Camagni and S. Sandroni, *Optical Remote Sensing of Air Pollution* (Elsevier, Amsterdam, 1984), 422 pp.
8. J.A. Davidson, R.E. Shetter, B.A. Anderson, and J.G. Calvert, *J. Phys. Chem.* **91**, No. 23, 5858 (1987).
9. H.J. Kolsh, P. Raivoux, J.P. Wolf, and L. Woste, *Appl. Opt.* **28**, No. 11, 2052 (1989).
10. R. Atkinson, T.J. Wallington, A.M. Winer, and J.N. Pitts, *J. Phys. Chem.* **90**, No. 21, 5393 (1986).
11. E.D. Hinkley, ed., *Laser Monitoring of the Atmosphere* [Russian translation] (Mir, Moscow, 1979), 416 pp.
12. E.V. Browell, S. Ismail, and S.T. Shipley, *Appl. Opt.* **24**, No. 17, 2827 (1985).
13. *Geophysical Reference Book* (Nauka, Moscow, 1965), 571 pp.
14. H.D. Metter, *J. Chem. Phys.* **49**, No. 4, 1784 (1968).
15. K. Miyazaki, H. Sakai, and T. Sato, *Opt. Lett.* **11**, No. 12, 797 (1986).
16. P. Warneck, F.F. Marmo, and J.O. Sullivan, *J. Chem. Phys.* **40**, No. 4, 1132 (1964).
17. B.A. Thompson, P. Harteck, and R.R. Reeves, *J. Geoph. Res.* **68**, No. 24, 6431 (1963).
18. N. Takeuchi, H. Shimizu, M.O. Kuda, *Appl. Opt.* **17**, No.17, 2734 (1978).
19. B.G. Heikes and A.M. Thompson, *J. Geoph. Res.* **88**, No. C15, 10 (1983).
20. S.P. Perov and A.Kh. Khrgian, *Current Problems of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1980), 290 pp.
21. V.M. Klimkin and V.N. Fedorishchev, *Atm. Opt.* **2**, No. 2, 174–175 (1989).
22. W.C. Stockwell and J.C. Calvert, *J. Photochem.* **8**, No. 1, 193 (1978).