MONITORING OF THE ATMOSPHERIC POLLUTION BY AN INFRARED DIAL SYSTEM

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Received March 28, 1994

A differential–absorption lidar (DIAL) system has been developed based on a CdSe *optical parametric oscillator (OPO) continuously tunable over the spectral range from* 8 *to* 13 μm. *Using this system transmission spectra and absorption coefficients for ammonia* (NH_3), *hydrazine* (H), *nonsymmetrical dimethylhydrazine* (NDMH), *tetramethyltetrazene* (T) *were obtained at laser lines corresponding to informative portions of the spectral range from* 8 *to* 13 μm. *Gas concentarations in a cell placed at an 80 m long sounding path were measured. Good agreement of the data obtained with the lidar and those obtained using standard chemical procedures was observed.*

In this paper we present the results of test experiments with a DIAL system based on a CdSe optical parametric oscillator (OPO) continuosly tunable over the spectral range from 8 to 13 μm.[1] The optical arrangement of the lidar is presented in Fig. 1.

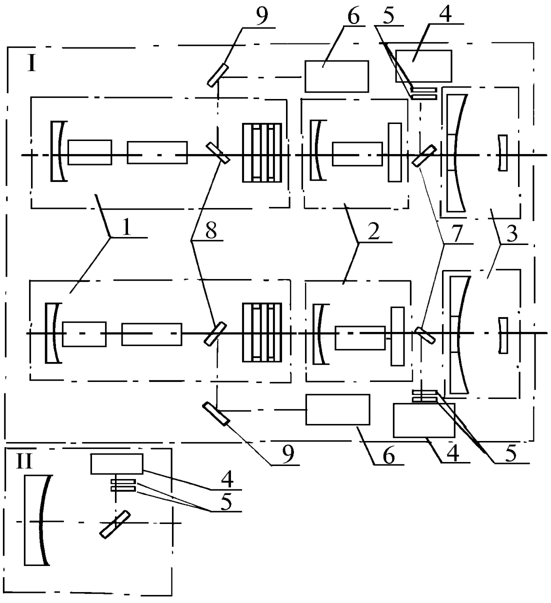

FIG. 1. Optical arrangement of the lidar: transmitter (I) and recording system (II); YAG: Er^{3+} *laser (1), a* CdSe *optical parametric oscillator (2), a correcting telescopic system (3), a photodetector (4), filters (5), a* He–Ne *laser (6), polished dividing* BaF_2 (ZnSe) *plates (7), polished quartz, KI, plates (8), and aluminum coated mirrors (9).*

The lidar transmitter includes two tunable OPO. A correcting Gregorian telescopic system that consists of two spherical reflecting mirrors is used at the output of every channel of the laser transmitter. Such an optical system enabled us to reduce the laser beam divergence from 3 to 0.3 mrad.

The band–pass filters can be placed in reference channels of the transmitter and in front of a photodetector in the detecting system to separate out either long–wave or short–wave portion of sounding radiation.

The unit of recording and information processing is a device that transforms the electrical signals delivered from the detector into the data employed by imaging system according to assigned algorithm.

The transmitter and the receiving optical system of the lidar are mounted on a single rotable table that enables one to change the sounding direction quickly and precisely from – 180° to + 180° in azimuth angle and from –45° to +45° in elevation angle.

Using this lidar the transmission spectra and absorption coefficients at laser lines within the informative portions of the spectral range from 8 to 13 μm containing absorption lines and bands of ammonia (NH_3), hydrazine (H), nonsymmetrical dimethylhydrazine (NDMH) and tetramethyltetrazene (T) were obtained. The block–diagram of the experimental arrangement is shown in Fig. 2.

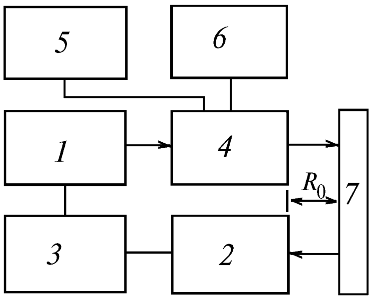

FIG. 2. Block–diagram of the arrangement for spectral measurements: the lidar transmitter (1), detecting system (2), the recording and processing unit (3), the cell (4), the installation for production of gas examined at required concentration (5), the installation for measurement of gas concentration in the cell (6), a screen (7), R_0 *is the distance from the cell to the screen.*

The measurements were carried out using a cell. A flow of gas at a certain concentration was created in the cell with a dynamic installation. The required concentration of the gas being under investigation was creared in the following way: nitrogen passed a chamber at a rate of 1–2 l/min during 30 minutes filled by either pure substance or solution of the substance in an inert solvent. The

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chamber could be fitted also with a valve for input of a substance. The gas concentration in the cell was measured before and after the experiments by photoelectrocalorimetric method. After initial determination of the gas concentration the ten–fold gas exchange was allowed in the cell before the spectral measurements started.

Spectral measurements were carried out at a gas pressure of 1 atm in order to model the atmospheric conditions for collisional broadening of absorption lines of the gases examined. Nitrogen of 99.99% purity was used as a buffer gas instead of air. Therefore, the destruction of molecules under influence of oxygen was avoided. The transmission spectra of NH_3, H, NDMH and T within the informative portions of the spectral range from 8 to 13 μm, were measured. Figures 3 and 4 present the transmission spectra measured for the above–mentioned gases. Data obtained in Ref. 3 are also presented for comparison. The absorption coefficients were calculated at the wavelengths corresponding to the minimum and maximum transmittance using the following equation:

$$\alpha(\lambda) = \left| \ln\left(\frac{P_{\mathrm{k}}\, P'_{0\mathrm{k}}}{P_{0\mathrm{k}}\, P'_{\mathrm{k}}}\right) \right| \Big/ \; p\,L\ . \qquad (1)$$

Here $P_{0\lambda}$, P_λ are the values of laser radiation intensity at the input and the output of the cell filled with the mixture of a gas with nitrogen; $P'_{0\mathrm{k}}$ and P'_{k} are values of the laser radiation intensity at the input and the output of the cell filled with nitrogen alone; p is the partial pressure of a gas examined; L is the cell length; λ is the laser radiation wavelength. The results of calculations are presented in Table I.

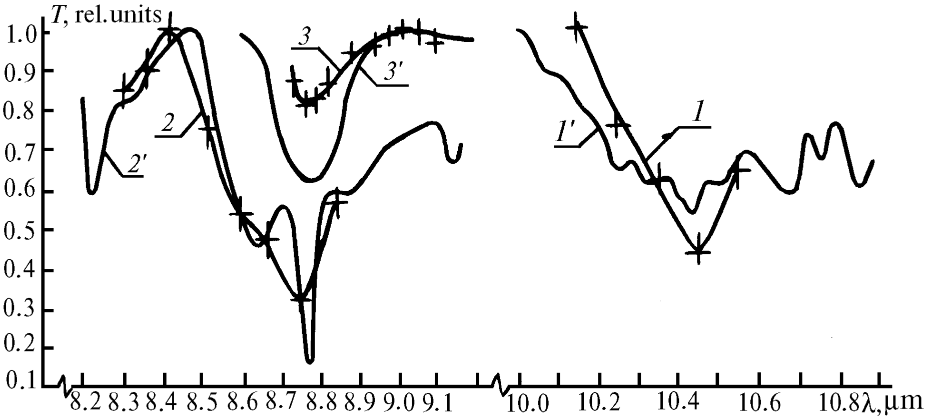

FIG. 3

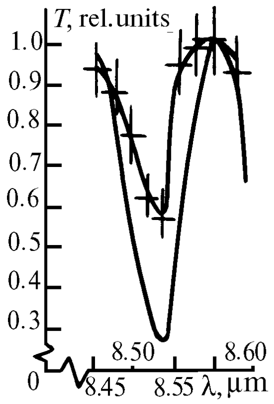

FIG. 4

FIG. 3. Transmission spectra of H *(1, 1'),* NDMH *(2, 2') and* T *(3, 3') obtained at laser wavelengths of the lidar and with a "Perkin Elmer Model 21" spectrophotometer (Ref. 3).*

FIG. 4. Transmission spectra of NH_3 *obtained at laser wavelengths of the lidar (+) and with a "Perkin Elmer Model 21" spectrophotometer (Ref. 3) (bottom solid line).*

TABLE I. Absorption coefficients of H, HDMH, T, *and* NH_3 *at the sounding wavelengths.*

Gas	λ_1, λ_2 μm	$\alpha \pm \delta\alpha$ $(\mathrm{atm \cdot m})^{-1}$
H	10.15	178±35
	10.45	684±140
NDMH	8.42	67±13
	8.75	549±110
T	8.76	758±150
	9.01	144±30
NH_3	8.54	156±30
	8.60	30±7

Note: δ is error.

To find the error of the measurement of α that can be caused by output frequency variation of CdSe OPO due to variable sounding angle and unstable ambient temperature, five runs were carried out with ~50 readings in each run. Variation of the air temperature during the experiments was about 5°C. The results obtained are presented in Table II.

The error of α measurement did not exceed 4% for each of gases. The low values of errors were caused by large ratio of the laser width to the width of gas absorption band. The vibrational–rotational structure of the absorption bands was not resolved under the conditions of our experiments. Therefore, since lidar output line width was $0.3\ \mathrm{cm}^{-1}$, it exceeded the width of separate absorption band, but it is at least an order of magnitude lower than the width of integral absorption band. The small variation of lidar wavelength ($\Delta\lambda \sim 10^{-4}$ μm for NDMH and NH_3 and $\Delta\lambda \sim 5 \cdot 10^{-3}$ μm for T and H) resulted in the low value of the error of α measurements (<4%).

TABLE II. Absorption coefficients of gases.

Gas	λ, µm	α, (atm·m)$^{-1}$	$\bar{\alpha}$, (atm·m)$^{-1}$	$\left\lvert\frac{\alpha-\bar{\alpha}}{\bar{\alpha}}\right\rvert_{\max}\cdot 100$, %	$\frac{\delta\alpha}{\bar{\alpha}}\cdot 100$, %
H	10.45	660; 684; 691; 695; 690	684	3.5	2.6
NDMH	8.75	560; 549; 531;565; 540	549	3.5	3.2
T	9.01	144; 148; 143; 145; 140	144	2.8	2.5
NH_3	8.54	154; 156; 150; 162; 158	156	3.8	3.6

Note. $\delta\alpha = t_{0.95;\,5}\cdot\delta\bar{\alpha}$, where $t_{0.95;\,5}$ = 2,8 (the Student factor); $\delta\bar{\alpha}$ is the rms deviation from the mean value of α.

The test experiments with the lidar system under field conditions were performed at a path 80 m long with a reflecting screen at the end of the path. Besides, the H, NDMH, T, and NH_3 concentrations were measured with respect to their background values in a cell placed on a path 80 m long. The measurements were performed at the wavelengths indicated in Table I. The signals reflected from the screen were recorded. Laser beam passed through either the cell filled with a mixture of the gas examined and nitrogen or the cell filled with nitrogen alone. The gas concentrations with respect to their background values were calculated using the following equation:

$$C = \ln\left(\frac{P_{\lambda1}\,P'_{\lambda2}}{P_{\lambda2}\,P'_{\lambda1}}\right) \Big/ \Delta\alpha\, L\ , \qquad (2)$$

where $\Delta\alpha = |\alpha_1 - \alpha_2|$.

TABLE III. H, NDMH, T, and NH_3 concentrations measured in the cell with the lidar and standard chemical techniques.

Gas	λ, µm	Lidar method $C \pm \delta C$, mg/m^3	Chemical method $C^* \pm \delta C^*$, mg/m^3	$\frac{\lvert C - C^*\rvert}{C}$, %
H	10.15 10.45	1350±350	1100±200	18.5
HDMH	8.42 8.75	1950±450	1800±350	7.7
T	8.76 9.01	3400±800	3100±600	8.8
NH_3	8.54 8.60	2200±500	1900±400	13.6

Table III presents the gas concentrations in the cell obtained in lidar experiments and by standard chemical techniques.

In our opinion, the systematic excess of the values of the gas concentrations observed in lidar experiments over the values obtained by chemical techniques can be attributed to the instrumental error.

The difference of the results does not exceed 20%. The values of error of the lidar measurements of the gas concentrations as large as 22.7–25.9% are primarily determined by large error (~20%) of standart chemical procedures of preliminary measurements of the gas concentrations that were used for calculation of absorption factors.

Thus, the absorption spectra for H, NDMH, T and NH_3 within the informative portions of the spectral range from 8 to 13 µm were measured using infrared lidar system. The absorption coefficients at the wavelengths corresponding to the minimum and maximum absorption of the gases were obtained. The gas concentrations in cell placed at a path of 80 m length were measured. Good agreement of the values obtained in lidar experiments with those obtained using standard chemical procedures was demonstrated for all gases studied.

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