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UNIVERSAL TRACE POLLUTANT DETECTOR FOR AIRCRAFT MONITORING OF THE OZONE LAYER AND INDUSTRIAL AREAS

I.V.FILIOUGUINE, S.V.KOSTIOUCHENKO, N.N.KOUDRIAVTSEV

MOSCOW INSTITUTE OF PHYSICS AND TECHNOLOGY
Moscow region, Dolgoprudny, Institutsky per. 9, MIPT,
141700 USSR, Fax. (095) 408-56-77

Abstract.

A method of monitoring the trace impurities of nitrogen oxides based on controlling of luminescence of NO molecules excited by nanosecond gas discharge have been developed having pptv-ppbv sensitivity and temporal resolution less than 0.01 s.

Introduction.

Measurements of contaminations of the trace pollutant gases such as NO, NO_x in the Earth atmosphere at altitude range 10-30 km is important for ozone layer conditions control [1]. Several methods have been developed for nitrogen oxides trace contaminations measurements in air. One group of them is based on monitoring of absorption of NO molecules in UV-range of spectrum [2]. But the most spread out are methods based on the chemilumenescence intensities measurements under injection of ozone molecules in the mixtures, containing NO [2].

These methods have high sensitivity up to ten pptv, 1.0-10.0 s response time, reliability and simplicity in practical realization [1]. Modern NO_x control systems for aircrafts and high-altitude balloons are based on chemilumenescence method [1,3]. But in these systems several expensive high technology elements such as Au catalysts converter are utilized. In addition the resolution time of these systems at high sensitivity limit is more than approximately one second which is unsufficient for high-speed aircraft monitoring.

In this study a new method of monitoring the trace impurities of nitrogen oxides based on controlling of luminescence of NO molecules excited by nanosecond gas discharge have been proposed as well as a control system for aircrafts utilizing having pptv-ppbv sensitivity and time resolution better than 0.01 s.

The developed detector for NO and other pollutant molecules trace concentration measurements has been described. The trace concentrations of these molecules are controlled by means of their radiation arising from fast 10-50 ns decay of some electronic levels excited in nanosecond gas discharge [3]. The air under the monitoring is pumped through a special discharge gap consisted of the quartz tube with two electrodes at its ends. The discharge gap has a coaxial geometry to be fine electrodynamically adjust to the nanosecond voltage generator. The high voltage impulses are repeated with frequency 30-100 Hz according to the air flow velocity in the tube. An ordinary optical system have been used to collect this radiation and to direct it to the monochromator or array of band pass filters.

Physical principals.

The main idea of proposed method is in very fast excitation of NO molecules with subsequent recording its luminescence in nanosecond time of scale when chemical reactions don't disturb an initial gas mixture contamination as well as nonradiative decay processes don't disturb of initially excited NO* molecules concentration. The gas is excited by breakdown ionization wave (BIW) developing from high voltage electrode and propagating with sub-light velocity through gas when high voltage nanosecond electrical pulse is put to the electrodes situated at the ends of the gas gap . The typical electrical pulses parameters are as follows: U=25-40 kV pulse amplitude, Δt=1-5 ns rise time, t=20-60 ns duration, n=20-100 Hz repetitive frequency conjugated to gas flow velocity in a discharge gap to have a full removing of the discharged gas from the gap.

In the BIW the main drop of the electrical potentials occurs in the neighbor of its front providing high reduced electrical field strength about 50-500 Td. At these parameters of the gas discharge its energy is mainly converted into electronics and vibrations of the particles, giving rise the significant concentrations of excited particles and so providing the high sensitivity of the method.

Laboratory set-up.

The laboratory set-up of NO defector for aircraft utilizing is represented in fig 1. The probes from ambient air are continuously supplying by gas flowing system (1) with electromagnetic valves and diaphragms to maintain gas pressure in the discharge gap (4) in the range P=3.0+0.3 Torr for different altitudes and flight speeds, as well as to gas samples removing from it with the velocity 50-100 samples per second. The sensitivity of our system is calibrated by mixture with known NO trace concentration from taken from vessel (5) and pumping through the discharge gap.

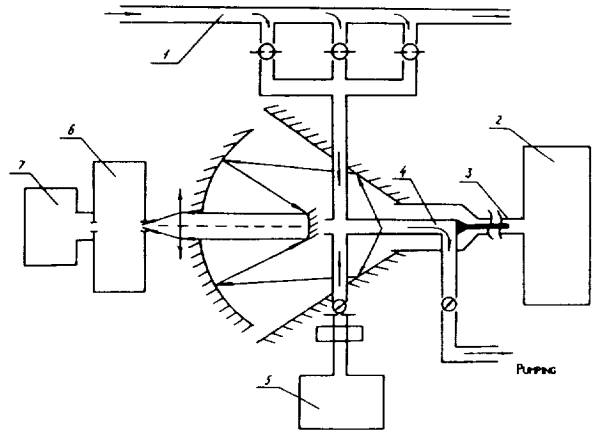

Fig.1. Experimental set-up.

The high voltage pulses from nanosecond generator (2) through coaxial line (3) are supplied to the conic high voltage and qraunded low voltage electrodes. The screen of coaxial cable is connected to the screen of the discharge tube. A radiation collection system, consists of several flat and spherical mirrors , lenses supply radiation to low-size monochromator (6). A high-sensitivity photomultiplier (7) is used for registration UV radiation.

Theory.

At the pressure in the discharge gap P= 5 Torr the nanosecond discharge provides a hig y uniform, strong nonequlibrated excited cold plasma. At these parameters the average electron energy is $\bar{\varepsilon}$=4.0-7.0 ev, their concentration $[N_e]>10^{12}$ cm^{-3} [3,4]. So, a strong radiation from air particles O_2, N_2 and trace contaminations as NO are presented in discharge afterglow. In addition continuous electrons deceleration radiation and recombination chemilumenescence present in the spectrum to. Picking

out the radiation from short leaving electronic states of impurities molecules in the appropriate spectral bands it's possible to have monitoring of trace contamination with high sensitivity and temporal resolution.

According to [5] the cross section of excitation of NO states by electron impacts is represented vs electron energy in the form:

$$\sigma^{m\ n}_{v''v'}(\varepsilon)=[M_e(\Delta E^{m\ n}_{v''v'})\ ]^2\varphi\ (\varepsilon/\Delta E^{m\ n}_{v''v'})*q^{m\ n}_{v''v'}$$

where Frank-Condon factors for states NO $(A^2\Sigma^+)$ is: $q^{00}_{v''v'}=0.1622$, $q^{10}_{v''v'}=0.3301$ [6], $\Delta E^{m\ n}_{v''v'}$ - energy of radiation transition.

The electronic radiative transition strength for variational v'=0-3 levels of NO $(A^2\Sigma^+)$ is $[M_e]^2=8.4*10^{-18}$ cm^2, the function $\varphi(x)$ in Bete-Born approximation is:

$$\varphi(x) = \varphi(E/\Delta E) = (\Delta E/E)*\ln(E/\Delta E).$$

In assumption of Maxwell distributions of electrons and ΔE=5.0 ev , the frequency of excitation of NO electronics levels is:

$$v^*= 8\pi*[NO]*\ M_e^2*q*(1/m^2)*(m/2\pi kT_e)^{3/2}$$

$$*\int_{\Delta E}^{\infty} \exp(-\frac{\varepsilon}{kT})*\ln\frac{\varepsilon}{\Delta E}\ d\varepsilon,$$

where T_e- electrons temperature, m - their mass.

At our conditions: P=3 Torr, T=300K, and [NO]=1 ppbv, kT_e=5 ev, the frequency of NO $(A^3\Sigma^+)$ state excitation v^* is about 7 s^{-1}., at kT_e=4 ev- v^*=5 s^{-1}. Hence, during the time of the discharge action t=40 ns at the typical electron concentration $n_e=10^{12}$ cm^{-3}, $\varepsilon=kT_e$=5 ev the concentration of NO molecules excited in the $(A^3\Sigma^+)$ state may be evaluated as:

$$[NO] = tn_e n^*=10^{15}\ cm^{-3}.$$

The radiative time of this electronic state is t_r=200ns [6], providing average radiation power during 200 ns afterglow with power $W = [NO]/t_r = 4*10^{-8}$ W/cm^3. This radiation intensity may be easily recording by ordinary optical systems. No disturbances of NO excited states concentration due to fast chemical reactions and nonradiative quenching are exist at this time interval after discharge. Recording the radiation spectral distribution from highly purified N_2+O_2 mixtures excited by nanosecond gas discharge at pressures 1-10 Torr (fig 2,3) we have found, that there are several transparent "windows" in the N_2+O_2 mixture spectrum, $\Delta\lambda$=1010-1024 nm (fig.2) and $\Delta\lambda$=1087-1110 nm (fig.3). The most convenient is spectral window $\Delta\lambda$=1087-1110 nm. in the near infrared. In these windows a strong radiation from several NO. transitions is presented, providing reliable selection of radiation of NO molecules.

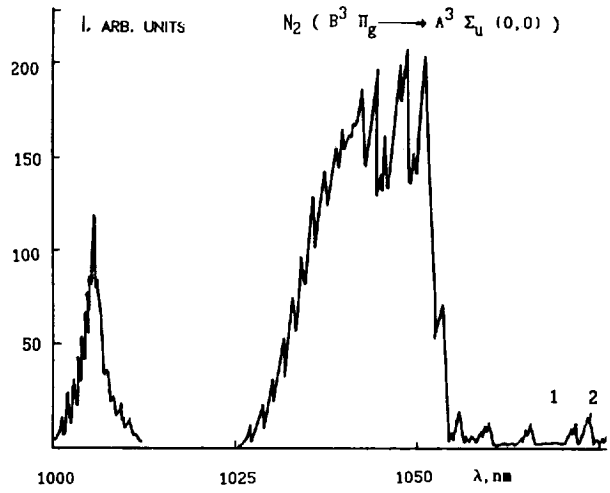

Fig.2. Radiation intensity in spectral range λ=1000-1070 nm from ealiar afterglow in N_2+ O_2mixture.

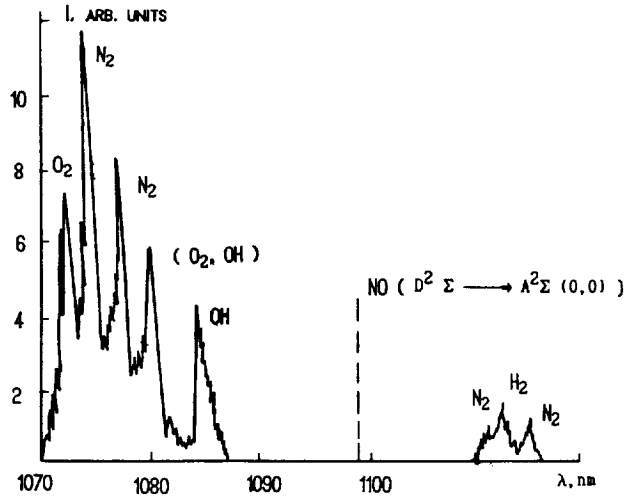

Fig.3. Radiation intensity in spectral range λ=1070-1150 nm from ealiar afterg low in N_2+ O_2mixture.

The sensitivity of this monitoring system is mainly defined by radiation noise in this spectral region by continuous-wave electrons decelerating and recombination radiation. The intensity of electrons decelerate radiation is represented by formula [4]:

$$dI = C_0 * \frac{N+N_e}{T_e^{1/2}} * \exp(-\frac{h\nu}{kT_e}) * d\nu,$$

where $C_o = \frac{16}{3} * (\frac{2\pi}{3}) * \frac{e^6}{m^{3/2} c^3 k^{1/2}} =$

$1.08*10^{-38}$, erg*cm^{3}K$^{1/}$.^{2}

For λ=.1000 nm, Δλ=.10 nm. the electrons decelerating radiation intensity may be evaluated as $W=6*10^{-11}W/cm^3$, that is three order of magnitude lower, that radiation of NO molecules at initial concentration [NO]=1 ppbv. Decelerating radiation decreases sharply, when the discharge is turned off with the characteristic time t =1nc, which is much lower than afterglow from short-living electronic states duration. Approximately the same value has a continuous recombination radiation. So, in principal, the sensitivity of this method may be estimated as 10 pptv. The temporal resolution of this method, is restricted only by possibilities of gas pumping through discharge gap and is less than 0.01s.

Conclusion.

A new method of NO trace contamination control with theoretical sensitivity up to 10 pptv and high temporal resolution adopted to spacecrafts and balloon utilizing have been developed. This method is based on a very sharp and effective excitation of the gas mixture by discharge in the form of breakdown ionization wave with subsequent radiation recording from short living electronics states of trace impurities. In laboratory experiments the sensitivity of NO determination up to 1.0 ppbv have been achieved with possibilities to further improving.

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