PHOTOACOUSTIC INVESTIGATIONS OF ATMOSPHERIC GASES

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In the paper the idea of testing of atmospheric air by photoacoustic method is presented. The base of photoacoustic effect theory in gas is presented. The paper concerns also preliminary results of photoacoustic experimental investigation, too.

Keywords: photoacoustic phenomena, photoacoustic cell, atmospheric air testing.

1. INTRODUCTION

Pure air (80% of air in troposphere), excluding well-known components as nitrogen and oxygen, consists of i.e. trace gases. Disadvantageous atmospheric phenomenon like greenhouse effect, acid rains, ozone hole etc. are caused by perturbation of air composition. Test of air composition, especially trace gases are important element of protection of environment. Trace gases investigation usually is made by special monitoring, but also in laboratory scale analysis. Between many laboratory techniques, photoacoustic spectroscopy is dynamic developing method for the sake of measures of ultralow concentration of the gases [1,2].

Photoacoustic effect can be divided into three main steps: heat emission caused by nonradiative deexcitation of the molecules excited by radiation, acoustic and thermal wave generation in sample and signal measure in photoacoustic cell with microphone. That phenomenon was first observed by A. G. Bell in 1880. His experiments resulted in the construction of i.e. photophone. A. G. Bell was found that photoacoustic effect occurs in all states. Progress in photoacoustic research was connected with discovery of laser.

2. THEORY OF PHOTOACOUSTIC EFFECT IN GASES

Theory of photoacoustic effect in gases was first presented by L. Kreutzer [3], and then by same other authors [4,5]. It is connected with two effects: heat production as a result of radiation absorption and caused by that effect acoustic wave generation.

Incident radiation is absorbed by the molecules and then rotational, vibrational and electronic energy levels are excited. Assume that absorbing gas have concentration N and molecules can exist only in one of two energetic states: excited (particles concentration N') and fundamental (concentration N-N'). Assuming also linearity of the effect occurring during absorption of light in gas, one can calculate the excited particles concentration from relation [1]:

$$\frac{dN'}{dt} = N\Phi\sigma - \frac{N'}{\tau} \tag{1}$$

Here Φ denote incident photon flux and σ the absorption cross section.

The heat source is generated in gas as a result of emitting energy produced in deexcitation processes of atoms. There are two types of heat sources depending on excitation type: modulated or impulse ones. For typical photoacoustic experiments with modulated radiation beam a power density of emitting heat is proportional to intensity of incident wave and it depends on absorption parameters. But for short laser impulse with high enough intensity of light or for continuously working lasers with high power optical saturation can cause non-linear relation between emitting heat and light intensity.

Heat energy conversion into acoustic signal can be written using P. Morse and K. Ingard [6] theory. Authors, starting from conservation laws of energy, momentum and mass and thermodynamic state equations for analyzing gas, have find heterogeneous wave equation, for acoustic pressure in existence of a heat source. This equation has two independent solutions: the little attenuation acoustic wave and the thermal wave. It has turned out that, thermal wave and acoustic wave are special separated and they variously behave themselves. For these reasons they may be separately treated. In trace gases analyses the acoustic signal (acoustic wave) has been mainly investigated. One usually investigates an acoustic signal in trace gases investigations and experiments are carried out in i.e. photoacoustic cell.

Amplitude of photoacoustic signal is proportional to heat power density and inversely proportional to modulation frequency. Photoacoustic signal also depends on boundary conditions characterized by type and photoacoustic chamber geometry [7].

3. PHOTOACOUSTIC SIGNAL ANALYSIS

For only one component gas there is registered signal, which in form [8] can be presented:

$$S = CPN\sigma \tag{2}$$

where C – cell constant found experimentally, P – power of radiation source, N – molecules concentration, σ - absorption cross-section. Minimum detectable absorption coefficient $\alpha_{\min}$ is given by:

$$\alpha_{\min} = \frac{S_{\min}}{CP} \tag{3}$$

where $S_{\min}$ is the noise-limited minimum microphone signal.

Minimum detectable concentration $c_{\min}$ of a species with absorption cross section σ mixed with a nonabsorbing gas at a total number density N_{tot} is given by:

$$c_{\min} = \frac{1}{N_{tot}} \frac{\alpha_{\min}}{\sigma} = \frac{S_{\min}}{N_{tot} CP\sigma} \tag{4}$$

In practical case one works with multicomponent gases it is necessary to analyze the signal for n different gases using a group of wave lengths λ_i (for i=1...) chosen according to absorption spectrum for pure components. That is the reason why for multicomponent gases registered signal is expressed in form:

$$S(\lambda_i) = S_i = CP_i N_{tot} \sum_{j=1}^{n} c_j \sigma_{ij} \tag{5}$$

for: $i = 1...m$, $j = 1...n$ and $m \geq n$, $P_i = P(\lambda_i)$ power of the laser for wavelength λ_i, c_j concentration of j-th component with absorption cross-section σ_{ij} for λ_i. From relation showed above one can derive the relation for concentration of j-th component:

$$c_j = \frac{1}{CN_{tot}} \sum_{i=1}^{m} [\sigma_{ij}]^{-1} \frac{S_i}{P_i} \tag{6}$$

$[\sigma_{ij}]^{-1}$ is inverse matrix of absorption cross-section σ_{ij}.

In order to getting an information about concentration from the registered signal there is need to use database values on absorption cross-section of given element and their compounds exp. HITRAN database [9] can be applied.

For impulse excitation signal can by written as follows [10]:

$$S(E,\lambda) = C\alpha(\lambda)E \tag{7}$$

where: C-cell constant, $\alpha(\lambda)$-absorption parameter, E-energy of light impulse. But there is much harder analysis of photoacoustic signal in that case [10].

4. EXPERIMENTAL INVESTIGATIONS

For some time in Institute of Physics at Silesian Technical University there are making investigations on photoacoustic effect in gases [2]. For photoacoustic investigations there was projected and built photoacoustic cell. Moreover there were created the set-ups for those experiments for gases excited by continual, modulated radiation beams and optional, by impulse excitation.

The idea of photoacoustic cell on fig. 1 is shown.

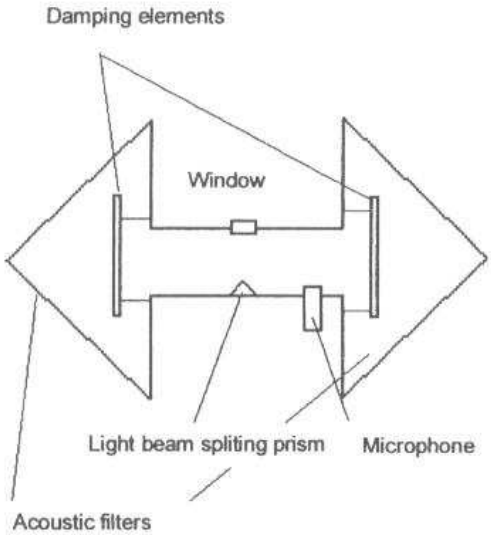

Fig. 1. The photoacoustic cell.

The presented cell is the multipass one with resonance at 1000 Hz. It can work in resonance, as well as out of resonance regimes.

In elaborating set-up as the light source the impulse dye laser is used. Optionally the xenon lamp will be applied, too.

Photoacoustic signal is registered by microphone using digital oscilloscope for impulses and lock-in nanovoltmeter for modulated light source. Set-up controlling and archiving dates is made thanks to GPIB bus.

Some results obtained in impulse investigation case are presented on fig. 2.

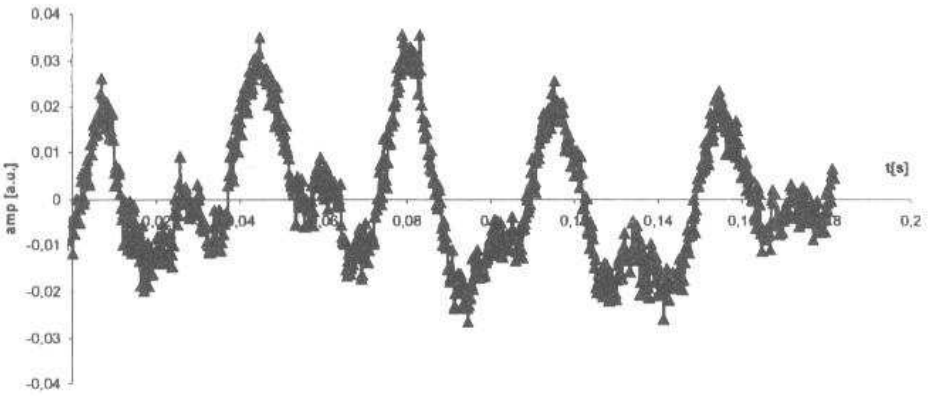

Fig. 2. Photoacoustic signal for impulse excitation after noise correction.

As it was written above an interpretation of the signal is rather hard. In modulated light source case there was found that experimental signal is to low. It is a result of low power of light source. Further investigations are concentrated on signal analysis, as well as on interpretation of impulse signal results received using with CO_2 laser as a light source. The results of experimental investigations will be published in near future.

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