ULTRASONIC MID-IR-LASER PHOTOACOUSTIC DETECTION OF TRACE GASES FOR APPLICATIONS IN TECHNOLOGY AND LIFE SCIENCES

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The laser photoacoustic (PA) spectroscopy is one of the most sensitive techniques applied for the local non-contact analysis of trace amounts of chemical compounds in gas media [1]. The PA technique is distinguished by a high sensitivity at the (sub) ppb level with the detectable absorption of 10^{-10} cm^{-1}, a short time resolution (down to a few seconds) and the capability to detect a large number of chemicals [2]. The most appropriate light sources for the technique are lasers operating in mid-IR spectral region. They are powerful carbon dioxide and carbon monoxide CW lasers and, since recently, CW parametric oscillators and quantum cascade lasers. For instance, the CO_2-lasers can be applied successfully in order to detect selectively compounds incorporating such chemical bonds as C-O, C-N, C=S, P=O, C-F, S=O, Si-O-, Si-H, P-OC, P-OH, S=O, N-H, P-H, As-H and others [3]. The use of rare isotopic species in the laser active medium allows both to widen the wavelength range (that is, to increase the number of substances to be detected) and to reduce essentially (more than 100 times) a deleterious effect of the background absorption by atmospheric air on the measurements [4]. The mid-IR-laser PA technique is a promising approach to inexpensive *in situ* multi-component analysis of atmospheric air in environmental pollution monitoring, exhaust gas monitoring, industrial process control, and leak detection [1]. The technique finds an expanding application in biology-related areas for sensitive detection of CO_2, C_2H_4, CH_4, NO_2, N_2O, H_2S, O_3, NH_3, C_2H_6, C_2H_6O, C_5H_{12} and others gases being involved in the metabolic reactions of living systems.

The principle of the technique is based on measuring the amplitude and phase of acoustic pressure oscillation arising due to absorption of a modulated laser beam by molecules of the gas inside a PA cell-resonator. The highly sensitive PA detection is realized if the modulation frequency coincides with an acoustic mode of the cell. The modulation frequency and the cell sizes should be correlated: the frequency increases with reducing the sizes. Traditionally, the laser beam is modulated with the help of mechanical choppers. Due to the sluggishness the choppers are able to excite the cell resonances at audio frequencies. It implies that the characteristic sizes of the PA cell are measured by centimeters. The cell volume ranges from tens of cubic centimeters to a few liters [5, 6]. As a result, the minimal rate of gas leak detectable in the

”audio” PA experiments is limited by the magnitude of ~10^{-9} cm^3/s (~10^{10} molecules per second). Such a sensitivity parameter is insufficient high in order to meet the biological and technical applications, which need the highly sensitive detection of gas leaks to be emitted by small-sized objects. The developed models of PA detector are exceeded significantly by the best commercial leak detectors in the sensitivity (~10^{-11} cm^3/s for helium mass-spectrometer-based systems [7]) or in the sizes (halogen leak detectors). The potential of the traditional “audio” PA technique for technical and biological applications associated with the local gas analysis is restricted.

A reasonable way of enhancement of the leak-detection sensitivity is to reduce the volume of the acoustic resonator (that is, the PA cell). The way requires the laser beam switching at higher frequencies. Of special interest is the switching in the range of ultrasonic frequencies up to the submegahertz scale where the absorption of acoustic wave is slight. The negative role of the lag of the vibration-translation energy redistribution with respect to the modulation (for instance, the effect of dynamic cooling) is expected to be small for a large number of volatile chemicals. The implementation of the ultrasonic approach to the PA technique will result in reducing the PA-cell sizes down to a few millimeters.

Combining the high sensitivity inherent in the traditional PA-approaches with an ability to probe the gas inside such a small-sized PA cell gives a possibility to analyze chemicals to be emitted by individual small-sized objects with an extremely low emission rate. For instance, the minimum detectable absorption of 10^{-10} cm^{-1} obtained in PA experiments [6] corresponds to a few ppt for the ethylene concentration or to a few tens of ppb for the carbon dioxide concentration (when a CO_2-laser is applied). At such detectable concentrations the application of a miniature PA cell (the cell volume is ~1 mm^3) allows to sense ~ 10^5 C_2H_4 molecules or ~ 10^9 CO_2 molecules. For comparison, in the aerobic reaction an individual cell of living organism emits carbon dioxide with the rate from 10^8 to 10^9 molecules per second [8]. In the photosynthesis reaction an individual cell of plant can absorb CO_2 with the rate higher than 10^{11} molecules per second [8]. A crude estimation shows that the application of the proposed approach can provide detecting the gas leak to be emitted by an object with the rate down to ~10^{-14} cm^3/s. The detection sensitivity will be increased 10^3 – 10^6 times compared to the traditional PA approaches and more than 100 times in relation to the mass-spectrometer-based leak-detection systems. In contrast to the systems, the ultrasonic PA leak detector needs no expensive vacuum chambers and can be applied to *in situ* localization of leak for a large number of substances (for instance, *F*/*Cl*-containing

compounds) to be emitted in atmospheric air. The approach is a promising line in order to create compact models of the high-sensitivity laser PA leak detector.

The highly sensitive leak detection is a promising commercial application for the technique. Possible areas of the PA leak detector application are the automobile industry (testing of fuel systems, aluminum wheels, air suspension systems, airbag inflators, air conditioning systems), the HVAC Technology (evaporators, compressors, condensers, accumulators, hoses, valves), the Vacuum and Over Pressure Technology (armatures, fitting, fire extinguishing systems, tanks) and the Packaging Technology (packing for pharmaceutical products and grocery items). A preliminary estimation show that the ultrasonic gas-leak PA detector on the basis of a compact RF waveguide CO_2-laser compares with the best commercial halogen leak-detecting devices in the cost and sizes. The estimated detector is expected to will outperform significantly the existing devices in the sensitivity. A mid-IR-laser PA gas analyzer can be used in order to sense explosive substances in airports and railway stations or to localize a tightness imperfection for the tubing with extremely toxic compounds (stibin, diborane, phosgene, phosphine, arsine, and others) in semiconductor plants. The approach is expected to find the application in Life Sciences (entomology, microbiology, cell biology, biochemistry etc.) focused into the metabolic processes occurring in small-scale biological samples: small animals and plants, their organs, tissue pieces or microscopic objects down to individual cells. The ultrasonic PA detector can be considered also as a material-economy tool for analyzing the chemicals in nanochemistry and other nanotechnology applications, which operate with the smallest amounts of substances.

A more detailed discussion of the theoretical background, advantages/problems, and possible application areas for the ultrasonic approach to PA detection of trace gases will be done in the report.

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