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Benzene Monitoring Using Laser Difference Frequency Spectroscopy

Weidong Chen, Fabrice Cazier, Daniel Boucher

MREID, Université du Littoral, 145 Av Maurice Schumann, 59140 Dunkerque, France

Frank K. Tittel

Rice Quantum Institute, MS 366, Rice University, 6100 Main St., Houston, TX 77005, USA

There is considerable interest in the detection of volatile organic compounds (VOCs) in the atmosphere because of their atmospheric reactivity. The need for identifying and quantifying VOCs levels in the atmosphere and industrial process control has led to the development of VOCs measurement techniques: chromatography coupled with mass spectrometry, Fourier transform spectroscopy, and laser spectroscopy. Laser absorption spectroscopy offers the advantage of highly selective in situ and real time measurements with detection sensitivities in the ppm to ppt range.

In this paper the feasibility of benzene (C_6H_6) concentration measurements by using mid-infrared laser absorption spectroscopy is reported. The spectrometer is based on laser difference-frequency generation (DFG) by mixing of two Ti Sapphire laser in a GaSe nonlinear crystal [1-2]. The infrared radiation, with an output power in the range of some tens nW, was continuously tunable from 8 to 19 μm .

A 10-liter glass flask was used for the preparation of benzene trace gas samples. The flask was filled with ambient air at a pressure of ~ 250 mbar, and an accurately weighed sample of the liquid benzene contained in a microsyringe was injected into the flask. The benzene gas mixture was then introduced into the absorption cell at a reduced pressure in the range of some tens mbar. C_6H_6 absorption lines of the ν_4 R(6) and $\nu_4 + \nu_{20} - \nu_{20}$ R(9) near 676.62 cm^{-1} were selected for the concentration measurements. The signal-to-noise ratio of ~ 20 deduced from the spectroscopic measurement yields a minimum detectable path-integrated concentration of ~ 1 ppm-m.

References

- [1] W. Chen, G. Mouret, D. Boucher, *Appl Phys* **B67**, 375 (1998)
- [2] W. Chen, J. Burie, D. Boucher, *Spectrochimica Acta* **A55**, 2057 (1999)

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Rapidly Tunable 2.5 kW CO₂ Laser Operating in Single-frequency and Two-wavelength Modes for Pollution Monitoring, Lidar and Scientific ApplicationsS.N. Bagayev, G.N. Grachev, V.F. Zakharyash, V.M. Klementyev, V.A. Orlov,
A.G. Ponomarenko, A.R. Sametov, V.B. Shulyat'ev
Institute of laser physics SB RAS

Pr. Lavrent'eva 13/3, Novosibirsk, 630090, Russia, tel: (3832)301863, fax: (3832)333478

The results of the development and investigations of the radiation characteristics of a rapidly tunable CO₂ laser to determine possibilities of its use in systems of Doppler location, distance measurements, and pollution monitoring with a large (up to 20-50 km) radius of action are presented.

The laser has been developed on the basis of the CW 3 kW CO₂ laser. An optical resonator of the laser has been developed on self filtering scheme. High beam quality is provided by this scheme (M^2 close to 1,6). The laser is equipped by three accessory units in a feedback arm to provide a variety of operation modes.

1. Single-frequency CW mode with capability of monotone line tuning (about 70 lines in all) with maximum output power up to 2,6 kW
2. The mode with simultaneous two-wavelength lasing at 40 pairs of adjacent laser lines with maximum total power up to 2,5 kW
3. The mode with rapid tuning of the generation line (with about 10^{-6} s transition time) in combination with an opportunity to form any given spectral-temporal sequence.
4. The mode of rapid tuning of a two-wave simultaneous generation in neighboring spectral lines (in particular, in lines from different branches and bands, more than a thousand of combinations) with the possibility of using Q-switching with wide ranges of power control (up to 100 kW), repetition frequency (up to 20 kHz), shape of laser pulses.
5. Repetition rate Q-switching mode with high peak power (up to 800 kW) and average one (up to 2,8 kW) with pulse repetition rate control in the range of 1-100 kHz.

It should be particularly emphasized that two-wavelength radiation is formed in single resonator with intersection of beams that is close to complete in the near and far fields. It generates a coherent super-position amplitude modulation wave. The experimental measurements have shown that the total amplitude of deviation in 1 ms was $\sim 10^{-8}$ for single-frequency mode and $\sim 10^{-7}$ for the difference frequency in the two-wavelength mode. At the same time, calculations by using the measured spectrum of turbulent fluctuations of the gas flow density fluctuations of an active medium have shown that the contribution of turbulent fluctuations into the spectral width of laser or modulation wave in the entire spectral range of frequency perturbations more than 1 kHz gives a relative instability no more than 10^{-9} . Hence, the results of the works performed show that the use of this laser is promising in the following areas:

1. Single-frequency generation mode makes it possible to use this laser as a radiation source for the laser Doppler radar with high range of performance and achievable (in principle) accuracy of determination of the objects' velocity at the level 0.1 m/s (in case of frequency stabilization at the level 10^{-9}).
2. Two-wavelength mode will make it possible to increase substantially a range of laser system for range finders and for measuring a small displacement in which the method of phase detecting of difference frequency of a modulation wave.
3. With rapid frequency tuning mode and opportunity to form the given spectral-temporal sequence of the generation for the development of laser systems for the ecological monitoring with the capacity to determine a pollution source with accuracy up to tens of meters, which could monitor the state of the air in the large industrial regions and megapolises.