Trace HCN Quantification Using Quartz Enhanced Photoacoustic Spectroscopy

A.A. Kosterev and F.K. Tittel
Rice Quantum Institute, Rice University, 6100 Main St., Houston, TX 77005, USA
Tel.: 713 348 5418, akoster@rice.edu

Abstract: Detection of trace HCN concentrations in dry nitrogen and ambient air was performed by means of quartz enhanced photoacoustic spectroscopy using a near-infrared DFB laser source. A normalized detection sensitivity of $2.5 \cdot 10^{-9}$ $cm^{-1}W/\sqrt{Hz}$ was achieved.

OCIS codes: (280.3420) Laser sensors; (300.6430) Spectroscopy, optoacoustic and thermo-optic

Hydrogen cyanide (HCN) is a highly toxic species that is contained in the exhaust of vehicles, in the smoke of burning nitrogen containing plastics, and is also used as a warfare chemical agent. Therefore, HCN concentration monitoring is important for industrial safety, fire detection in aircraft cargo bays, and homeland security. A quartz enhanced photoacoustic spectroscopy (QEPAS) approach which was first reported in 2002 [1] allows to significantly reduce the size of the laser-based chemical sensor while improving its immunity to environmental noise and thus can be the basis for portable trace gas sensors. The principles and implementation of QEPAS are described in more detail in [2]. Briefly, this technique is based on the utilization of a sharply resonant quartz crystal as an acoustic transducer. In this presentation we shall report QEPAS performance when applied to HCN detection in dry nitrogen and normal laboratory environment air with a 50% relative humidity.

The optical layout of the QEPAS based sensor is shown in Fig. 1. A fiber-coupled telecommunication DFB diode laser (JDS Uniphase) emitting >60 mW of optical power is used as the excitation source to probe the HCN absorption at 6539.13 cm^{-1}. The absorption detection module (ADM) consists of a quartz crystal tuning fork (TF) resonant at ~32.8 kHz and two 2.5 mm long pieces of 0.4 mm diameter glass tubing which form a half-wave longitudinal acoustic resonator. QEPAS detection was performed in a 2*f* wavelength modulation mode. A fiber beamsplitter is used to direct 1% of the laser radiation to a reference cell. The fiber-coupled sealed reference cell (27 mm pathlength) with a built-in photodiode contains a mixture of 40 Torr HCN and 160 Torr N_2 and is used to lock the laser wavelength to the target HCN absorption line by means of a 3*f* technique as described in [2]. The optical power delivered to the ADM through a sapphire optical window (not shown) was measured to be 50 mW. A spherical mirror M was used to refocus the radiation back to the ADM and was found to increase the photoacoustic signal ~1.7 times, as predicted.

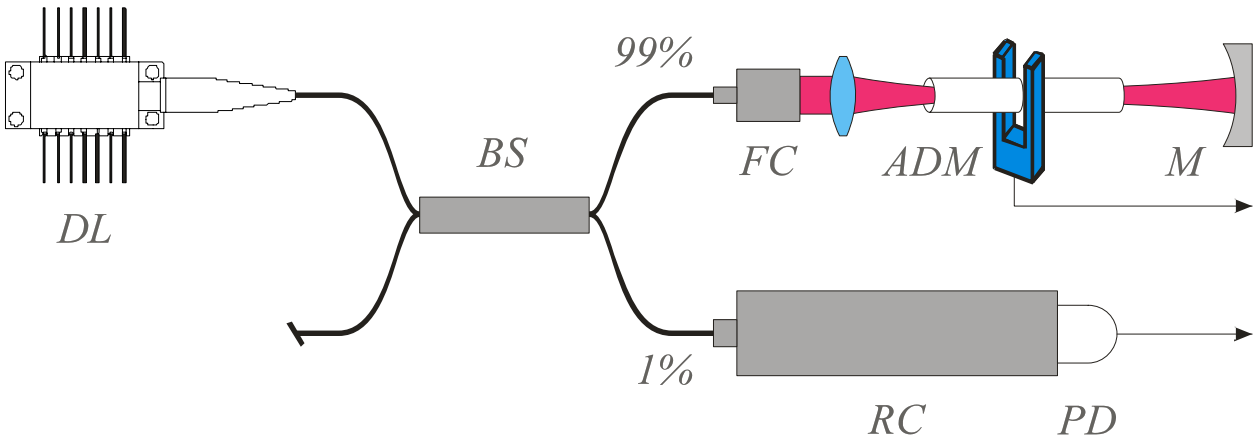

Fig. 1. The QEPAS-based trace HCN sensor architecture. DL – fiber-coupled DFB diode laser, BS- fiber beamsplitter, FC – fiber collimator, ADM – absorption detection module, M – back-reflecting spherical mirror, RC – fiber-coupled reference cell, PD – photodiode.

A permeation tube based trace HCN generator was used for the sensor calibration. The sampled gas pressure and the laser wavelength modulation index were optimized to achieve the highest signal to noise ratio (SNR). The optimum pressure for NCH sensing in dry N_2 as a carrier gas was found to be 300 Torr. This points to a relatively slow V-T energy transfer in this system (a condition $\tau_{V\text{-}T}\omega<<1$ is not satisfied), because it was established earlier that the highest QEPAS signal for fast-relaxing molecules such as NH_3 and C_2H_2 is observed at 50-60 Torr. If the laboratory environment air with a 50% relative humidity at +24ºC is used as the carrier gas, the optimum pressure becomes 60 Torr, and the SNR is 3 times higher compared to the dry N_2, 300 Torr. Thus, H_2O of air promotes the energy transfer from the initially excited molecular vibration of HCN to translational degrees of freedom of the carrier gas. Such an effect of the H_2O presence is well known in photoacoustic spectroscopy.

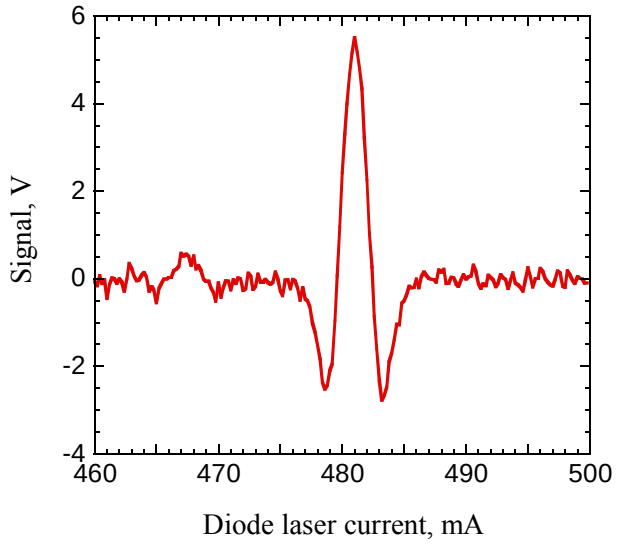

Fig. 2. QEPAS spectrum: 6.25 ppm of HCN in air. Vertical axis is a lock-in amplifier output.

Fig. 2 shows an example of the QEPAS scan (2*f* data) of an air sample with 6.25 ppmv of HCN at 60 Torr total pressure. The stronger absorption line in the center is the HCN line (6539.13 cm^{-1}), while the weaker line to the left is caused by the presence of H_2O. This spectrum is acquired with 1s lock-in amplifier time constant. The noise-equivalent HCN concentration estimated based on the SNR of this spectrum is 150 ppbv. For comparison, the current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for hydrogen cyanide is 10 ppmv as an 8-hour time-weighted average (TWA) concentration.

The normalized noise equivalent absorbance (NNEA) based on the same data set is calculated to be $2.5\cdot10^{-9}$ $cm^{-1}W/\sqrt{Hz}$. This number is consistent with our results for NH_3, H_2O, and C_2H_2, and as good as the typical NNEA reported for the conventional photoacoustic sensors.

References

[1] A .A. Kosterev, Yu. A. Bakhirkin, R. F. Curl, and F. K. Tittel, "Quartz-enhanced photoacoustic spectroscopy," Optics Letters **27**, 1902-1904 (2002)

[2] A. A. Kosterev, F. K. Tittel, D. Serebryakov, A. Malinovsky and A. Morozov, "Applications of quartz tuning forks in spectroscopic gas sensing", Review of Scientific Instruments **76**, 043105 (2005)