SPIE Newsroom

10.1117/2.1201601.006295

Mid-IR laser-based sensor for hydrogen peroxide detection

Nancy P. Sanchez, Yajun Yu, Lei Dong, Robert J. Griffin, and Frank K. Tittel

A continuous-wave external-cavity quantum cascade laser is integrated with a multipass absorption cell to target a hydrogen peroxide interference-free absorption line at 1234.055cm^{-1}.

Hydrogen peroxide (H_2O_2) is a strong oxidizing agent that is associated with the generation of hydroxyl radicals in the atmosphere. It is also involved in several environmental processes, including the degradation of pollutants in water by advanced oxidation processes.[1,2] In addition, H_2O_2 is relevant in the medical field as a reactive oxygen species used as a biomarker of lung and airway-related inflammation. Mid-IR laser-based sensor systems, with minimum detection limits (MDLs) at the parts-per-billion (ppb) level, have previously been reported for monitoring of H_2O_2.[3–5] Although these configurations have high sensitivity levels and continuous real-time detection capabilities, they are subject to interference from water lines in the selected spectral regions, which is a potentially significant concern for their field operation.[3] For future development of mid-IR laser-based sensor systems, it is therefore necessary to explore alternative strong, interference-free H_2O_2 absorption lines.

The strong oxidation potential of H_2O_2, its relatively broad germicidal spectrum, and the innocuous character of its decomposition products (water and oxygen) have led to the extensive use of this species for decontamination and sterilization of clean production sites and healthcare facilities.[6–8] Vapor phase hydrogen peroxide (VPHP) units—in which aqueous H_2O_2 solutions are used to generate gas-phase H_2O_2 concentrations of 200–1200ppm—are normally used in H_2O_2-based sterilization/decontamination techniques. Other applications of H_2O_2 include its use as a bleaching agent in the production of pulp and paper, and for sterilization of packing materials and medical devices. Potentially high levels of H_2O_2 can be observed at production and decontamination sites, and therefore monitoring the concentration of this species is crucial for evaluating exposure risks (e.g., above the US Occupational Safety and Health Administration Agency's average permissible exposure levels).

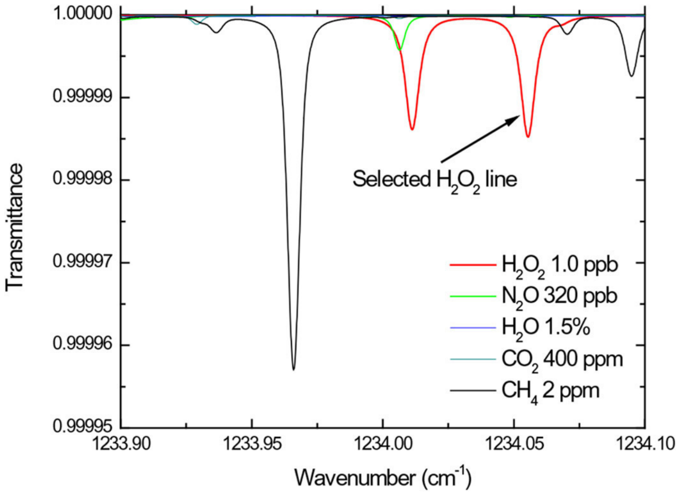

Figure 1. *Transmittance of hydrogen peroxide (H_2O_2) at a pressure of 20Torr, temperature of 293.15K, and with a 76m optical path length. The potential interferences from other gas species—water (H_2O), methane (CH_4), nitrogen oxide (N_2O), and carbon dioxide (CO_2)—are illustrated. Data taken from the high-resolution transmission molecular absorption (HITRAN) database.*

In this work,[9] we addressed the potential interference from water and other trace gas species during the detection of H_2O_2. To that end, we chose to study an interference-free absorption line at a wavenumber of 1234.055cm^{-1} (see Figure 1). We have thus developed a sensor system for the specific and selective detection of H_2O_2, which is based on this interference-free absorption wavelength.

In our sensor system we use a continuous-wave external-cavity quantum cascade laser (CW EC-QCL) that has a mode-hop-free (MHF) tuning range of 1225–1285cm^{-1}. We couple this EC-QCL with a commercial multipass absorption cell that has an optical path length of 76m. We use wavelength modulation spectroscopy, with second harmonic detection, for data processing. The modulation amplitude and pressure levels in our sensor

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system have been optimized for sensitive detection of H_2O_2. The actual configuration of our developed sensor system is shown in Figure 2.

We performed a calibration of our sensor system by generating different concentrations of gas-phase H_2O_2. To realize these different gas concentrations, we allowed air to flow over aqueous solutions (between 0.1 and 2% w/w) of H_2O_2. We used the standard high-resolution transmission molecular absorption (HITRAN) database to determine the corresponding concentration of H_2O_2 in the gas phase, based on the direct absorption signal at each mixing ratio level. The response of the sensor system at different H_2O_2 concentrations is illustrated in Figure 3. We find that there is a linear relationship between the system response and the concentration of H_2O_2. We also observe stability in the response at different mixing ratios.

Our current configuration for the sensor system allows detection of H_2O_2 at the ppb level (MDL of about 25ppb for a 280s optimum integration time). This configuration has the potential for continuous monitoring of H_2O_2 at industrial sites, as well as at locations that are undergoing VPHP-based decontamination. The relatively compact layout of our sensor means that it can be deployed at a variety of locations for the determination of average permissible exposure levels of gas-phase H_2O_2. In addition, our system has no restrictions associated with the relative humidity of the measurement sites. The interference-free absorption line that we selected for our sensor system, together with the MDL that we can achieve, also means that our system is suitable for the direct analysis of exhaled breath (in which water concentrations close to the saturation level are expected).

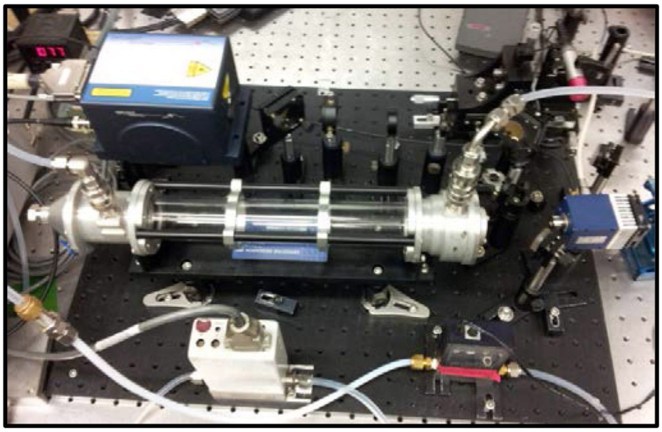

Figure 2. *Photograph of the H_2O_2 sensor system configuration. The sensor architecture consists of a Daylight Solutions 21080-MHF CW EC-QCL (mode-hop-free continuous-wave external-cavity quantum cascade laser), optical components for focusing and improving the laser beam shape (wedge beam splitter, 400μm pinhole, mirrors, and two lenses with focal lengths of 4 and 5cm), an Aerodyne Inc. AMAC-76 multipass absorption cell, and a PVMI-3TE-8 Vigo mid-IR detector.*

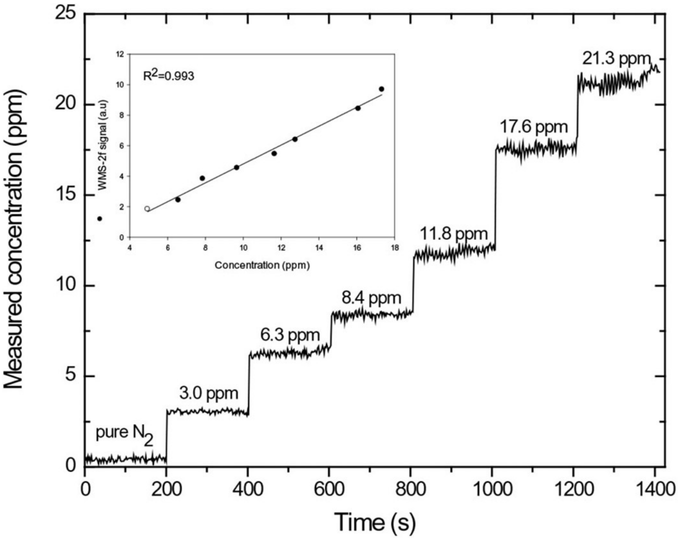

Figure 3. *Response of the sensor system to different concentrations of H_2O_2 at 20Torr. R^2: Coefficient of determination.*

In summary, we have developed a sensor system that is based on the integration of a CW EC-QCL (with an MHF operating range of 1225–1285cm^{-1}) and a commercial multipass absorption cell (with a 76m optical path length) for the detection of H_2O_2 at the ppb level. With an optimized configuration, we can achieve an MDL of about 25ppb with a 280s integration period. From the results of our calibration tests, we find that the sensor system exhibits a linear response at different H_2O_2 concentrations, when it is operated at optimum pressure and modulation amplitude. We have targeted a specific interference-free H_2O_2 absorption line at 1234.055cm^{-1}, which alleviates interference issues that have been reported in previous mid-IR-based H_2O_2 sensing systems. Our system is therefore suitable for the monitoring of H_2O_2 at industrial sites, in decontamination/sterilization locations using VPHP, and in medical applications. In our future work we will focus on further improving the sensitivity of the sensor system. We aim to reduce its MDL to a level that makes it suitable for use in additional circumstances (e.g., the monitoring of atmospheric concentration of H_2O_2).

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References

1. R. Andreozzi, V. Caprio, A. Insola, and R. Marotta, *Advanced oxidation processes (AOP) for water purification and recovery*, **Catalysis Today 53**, pp. 51–59, 1999.
2. H. Sakugawa, I. R. Kaplan, W. Tsai, and Y. Cohen, *Atmospheric hydrogen peroxide*, **Environ. Sci. Technol. 24**, pp. 1452–1462, 1990.
3. Y. Cao, N. P. Sanchez, W. Jiang, W. Ren, R. Lewicki, D. Jiang, and R. J. Griffin, *Multi-pass absorption spectroscopy for H_2O_2 detection using a CW DFB-QCL*, **Adv. Opt. Technol. 3**, pp. 549–558, 2014.
4. J. B. McManus, M. S. Zahniser, D. D. Nelson Jr., J. H. Shorter, S. Herndon, E. Wood, and R. Wehr, *Application of quantum cascade lasers to high-precision atmospheric trace gas measurements*, **Opt. Eng. 49**, p. 111124, 2010. doi:10.1117/1.3498782
5. W. Ren, W. Jiang, N. P. Sanchez, P. Patimisco, V. Spagnolo, C. Zah, F. Xi, L. C. Hughes, R. J. Griffin, and F. K. Tittel, *Hydrogen peroxide detection with quartz-enhanced photoacoustic spectroscopy using a distributed-feedback quantum cascade laser*, **Appl. Phys. Lett. 104**, p. 041117, 2014. doi:10.1063/1.4863955
6. M. Finnegan, E. Linley, S. P. Denyer, G. McDonnell, C. Simons, and J.-Y. Maillard, *Mode of action of hydrogen peroxide and other oxidizing agents: differences between liquid and gas forms*, **J. Antimicrobial Chemotherapy 65**, pp. 2108–2115, 2010.
7. A. Kahnert, P. Seiler, M. Stein, B. Aze, G. McDonnell, and S. H. E. Kaufmann, *Decontamination with vaporized hydrogen peroxide is effective against Mycobacterium tuberculosis*, **Lett. Appl. Microbiol. 40**, pp. 448–452, 2005.
8. N. A. Klapes and D. Vesley, *Vapor-phase hydrogen peroxide as a surface decontaminant and sterilant*, **Appl. Environ. Microbiol. 56**, pp. 503–506, 1990.
9. N. P. Sanchez, Y. Yu, L. Dong, R. J. Griffin, and F. K. Tittel, *Detection of hydrogen peroxide based on long-path absorption spectroscopy using a CW EC-QCL.* Presented at SPIE Photonics West, 2016.