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Hollow Waveguide Gas Sensor for Mid-Infrared Trace Gas Analysis

Seong-Soo Kim[1], Christina Young[1], James Chan[2], Chance Carter[2], Boris Mizaikoff[1]
[1]Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta, GA, 30332-0400, USA,
boris.mizaikoff@chemistry.gatech.edu
[2]Lawrence Livermore National Laboratory, Livermore, CA 94550

***Abstract*—A hollow waveguide mid-infrared gas sensor operating from 1000 cm^{-1} to 4000 cm^{-1} has been developed, optimized, and its performance characterized by combining a FT-IR spectrometer with Ag/Ag-halide hollow core optical fibers. The hollow core waveguide simultaneously serves as a light guide and miniature gas cell. CH_4 was used as test analyte during exponential dilution experiments for accurate determination of the achievable limit of detection (LOD). It is shown that the optimized integration of an optical gas sensor module with FT-IR spectroscopy provides trace sensitivity at the few hundreds of parts-per-billion concentration range (ppb, v/v) for CH_4.**

I. Introduction

Mid-infrared (IR) spectroscopy has a long history in chemistry and physics, and is a well-established research field for optical sensor technologies in recent decades. Each chemical species is characterized by distinctive IR spectroscopic response patterns resulting from vibrational and rotational transitions excited in this frequency regime, thereby providing a rigorous platform for gas sensing applications. Recent technological advances have triggered a renaissance in the field of mid-infrared spectroscopy translating benchtop-style IR instrumentation into field-applicable compact IR sensing devices. Novel light sources such as e.g., quantum cascade lasers, new light delivery systems such as e.g., hollow waveguide optical fibers, and advances in detector and Fourier transformation infrared spectrometer (FT-IR) technology yield mid-IR gas sensing devices that are more sensitive, faster, and more reliable [1-6]. These advances in fundamental IR technology reflect in increasingly adopted IR gas sensing schemes applied in environmental monitoring, harsh process environments, and biomedical research.

II. Experiments

The demonstrated IR gas sensing system comprises a Bruker 55 FT-IR spectrometer – which will be replaced with a more compact portable FT-IR device for field measurements - a hollow waveguide gas cell, beam control optics, and a liquid nitrogen cooled compound semiconductor mercury-cadmium-telluride (MCT) detector. Figure 1. shows a generic system diagram. Metallic reflection style hollow waveguides have been used for this first prototype. The light guiding mechanism of a metallic hollow waveguide is reflection of radiation at the metallic surface coating the inside of the hollow core of a silica fiber, which is different from that of conventional dielectric optical fibers or photonic band gap fibers. Conventional dielectric optical fibers take advantage of total internal reflection for radiation propagation. Ideally, there are no reflection losses observed at the dielectric interface where total internal reflection occurs. However, only few materials provide the required broad range of optical transparency in this spectral regime. Furthermore, this type of optical fiber core using high index dielectric materials are of limited applicability for hollow core structures. Recently, photonic bandgap structures have attracted increasing attention for fabricating channel waveguides in integrated optical circuits or for hollow core optical fibers [7-9]. These materials guide radiation by forming a stop band provided by periodic structures of alternating refractive index regardless of the incident angle of the radiation. Thereby, it is possible to fabricate abrupt 90 degree bendings within such photonic bandgap optical waveguides. However, the challenge is to design very broad optical stop bands by appropriately adjusting the period of these lattices. It is well established that reflection from metallic surfaces is least sensitive to optical wavelength change.

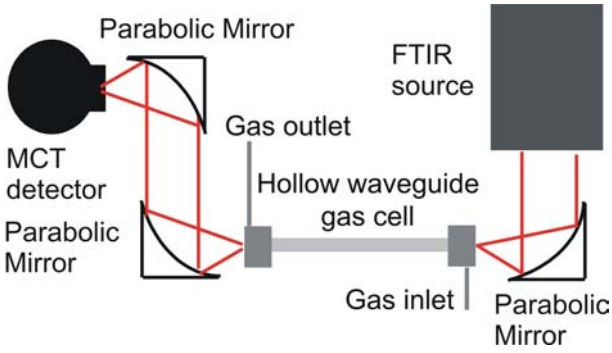

Figure 1. Integrated mid-infrared gas sensing system using a hollow core optical fiber and a FT-IR spectrometer.

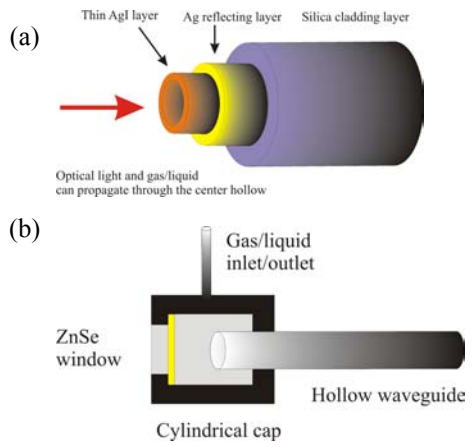

Figure 2. Hollow waveguide gas cell structure. (a) Structure of hollow core optical fiber from Polymicro Technologies, LLC. Silver is coated onto the inside surface of a silica hollow core fiber serving as a broadband mid-infrared reflection surface. The thin silver halide coating is a protective layer. (b) Assembly of hollow core waveguide and cylindrical end cap with ZnSe window. The cylindrical end cap has a small diameter tubing inlet for introducing gas phase or liquid phase samples into the hollow waveguide core. The mid-infrared transparent optical windows are made from ZnSe. The hollow core waveguide and the cylindrical end cap form a gas-tight assembly.

Hence, large diameter metallic hollow core waveguides are used to delivering CO_2 laser radiation over considerable distances, e.g., for surgical applications [10-12]. In this paper, we use metallic hollow core waveguides with a dual purpose: (i) for guiding broadband mid-infrared radiation to a certain distance in a confined volume, and (ii) to confine gaseous analytes inside the core of the hollow waveguide serving as a miniature gas cell. Therefore, maximum interaction between mid-infrared radiation and gaseous analyte molecules can be achieved. In this experiment, 1 m of hollow core waveguide with 750 μm inner diameter (Polymicro Technologies) has been used. These silica capillaries are silver coated at the inner surface, as schematically shown in Figure 2 (a). One of the most distinctive advantages of Ag/AgI hollow core waveguides is their broadband transparency covering the entire mid-infrared range, as silver provides high reflection from the visible to the far infrared region. Both ends of the hollow waveguide are connected to cylindrical end caps hermitically sealing the inside of the hollow core fiber, as shown in the Figure 2 (b). The end cap features ZnSe windows and gas/liquid inlet tubing welded to the aluminum body. Broadband mid-infrared radiation from the SiC glow-bar radiation source in the FT-IR spectrometer is coupled into the hollow waveguide through the ZnSe window using a 90 deg off-axis parabolic gold mirror with 2 inch effective focal distance, and 2 inch diameter along the minor axis of the mirror. Radiation emitted at the distal end of the hollow waveguide is collected by two identical off-axis parabolic mirrors with 1 inch effective focal distance, and 1 inch diameter along the minor axis of the mirror. Thus focused radiation was then coupled to a MCT detector (Infrared Associates, Inc.; model FTIR-16-1.0) using a current-mode pre-amplifier (model MCT-1000, Infrared Systems Development Corp.). The entire system was purged with nitrogen for more than 3 h prior to measurements for eliminating residual moisture and CO_2 from the optical path. Gas samples with different concentrations were prepared by the exponential dilution method [2, 13]. This method is widely used in gas chromatography for trace gas calibration. In this experiment, an exponential dilution flask (EDF) with 125 mL volume was used with a magnetic stir bar coated with glass. One end of the EDF is connected with an inert carrier gas tank via a gas regulator. The flow of nitrogen as a carrier gas was set to constant rate of 41 mL/min. The other end of the EDF is connected to the gas inlet of the HWG gas cell. For each experiment, well-known volumes of 100 % pure analyte were injected into the EDF. The analyte concentration, $C(t)$, at any instance is therefore given by

$$C(t) = C_0 \exp(-\alpha t), \qquad (1)$$

where C_0 is the initial concentration of the analyte in the EDF after injection and α is the ratio of the carrier gas flow rate to the EDF volume.

III. Results

2 mL of CH_4 were injected into the EDF using a constant nitrogen inert carrier gas flow at 41 mL/min at stable flow conditions. For ensuring the reproducibility of the sample preparation, each gas sample was three times successively introduced via the EDF. After the detected absorption peak of the analyte dissipated and the baseline was recovered, the next injection into the waveguide gas cell was performed. During these measurements, the entire beam path was kept purged with nitrogen.

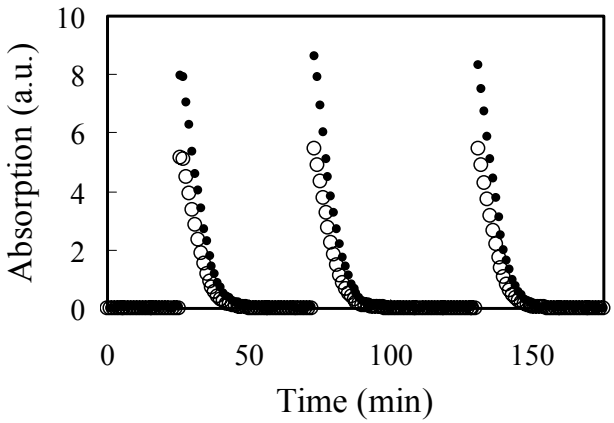

Figure 3. Reproducibility experiments for single analyte injections using exponential dilution. The next injection of analyte follows after the absorption peak from the previous injection entirely dissipates, and the baseline has been fully recovered. The white circles in the graph represent the CH_4 absorption peak intensity change vs. time at 1304 cm^{-1}, and the filled circles at 3016 cm^{-1}.

Analyte		CH_4	
Wavenumber (cm^{-1})		3016	1304
Mode of vibration		Asymmetric stretching	Bending
LOD (ppb v/v)	1st injection	11,800	85.8
	2nd injection	22,700	614
	3rd injection	43,660	614
Ave. LOD (ppb v/v)		26,053	438
STDev. (ppb v/v)		16,192	305

Table 1. Mid-infrared trace gas analysis results for each injection.

In the following, the achievable limit of detection for CH_4 was calculated and summarized in Table 1. Molecular-specific fundamental rotational and vibrational transitions active in the mid-infrared provide strong absorption features conducive for sensitive and selective infrared optical sensing in the gas phase. Methane selectively absorbs IR radiation at specific wavelengths resulting in a loss of transmission through the waveguides. Methane shows two strong absorption peaks within the range between 1000 cm^{-1} to 4000 cm^{-1}. These absorptions are resulting from two types of vibrations: asymmetric stretching vibrations and bending vibrations occurring at approximately 3016 cm^{-1} and 1304 cm^{-1}, respectively. While the peak height of the two CH_4 absorption modes at 1304 cm^{-1} and 3016 cm^{-1} are similar, the absorption peak at 3016 cm^{-1} is characterized by an increased peak width. Hence, the absorption peak at 1304 cm^{-1} provides a better signal-to-noise ratio (SNR) than the peak at 3016 cm^{-1}, therefore resulting in a lower limit of detection. Consequently, with a 1 m long Ag/AgI hollow core waveguide gas cell coupled to a FT-IR spectrometer LODs of approximately 438 ppb (v/v) for CH_4 with a standard deviation of 305 ppb (v/v) have been achieved. The progression of the spectra is presented in Figure 4. Currently, experiments with gas mixtures are in progress for demonstrating the quantitative discriminatory capability of FT-IR-based hollow waveguide gas sensors for multiple constituents.

IV. CONCLUSIONS

An integrated mid-IR gas sensing system using a 1 m long Ag/AgI hollow core waveguide gas cell coupled to a FT-IR spectrometer aiming at methane sensing was successfully established. The hollow core waveguide was used for efficiently guiding broadband mid-infrared radiation, while simultaneously serving as miniaturized gas cell. LODs for CH_4 were calculated at 438 ppb (v/v) and 26,053 ppm (v/v) for the absorptions at 1304 cm^{-1} and 3016 cm^{-1}, respectively. These experiments also confirm that the broadband nature of Ag/AgI hollow waveguides for radiation propagation provides strong resolving power to simultaneously discriminate multiple analytes in mixture at very low detection limits.

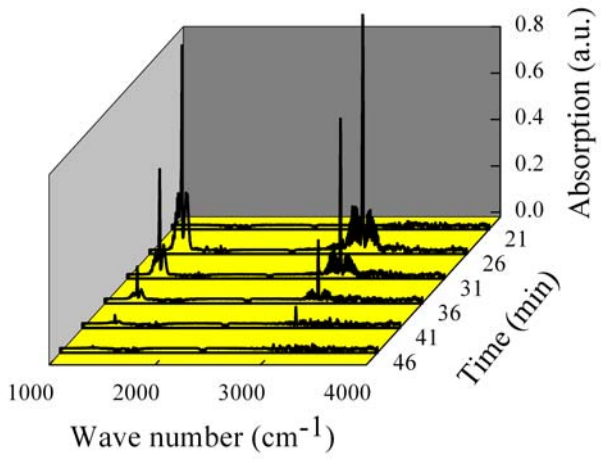

Figure 4. Time progression of CH_4 absorption spectra.

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