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In-water fiber-optic evanescent wave sensing with quantum cascade lasers

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ABSTRACT

The ability of detecting harmful chemicals is an important safety requirement for drinking water systems. An apparatus for in-water chemical sensing based on the absorption of evanescent waves generated by a quantum cascade laser array propagating in a silver halide optical fiber immersed into water is demonstrated. We present a theoretical analysis of the sensitivity of the system and experimentally characterize its real-time response and spectroscopic detection for injection of a sample chemical (ethanol) in a tube containing water.

1. Introduction

Water is polluted all over the world by highly toxic chemicals that are poured directly into it or into the ground by agriculture, industry, military and other sources. Since the toxicity of chemicals generated by these activities depends on their nature and ranges from highly toxic (e.g. organophosphorous pesticides or herbicides, such as Parathion, Diazinon or DDVP) to moderately toxic (e.g. halogenated hydrocarbons or ammonium perchlorate), it is not only necessary to detect their concentration but also to identify them inside a water system. A useful monitoring system should facilitate online monitoring in remote locations (e.g. inside water pipes or reservoirs), be sensitive, selective, robust, affordable and easy to operate.

Mid-infrared (mid-IR) spectroscopy is a powerful tool to identify organic molecules as most of them exhibit molecular fingerprints due to roto-vibrational modes absorbing in the mid-IR range [1]. Quantum cascade lasers (QCLs) [2] have demonstrated their ability as light sources for the spectroscopic detection of chemicals in the atmosphere reaching the part-per-billion sensitivity with the proper absorption cells [3]. Previous experiments were performed with such lasers operating in the mid-IR range for chemical sensing using a direct absorption method to detect phosphates [4], adenine and xanthosine [5], glucose and fructose [6], or carbon dioxide [7] in aqueous samples by using a specific flow cell and a propagation path of the order of 100 μm. This short optical path is constrained by the large absorption coefficient of water [8], being about 500 cm^{-1} (i.e. 20 μm attenuation length) in the spectral range from 8 to 10 μm, resulting in unpractical measurements using standard macroscopic transmission cells. On the other hand, the use of miniaturized cells would hamper the monitoring of large volumes of water. Measurement systems based on fiber-optic evanescent wave spectroscopy (FEWS) have been previously reported, either at visible wavelengths by using a surface plasmon resonance based sensor to detect pesticides [9], or in the infrared by using a silver halide fiber to measure in-water absorption of chemicals over a distance of few millimeters [10]. The latter system is based on attenuated total reflectance method allowing to measure the absorption of samples next to the fiber and relies on the high transparency [11] in the mid-IR range, non-toxicity and non-hygroscopy of silver halide fibers. By combining QCLs with silver halide optical fibers, droplets of specific chemicals in liquid phase were directly detected [12] by measuring the transmitted light spectrum, with a total immersed length below 25 mm.

Here, we present a sensing system for the *in situ* and real-time monitoring of chemical substances dispersed in water based on FEWS. The system integrates a multi-wavelength QCL array, a 80 cm-long silver halide fiber (AgClBr) contained in a PVC tube, and a fast mercury–cadmium–telluride (MCT) infrared detector. As the fiber is core-only, the evanescent tail of the electric field overlaps

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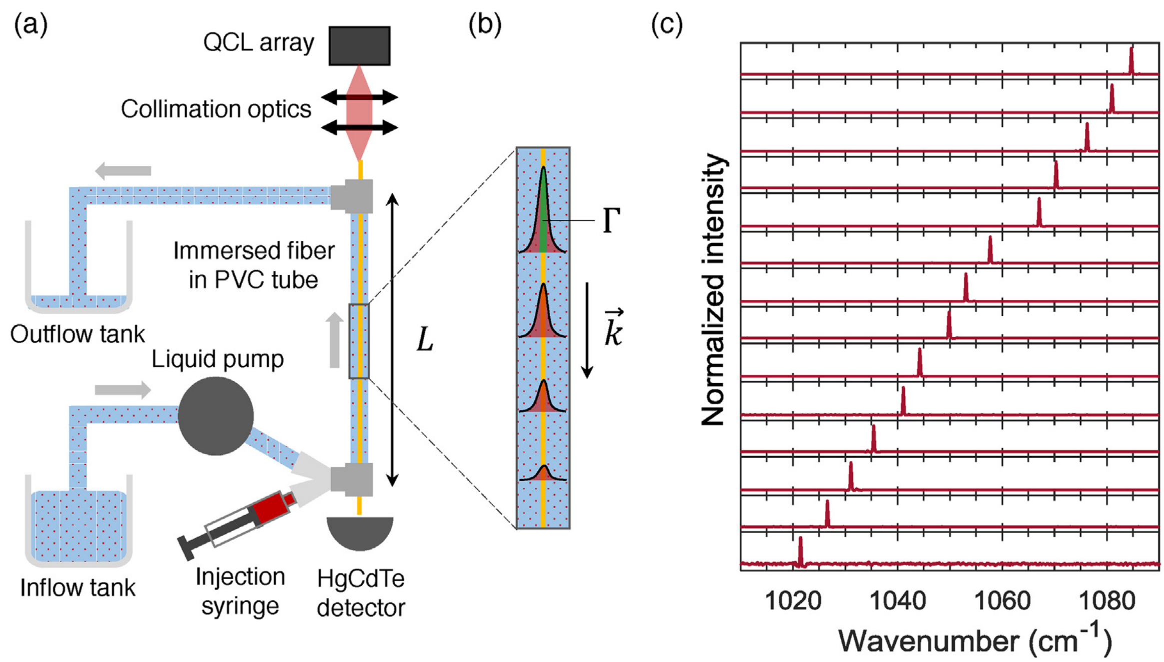

Fig. 1. (a) Schematic of the fiber-optic system for in-water chemical sensing. A silver halide fiber lies in a PVC tube (inner diameter 6.4 mm, length 80 cm). Water flows between two tanks propelled by a peristaltic pump. (b) Principle of fiber-optic evanescent wave sensing: as the light propagates along the immersed fiber (wavevector $\vec{k}$) with a confinement factor Γ, the evanescent tail overlaps with the liquid causing optical absorption. (c) Series of emission spectra produced by the different elements of the QCL array showing monochromatic emission from 1020 cm^{-1} to 1085 cm^{-1}.

with the chemical diluted in the water (or any other fluid such as air) and the variations of the transmitted intensity can be detected on the infrared detector. We first explore the sensitivity of such a system with a theoretical analysis, then we demonstrate in-water transmission of a mid-IR evanescent wave and the detection of traces of ethanol. This chemical is chosen as a sample chemical for the safety of the experimental protocol but its absorption properties in the mid-IR range can be considered as representative of the class of highly toxic molecules that we are targeting in this study. Two configurations were used for the experimental study: a time-resolved transmission measurement at a single frequency that allows to characterize the time response of the system, and a static multi-wavelength study aiming at the spectroscopic identification of the molecular fingerprint of the chemical at different concentrations.

2. Measurement setup

A schematic of the measurement set-up is shown in Fig. 1(a): a multimode AgClBr fiber (Ø=0.9 mm, L = 80 cm) is fed inside a clear PVC tube (capacity 30 mL), with tee-shaped connectors at both ends. One port of the tees provides the interface for the fiber with the outside of the tube where light is coupled in/out of the fiber. Epoxy glue is used to guarantee a water-proof interface. The other port of the tees allows the fluid to flow in/out of the tube upon the propulsion generated by a peristaltic pump.

The mid-IR light source of the system consists of a QCL array based on the master-oscillator power-amplifier array geometry [13]. The array is composed of 14 devices comprising two individual electrical sections: a power amplifier, and a distributed feedback (DFB) section. The active region of this device is a GaInAs/AlInAs broadband bound-to-continuum heterostructure grown lattice-matched on a conducting InP substrate by organometallic vapor phase epitaxy (OMVPE). The grating period of the DFB section is varied for each device in order to obtain single-mode operation at specific wavelengths between 9.2 and 9.8 μm. The QCL array is operated in pulsed mode with a repetition rate of 10 kHz and a pulse width of 80 ns. The emission spectrum of each device is measured using a Bruker 70 Fourier transform infrared spectrometer (cf. Fig. 1(c)).

The optical transmission of the fiber in the mid-IR is monitored by measuring the transmitted light generated from the different devices of the QCL array by using a thermoelectrically cooled mercury–cadmium–telluride (MCT) detector (Vigo PVI-4TE-10.6). The light pulses measured by the MCT detector are averaged using a box-car averager (Stanford Research Systems SR280) synchronized with the pulse generator and averaging over 300 pulses. The output signal of the box-car averager is acquired using a DAQ card (National Instruments BNC 2110).

The principle of FEWS is illustrated in Fig. 1(b): as the light generated by the laser propagates along the core-only fiber, the evanescent tails of the modes supported by the fiber overlap with the surrounding fluid and lead to a wavelength-dependent absorption of light in the fluid. As a consequence, the intensity decreases in the light wave along the whole fiber length. The efficiency of the evanescent wave absorption mechanism is determined by the fiber geometry (e.g. shape and size) [10].

3. Results and discussion

3.1. System analysis

The performance of the sensing system is limited by a compromise that depends on the fiber length L, the laser power P_{laser}, the noise level of the detector N_0 and the power coupling efficiency in and out of the fiber η. The bandwidth of the system for which the noise level is defined corresponds to the integration constant of the box-car averager used. This setting (300 samples at 10 kHz rate) is kept constant in all experiments leading to a bandwidth of approximately 30 Hz. This specific value was chosen to ensure fast response (within 100 ms) for the real-time study of the optical transmission.