Chapter 17
Optofluidic Jet Waveguide Sensor for Raman Spectroscopy

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An optofluidic sensor based on a liquid jet waveguide has been successfully applied in Raman spectroscopy. The jet waveguide is obtained by ejecting the solution under analysis through a capillary nozzle. A self-aligned configuration allows to couple the liquid waveguide with an optical probe consisting of two optical fiber respectively used to excite and to detect the Raman signal. As the numerical aperture of a water jet exceeds the one of any other liquid waveguide, a liquid jet ensures high collection and excitation efficiency. Unlike common approaches, this method removes the signal background coming from the substrate avoiding any necessity to contain the solution by means of solid walls. Proof-of-concept measurements performed by means of ethanol-water solution at different concentrations, show limit of detection already competitive with respect different approaches.

17.1 Introduction

Raman spectroscopy (RS) is a powerful analytical technique widely recognized as one of the main tool for molecular identification. Raman scattering and fluorescence emission are two competing phenomena, for this reason, the fluorescence contribution affects the performances of a sensor based on Raman effect. Once the fluorescence background becomes large relative to the Raman signal, its contribution can no longer be subtracted effectively. Several time consuming approaches for reducing fluorescence have been proposed including time-resolved detection, photolytic destruction of fluorescent impurities, and quenching with added reagents. More practical solution are obtained by means of expensive techniques as for instance shifted-excitation Raman difference spectroscopy (SERDS) or Fourier transform infrared spectroscopy (FT-IR).

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Besides the background noise reduction attempts, as spontaneous Raman scattering is a weak optical effect, different methods in effective collection efficiency have been proposed as for instance the use of liquid core waveguides (LCWs) [1] or by means of hollow core photonic crystal fibers (HC-PCFs) [2].

Moreover, recent advances in microfluidics have greatly broadened the applicability of RS in lab on a chip devices [3]. Several factors affects the practical reliability of an optofluidic sensor for Raman spectroscopy. In microfluidic devices the main factors are the signal weakness and the background contamination from the substrate. In LCW approach, long capillary are required to enhance Raman signal and Teflon AF2400, the most performing material for capillary fabrication, exhibits autofluorescence. Despite HC-PCFs offer high collection efficiency, they are usually filled through capillary action. This slow technique prevent their practical use in real time monitoring. Moreover, the formation of air gaps in sample distribution affects light guidance within the microchannels. In this work, we report the successful application of a liquid jet waveguide for Raman spectroscopy. This approach, by exploiting the waveguiding nature of a water jet, is able to avoid or minimize the previously mentioned issues.

17.2 Jet Waveguide Sensor

The ejection of a liquid through a round nozzle depends on different forces acting on the liquid: the viscous drag, the surface tension, the gravitational and the inertial force. Depending on the liquid velocity, different regimes can arise. At low velocity, the quasi-static balance between inertial and surface tension will result in the formation of droplets (dripping regime). By increasing the velocity above a certain critical value, the kinetic energy will overcome the liquid surface energy, leading to a jetting regime where a continuous jet formation is observed. The jet has a continuous shape forming a regular cylinder up to a certain length (named breakup length), and then it breaks up into drops. The breakup length first increases linearly with jet velocity reaching a maximum (linear regime) and then it begins to decrease until a minimum of the breakup length. All the measurements performed by our jet waveguide sensor have been obtained in linear regime.

As for LCW, in a water jet, the Raman signal can be efficiently guided by means of total internal reflection (TIR) but in this case the numerical aperture and consequently the collection efficiency is greater ($NA_{\text{water jet}} = 0.88 > NA_{\text{LCW}} = 0.32$). HC-PCFs own a numerical aperture considerably larger than LCWs (≈ 0.68 for water core)[4]. But even in this case, the HC-PCF numerical aperture is well below the one achievable by means of a water jet waveguide. Jet waveguide sensors have been successfully applied in fluorescence spectroscopy [5] but never employed in the proposed configuration for Raman spectroscopy.

The working principle is shown in Fig. 17.1. A liquid stream of the solution to analyze is generated by means of a stainless steel capillary with internal diameter ID = 0.508 mm. In order to excite and detect the Raman signal, a simple probe

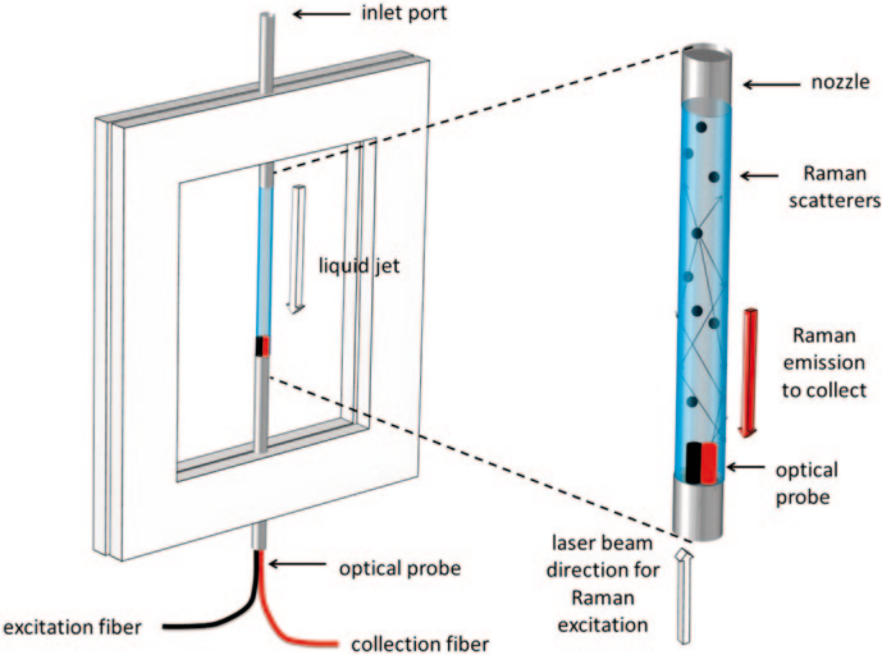

Fig. 17.1 Schematic of the optofluidic Raman sensor based on a water jet waveguide

composed of two optical fiber (diameter d = 105 µm diameter, NA = 0.22) has been used. One fiber is employed to excite the solution, whereas the other one is used to deliver the signal towards a spectrophotometer. The liquid jet is directly coupled with the optical probe in an alignment-free configuration enabling the excitation of the whole stream and an effective collection of the Raman signal. In contrast to commonly used methods in Raman detection, this configuration completely avoids any fluorescence background from the substrate or from solid walls used to contain the solution. The liquid jet length considered in our measurements was l = 18 mm (distance nozzle-optical probe). This corresponds to an excited volume of around 3.53 µl.

In order to manufacture a suitable holding and alignment-free architecture a Polymethylmethacrylate (PMMA) frame was micromachined.

17.3 Experimental Measurements

A laser source at 532 nm ($P_{out} = 70$ mW) was coupled with the exciting fiber of the optical probe by means of a collimator providing the 44 % of the original emitted power. A syringe pump was used to drive the solution into the stainless steel capillary. The collecting fiber of the optical probe was directly coupled with a spectrom-

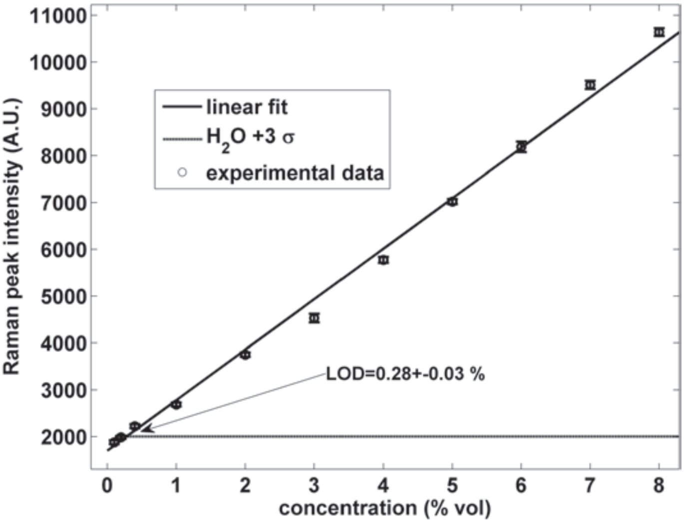

Fig. 17.2 Calibration curve for ethanol water solution ranging from 0.1 to 8 %. The horizontal line is drawn considering the blank measurement plus three times the value of its standard deviation. The LOD is 0.28 %

eter delivering the Raman signal towards this detector. The spectrometer used in the measurements was a Shamrock SR-3031(Andor Technology) employing a 600 lines per mm grating and a thermoelectrically cooled CCD camera (Newton, Andor Technology). An optical filter was employed to filter out the pump contribution at 532 nm in the detected spectra.

The performances of the system have been successfully tested considering ethanol-water solution at different concentrations. In particular for the measurements analysis, we have considered the Raman peak centered at 2932 cm^{-1} corresponding to the stretching symmetric vibration of the CH_3 group in water-ethanol system. Each experimental point of the calibration curve (Fig. 17.2) was obtained considering the average of 20 measurements performed with an integration time $t_{int} = 2$ s.

A limit of detection (LOD) of 0.28 ± 0.03 % for ethanol-water solution has been obtained. Despite this present setup is not intended as a fully optimized system, the attained value of the LOD (0.28 %) is competitive also if compared to more complex spectroscopic technique. For instance a LOD of 0.2 % is reported using FT-Raman spectroscopy [6]. Also the comparison with sensors based on hollow core shows the effectiveness in ethanol detection of the proposed device. For instance ethanol concentration at the 1 % level is reported for hollow core based sensor [7] (3 m long with internal volume of around 9 μl) using excitation wavelength at 532 nm.

17.4 Conclusions

An optofluidic sensor for Raman spectroscopy of liquid solutions has been developed. The NA provided from a liquid jet ensures very high collection efficiency, outperforming other liquid waveguides. Proof-of-concept measurements attest an LOD value which is suitable for sensing application. The intrinsic device simplicity establishes the basis for real world sensing applications and the absence of typical disadvantages affecting other approaches open new perspective in Raman spectroscopy.

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