Non-Intrusive Velocity Measurement of Millichannel Flow by Spontaneous Raman Imaging*

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Abstract

A non-intrusive measurement technique based on spontaneous Raman imaging was proposed for investigating microscale flow structures. It has the advantage that it does not require tracer particles or fluorescent dye to measure fluid velocity and scalar quantities. Raman scattering from ions in solution is substance specific and is observed as Raman spectra that contain peaks due to molecular species. The spontaneous Raman intensity from an electrolyte solution strongly depends on the electrolyte concentration. Thus, a bandpass filter attached to an EM-CCD camera detects only the strong Raman scattering at the selected Raman shift. The spontaneous Raman image obtained was converted to an electrolyte concentration distribution by using a calibration curve that expressed the relationship between the Raman intensity and the concentration. The flow velocity in a millichannel was calculated from the peak-value displacement of the time-series concentration distribution.

Key words: Non-Intrusive Measurement, Spontaneous Raman Imaging, Calibration Curve, Ion Concentration

1. Introduction

Novel technologies developed in the past decade have endowed nano/microfluidic devices with many functions that were unimaginable in the previous century. These functions are realized based on precise control of fluid motion in nano/microchannels. A slight change in the physical parameters of a thermofluid in a very small space drastically affects the functional capabilities of these devices. Thus, nano/micron-resolution particle image velocimetry (PIV)⁽¹⁻⁵⁾ and laser-induced fluorescence (LIF)⁽⁶⁻⁸⁾ have been used to measure fluid velocity and scalar quantities with high resolutions. However, they are not ideal measurement techniques for practical applications or medical diagnosis because fluorescent particles or a dye need to be injected directly into a flow. Consequently, the effects of the temporal-spatial distribution and the electrochemical properties of the particles or dye on the flow structure cannot be neglected^(9,10).

An alternative approach based on Raman spectroscopy⁽¹¹⁾ has been developed. Piorek *et al.*⁽¹²⁾ proposed using surface-enhanced Raman spectroscopy (SERS) to detect airborne water-soluble molecules. Ag nanoparticles were injected into an open microchannel and the aggregation process in surface-free flow was investigated. SERS gives a much more intense Raman intensity than spontaneous Raman spectroscopy; however, nanoparticles that enhance the scattering intensity act as contaminants. Roetmann *et al.*⁽¹³⁾ measured the

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Fig. 1. (a) Schematic concept of Raman scattering. (b) Spontaneous Raman spectroscopy image of a KCl solution⁽¹⁵⁾. (c) Spontaneous Raman spectra of a KCl solution and water⁽¹⁵⁾. (d) Instantaneous image of spontaneous Raman intensity from a KCl solution⁽¹⁵⁾. (e) Calibration curve expressing the relationship between spontaneous Raman intensity and KCl concentration⁽¹⁵⁾.

concentration distribution of ethanol and water in a micromixer using planar spontaneous Raman scattering. They visualized ethanol motion with a temporal resolution of 1 s; however, they did not determine the absolute ethanol concentration and velocity.

The objective of the present study is to develop a non-intrusive velocity measurement technique based on spontaneous Raman imaging. Raman scattering from ions in an electrolyte solution is substance specific and is observed as Raman spectra that contain peaks due to molecular species⁽¹⁴⁾. The present study focuses on the Raman intensity from ions in an electrolyte solution, which strongly depends on the ion concentration. Therefore, a calibration curve that expresses the relationship between the Raman intensity and the electrolyte concentration is used to obtain time series of the concentration distribution, whose peak-value displacement is utilized to calculate the flow velocity.

Fig. 2. Schematic diagram of spontaneous Raman imaging system.

Nomenclature

- t : time
- x : streamwise coordinate
- y : spanwise coordinate
- z : depthwise coordinate
- Δt : camera frame rate

2. Measurement Principle

When a material is irradiated by a laser beam, inelastically scattered light from the material has a different frequency from the incident light. The frequency difference corresponds to the energy level of a molecular vibration (see Fig. 1(a)). Conventional Raman scattering (i.e., spontaneous Raman scattering⁽¹⁴⁾) is detected using a Raman spectrograph equipped with a camera. Figure 1(b) shows a Raman image of a KCl solution and water⁽¹⁵⁾ obtained using a Raman spectrograph (Solar TII, Ltd., SL 100M) and an EM-CCD camera (Hamamatsu Photonics, C9100–12). In Raman spectroscopy, only one-dimensional information is obtained from a Raman image. The Raman intensity as a function of the Raman shift (the upper abscissa in Fig. 1(c) represents the wavelength calculated from the Raman shift and the laser wavelength) for a KCl solution differs from that of water. In particular, the Raman intensity is higher in the wavelength range 650–660 nm. When a bandpass filter whose transmissivity in this wavelength range is carefully designed is attached to the camera, a two-dimensional distribution of the Raman intensity is obtained (see Fig. 1(d)). The present study focuses on the effect of ion concentration on the Raman intensity. Thus, a calibration curve (see Fig. 1(e)) that expresses the relationship between the Raman intensity and the ion concentration is obtained; it is commonly used in micro-LIF^(6,16) and nano-LIF^(7,8).

3. Experimental Setup

Figure 2 shows a schematic diagram of the optical measurement system. A 14-bit EM-CCD camera (Hamamatsu Photonics, C9100–12) with 512×512 pixels² ($16.0 \mu\text{m}/\text{pixel}$) was mounted on an inverted microscope (Nikon Corp., TE–2000U) with a $4\times$ magnification objective lens ($NA = 0.13$). A continuous wave (CW) Nd:YVO₄ laser (Coherent, Inc., Verdi; 1.7 W) provided the excitation light (wavelength: 532 nm; incident angle: 30°). A bandpass filter (Semrock, Inc.) with the transmissivity profile shown in Fig. 3 was used because the

Fig. 3. Transmissivity profile of bandpass filter for NaCl solutions.

Fig. 4. (a) Top and (b) cross-sectional views of I-shaped millichannel.

Raman intensity from a NaCl solution differed significantly from that of water in the wavelength range 530–560 nm (see Fig. 5). The time and spatial resolutions were 91.9 ms (determined by the EM-CCD camera frame rate) and $32 \times 32 \mu\text{m}^2$ (based on the average of 8×8 pixels²), respectively. The CW laser had a beam diameter of 2.25 mm and the measurement area was set to $2 \times 2 \text{ mm}^2$.

Figure 4 shows a schematic diagram of an I-shaped millichannel consisting of PDMS and 170- μm -thick borosilicate glass. The width and depth were 5 and 0.7 mm, respectively. Ion-exchanged water was injected into the inlet by a syringe pump at a flow rate of 3 mL/min. A 1 mol/L NaCl solution with a volume of 80 μL was injected into the inlet, which was located 1 mm from the midpoint of the channel (on the left edge of the measurement area).

4. Results and Discussion

4.1 Relationship between spontaneous Raman intensity and electrolyte concentration

Prior to performing experiments on the channel flow, the relationship between the Raman intensity and the electrolyte concentration was examined at a temperature of 297 K. Measurements were performed using a closed cell⁽⁷⁾ for five different NaCl concentrations. Figure 5 shows spontaneous Raman spectra of these NaCl solutions obtained using a Raman spectrograph (Solar TII, Ltd., SL 100M; spectral resolution: 0.57 nm) and the EM-CCD camera. The abscissa indicates the wavelength calculated from the Raman shift and the laser wavelength (532 nm). A significant increase in the scattering intensity was observed in the wavelength range 530–560 nm. Thus, the bandpass filter with transmission characteristics shown in Fig. 3 was used. Since the Raman stretching band of Na^+ is almost the same as

Fig. 5. Spontaneous Raman spectra of NaCl solutions and water.

Fig. 6. Calibration curve expressing the relationship between spontaneous Raman intensity and NaCl concentration.

that of Cl^- ⁽¹⁷⁾, the present study considers the electrolyte solution without distinguishing between these two ions.

The calibration curve in Fig. 6 expresses the relationship between the spontaneous Raman intensity and the NaCl concentration obtained using the present imaging system. In a set of experiments, the scattering intensity from a millichannel with no solution was captured as a background image. The noise was then removed by subtracting this background image from captured images; thus, the measured data did not contain Raman scattering from borosilicate glass slides. The CW laser beam has a Gaussian profile; the influence of this variation in the excitation intensity on the Raman intensity was corrected⁽⁷⁾. To reduce pixel error, the results were averaged over 8×8 pixels²; this gave a standard deviation for the scattering intensity of 2.2%. In a set of experiments, the measured concentration was calibrated using this curve. The measurement uncertainty in these experiments was ± 0.08 mol/L at a 95% confidence level with a spatial resolution of $32 \times 32 \mu\text{m}^2$.

4.2 Simultaneous measurement of concentration and velocity of electrolyte solution

Immediately after injecting a 1 mol/L NaCl solution into the inlet, a time series of the two-dimensional Raman intensity was obtained. Figure 7(a) shows successive instantaneous images obtained at a frame rate of $\Delta t = 91.9$ ms. These images have a depth of field of $62 \mu\text{m}$. They were converted into two-dimensional concentration distributions (see Fig. 7(b)) using the calibration curve.

Fig. 7. (a) Successive images showing the temporary evolution of spontaneous Raman intensity from a NaCl solution. (b) Temporal evolution of instantaneous NaCl concentration distribution.

Fig. 8. Temporal evolution of NaCl concentration at $y = 2.33-2.66$ mm.

Concentration distribution maps were divided into six regions in the y -direction and the temporal evolution of the concentration in each region was calculated. Figure 8 shows the temporal evolution of the NaCl concentration at $y = 2.33-2.66$ mm. The peak value of the concentration moved in the streamwise direction; this allows the streamwise velocity to be easily calculated from the displacement of the peak concentration and the camera frame rate⁽¹⁰⁾. The mean streamwise velocity, as shown in Fig. 9, was calculated by the above method using seven successive images. Also the error bars are indicated in Fig. 9. The channel centerline corresponds to $y = 2.5$ mm. A nearly parabolic profile was observed. A

Fig. 9. Mean streamwise velocity profiles of a NaCl solution.

velocity measurement under the same experimental condition was performed using micro-PIV and 1- μm -diameter fluorescent particles. Moreover, a numerical simulation⁽¹⁸⁾ at the same flow rate was carried out and the result is shown in Fig. 9. The mean velocities at the centerline ($z = 0.35$ mm) determined by micro-PIV and the simulation were 6.6 mm/s and 6.56 mm/s, respectively, which are greater than that measured by the present imaging system (4.7 mm/s). However, it is difficult to specify the depth at which the Raman scattering originates in the present experiments, because the scattering intensity from the whole channel flow captured by the EM-CCD camera may result in the large error bars. Experiments using evanescent wave illumination are currently being undertaken to specify the depth position.

5. Conclusions

A non-intrusive imaging technique for measuring fluid flow was proposed based on Raman scattering imaging. The present study investigated the relationship between the spontaneous Raman scattering intensity and the electrolyte concentration. The present technique was applied to simultaneously measure the electrolyte concentration and the flow velocity. The measurement uncertainty of ± 0.08 mol/L was achieved with a spatial resolution of $32 \times 32 \mu\text{m}^2$.

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