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Experimental comparison of CARS and Raman spectroscopy for concentration measurements in microchannels

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1. Introduction

Micro heat exchangers, micromixers and microreactors have gained importance in chemical, pharmaceutical and life sciences applications. Due to the large wall surface to volume ratio these devices provide efficient mass and heat transfer. This may result in greater selectivity and higher yield for chemical reactions. Such microreactors are applied for chemical production, too. E. g., a micro heat exchanger with 27 cm^3 volume can transfer a thermal power of 200 kW at 7 t/h. For an optimum system design, a detailed understanding of the interplay of chemical reactions and transport processes in microchannels is necessary. It is important to measure concentrations of products in-situ under reaction conditions within microchannels with widths and depths of 200 µm with good spatial resolution. Laser Raman spectroscopy is used (fig. 1, left) and applied to monitor the oxidation of cyclohexane at 200 °C / 80 bars in a microreactor with a bonded 2 mm thick glass plate (fig. 1, right).

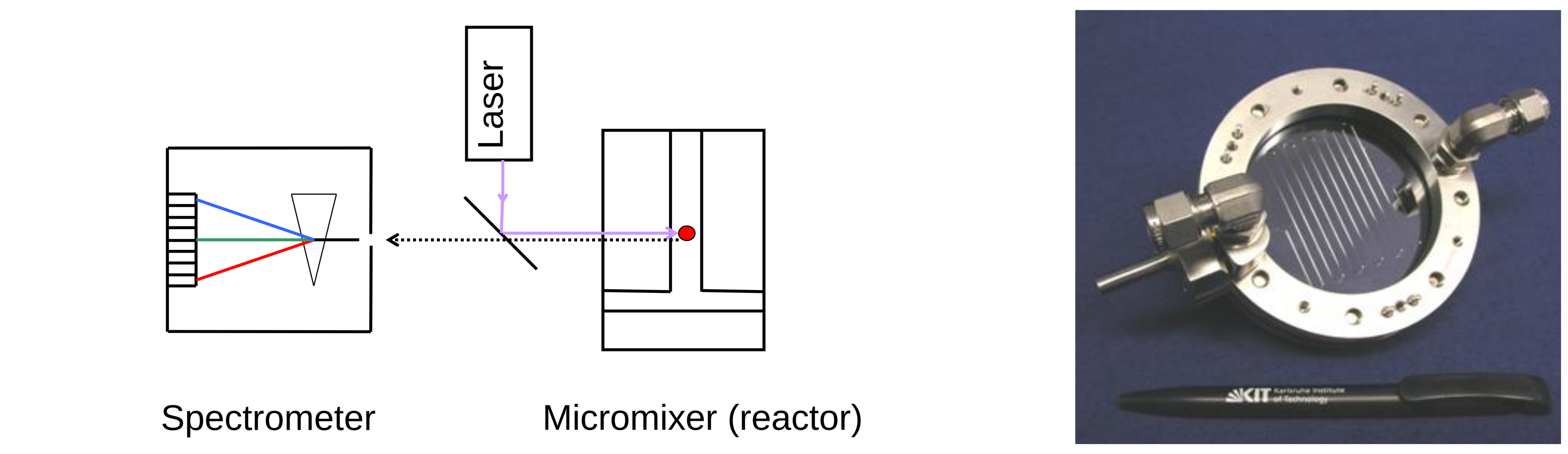

Fig. 1: In-situ analytics for micro chemical engineering and microreactor

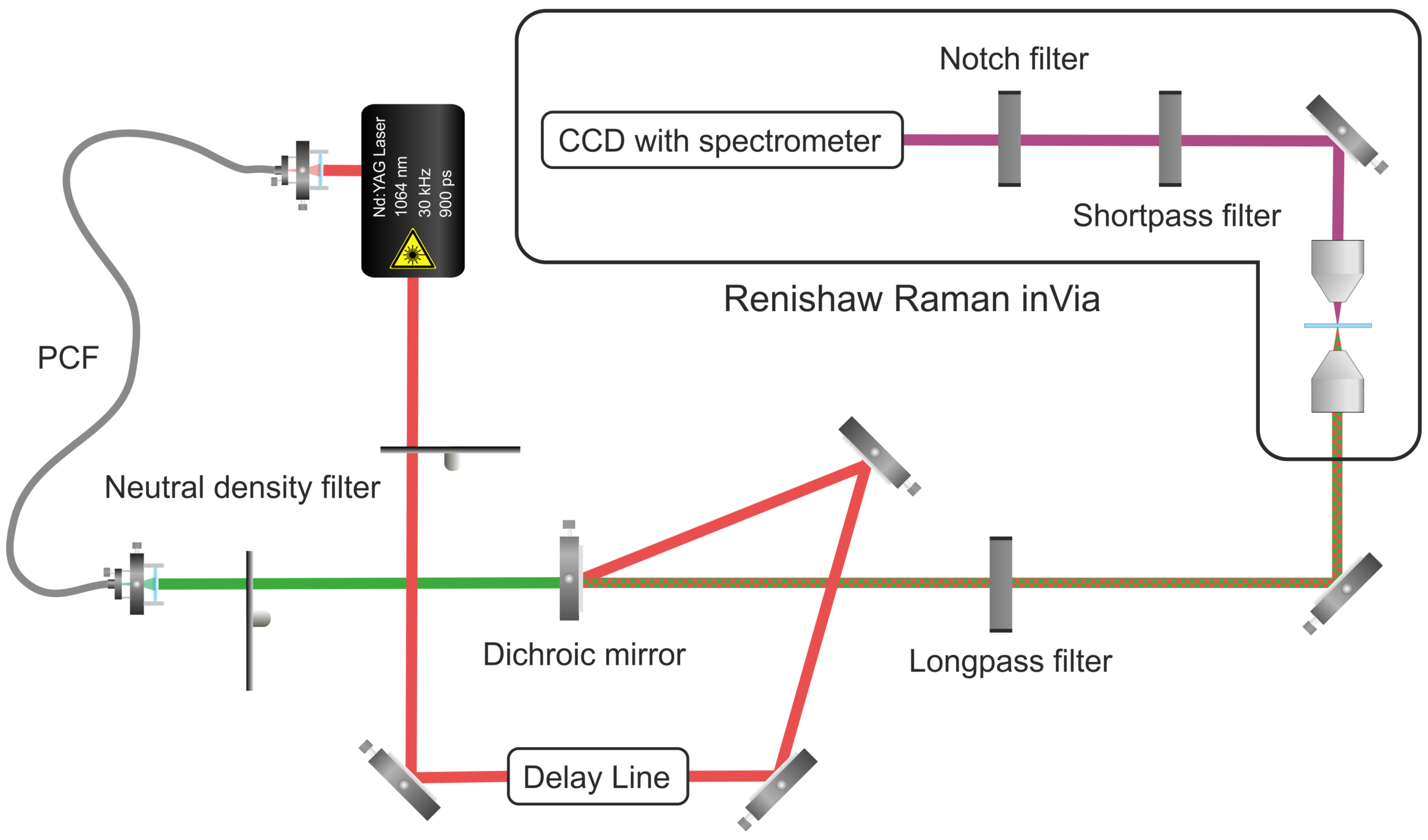

Fig. 2: CARS setup combined with Renishaw Raman inVia

2. Comparison of Raman and CARS

Raman spectroscopy on the one hand side gives undisturbed spectra, which are proportional to concentrations. Optical access is only required for one direction. However, sensitivity is low and measuring time large. If fluorescent molecules are present, Raman light may be completely hidden. CARS however, provides, under certain conditions, much higher signals and thus allows short measuring times. It is not disturbed by fluorescence due to the blue shifted anti-stokes signal. In addition, CARS has a smaller scattering volume and therefore, a better spatial resolution can be achieved. Measured CARS spectra often show a broad non-resonant background, which can be corrected with mathematical methods.

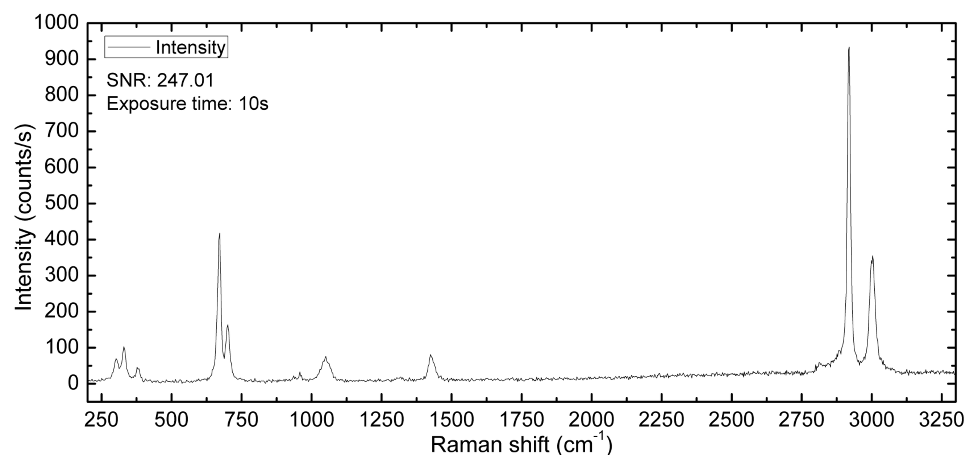

Fig. 3: Raman spectrum of DMSO in a 50 µm wide microchannel

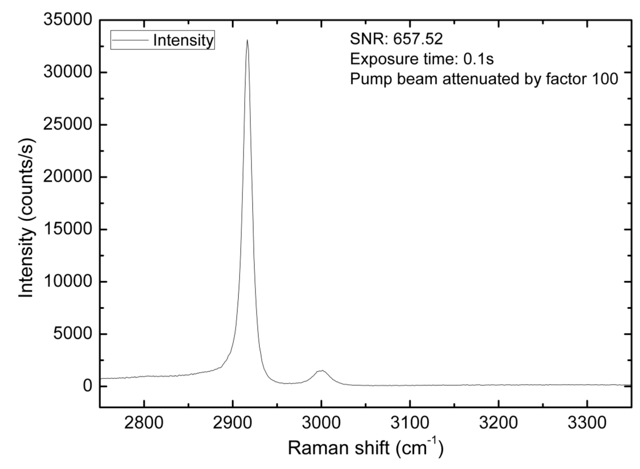

Fig. 4: CARS spectrum of DMSO

3. Experiments and Results

To compare Raman and CARS under similar conditions, DMSO was chosen as test fluid. It was filled in a cuvette with small depth and a microchannel with 50 µm width and 250 µm depth. Raman spectra were recorded using lasers at 488 nm, 633 nm and 785 nm. The CARS system* (fig. 2) consisted of a Nd:YAG laser, which is coupled into a photonic crystal fiber (PCF) to produce a broad spectrum, whereby an excitation wavelength range of 1080 nm – 1700 nm is used as Stokes beam. A second beam of the Nd:YAG laser (pump) is delayed and combined with the broadband beam (Stokes). Both beams are focused via microscope objectives into the cuvette and the CARS light is collected by another objective and guided to a spectrometer with attached CCD camera. Raman spectra and CARS spectra of DMSO were recorded between 200 cm^{-1} and 4000 cm^{-1}. Fig. 3 shows the Raman spectrum of DMSO in a microchannel (488 nm, 10 s) and fig. 4 the corresponding CARS spectrum (0.1 s). Measurements were performed with the set-up shown in fig. 5 using a 0.1 mm thin cuvette. Raman measurement was performed with an excitation power of 500 mW @ 785 nm and CARS with 100 mW for the pump and 70 mW for the Stokes beam. In fig. 6 CARS and Raman depth measurements of a 15 µm thick polymer film are presented. A resolution (FWHM) of ~60 µm for Raman and ~15 µm for CARS can be estimated.

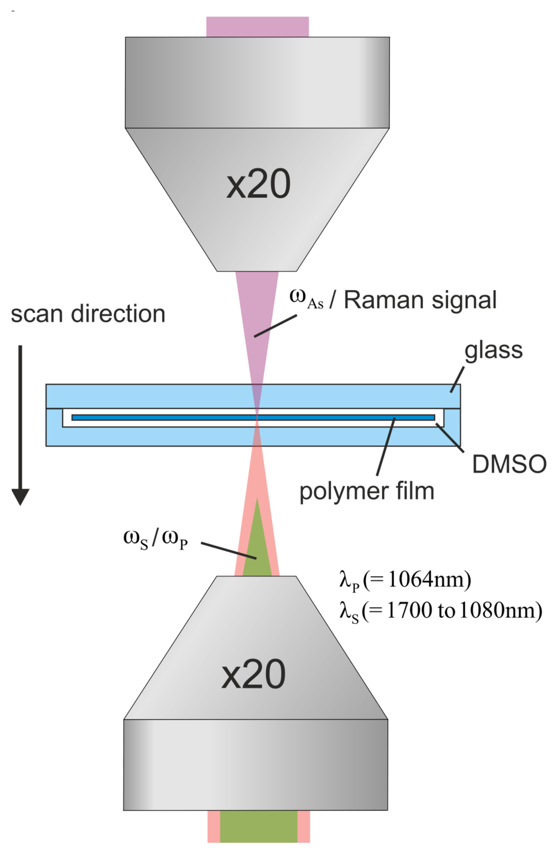

Fig. 5: Optical set-up for depth resolution

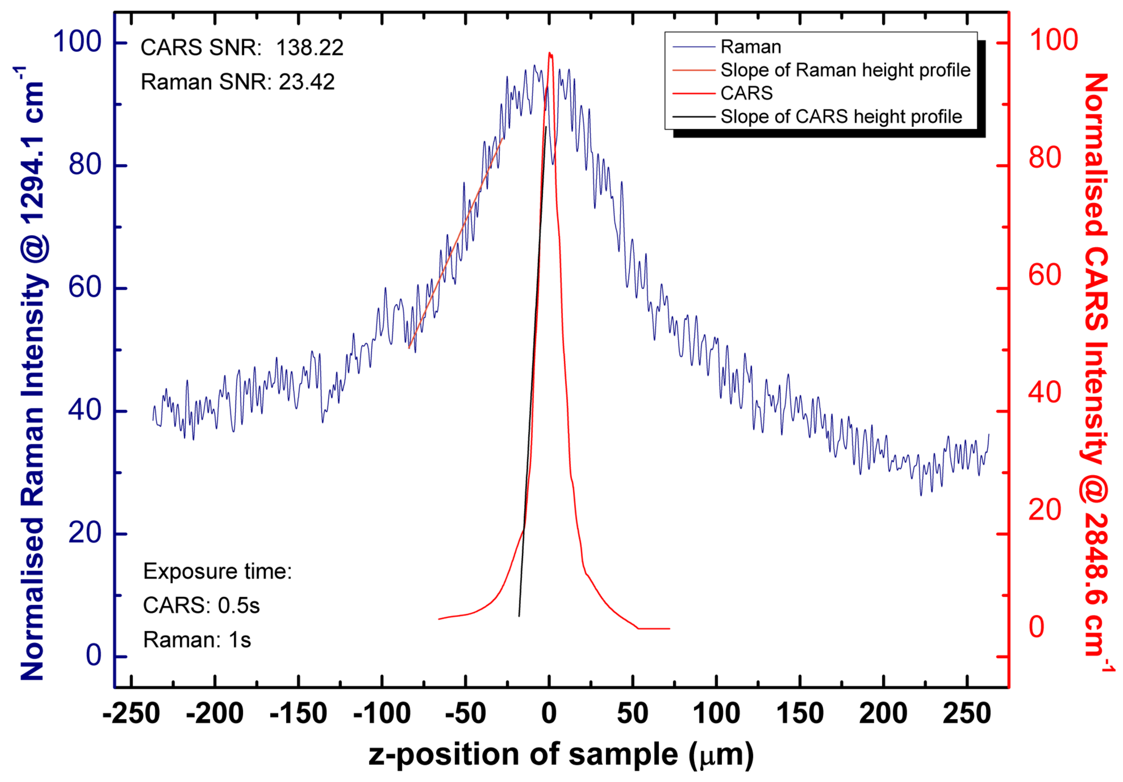

Fig. 6: CARS and Raman depth profiles of a 15 µm thick polymer foil

4. Conclusion

The measured intensity ratio and signal to noise ratio (SNR) between CARS and Raman signal strongly depends on wavenumber. At 3000 cm^{-1} the SNR of the CARS signal is about 30 times larger, considering the shorter exposure time. Microscope objectives with low magnification and low NA, but large working distance of a few millimeters, allow the use of 2 mm thick cover glasses for the microchannel. Therefore, space resolved measurements are possible up to 80 bars. Taking the strong signals and enhanced spatial magnification of CARS into account, fast mappings in microchannels and in other fast running dynamic processes can be performed. Broadband CARS using supercontinuum lasers as Stokes laser source makes it possible to build up a cost-effective set-up with good results especially for spatial and time-resolved (<1ms) measurements.

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