Pulsed 2-Dimensional Raman Spectroscopy on Microdroplets

By *Helge Moritz* and *Gustav Schweiger**

In this study, we used a technique based on pulsed Raman spectroscopy to determine the average concentration in the liquid phase and concentration distribution in the gas phase surrounding desorbing linear arrays of binary microdroplets. For this study, monodisperse microdroplets consisting of acetylene dissolved in acetone were generated by a modified vibrating orifice aerosol generator (VOAG). The 2-dimensional concentration fields of acetylene desorbed from the droplets were determined with a spatial resolution of about 40 µm both along the direction of the droplet chain and perpendicular to it. The detection limits for the gas and liquid phase concentrations were about 100 ppm and 1 mmol/l, respectively.

1 Introduction

For a detailed experimental investigation of mass transfer in aerosols or sprays, it is essential to determine the concentration of the individual chemical components in the vapor and the liquid phase. Because of the small mass of the particles and the transient nature of many processes, optical measurement methods are recommendable for *in situ* studies of microparticle systems. Raman spectroscopy on optically levitated microdroplets were first analyzed by Thurn and Kiefer [1]. The characterization of laboratory-generated microparticles by Raman spectroscopy up to 1990 was reviewed by Schweiger [2]. Raman studies of gas/liquid and gas/solid aerosol chemical reactions were reported by Davies [3] and Tang and Fung [4].

The intensity of scattered light from microparticles depends linearly on the local field, the scattering volume, and the molecular concentration as long as stimulated and nonlinear processes have not to be considered. However, Raman scattering on microparticles depends in a complicated way on the position of the scattering molecule within the particle, the size, and index of refraction. Despite the complicated relation between the angular Raman scattering of individual molecules and their position in the particle, the angular averaged total Raman intensity for homogeneous particles is simply a function of the particle volume, Schweiger [5], and Vehring and Schweiger [6]. If MDRs (morphology-dependent resonances) are excited, Raman scattering from the volume covered by the resonant mode is enhanced. The mode volume is more or less close to the surface, depending on the mode order. For inhomogeneous particles the ratio between Raman scattering on- and off-resonance may therefore be affected by concentration gradients in the particle. This was shown experimentally by Moritz and Schweiger [7], and Lin and Campillo [8] and analyzed theoretically by Lange and Schweiger [9].

Measurements on highly monodisperse droplet chains are possible with the vibrating orifice aerosol generator (VOAG) developed by Berglund and Liu [10], which has been stabilized by Lin *et al.* [11]. The VOAG uses a piezoelectric (PZT) crystal to oscillate an orifice, breaking a liquid jet into a chain of uniform droplets having controllable droplet size, spacing, and velocity. This technique has been used for high-precision optical studies, i.e., Devarakonda *et al.* [12], Ray and Nandakumar [13], Lin *et al.* [14], Eversole *et al.* [15], and Tzeng *et al.* [16].

Newly developed techniques allow the simultaneous measurement of the gas and liquid phase as shown by Vehring *et al.* [17]. They studied fast transport processes, such as absorption of SO_2 in and desorption of CO_2 from aqueous microdroplets generated with a VOAG. Profiles of gaseous CO_2 near the droplets could be measured with a spatial resolution of 50 µm.

For a detailed experimental investigation of heat and mass transport, the determination of the gas composition as close to the surface of the particles is desirable. However, due to slight random changes in the droplet position, no measurements can be made closer to the surface of the droplet than approximately 100 µm. To overcome this limitation of the spatial resolution, we employed pulsed 2-dimensional Raman spectroscopy in this investigation.

Various theoretical models exist to describe heat and mass transfer processes from microdroplets. Some authors [18,19] use the "d^2-law" [20] or related models. Most of the models were developed for isolated single particles. These models are of limited benefit for the investigation of transport processes in droplet chains. The interdroplet separation distance is so small that droplet-droplet interactions become significant. Based on a point source model (PSM), Ray and Davis [18] have taken these effects into account and developed simple algebraic expressions for steady-state evaporation of finite as well as uniformly distributed infinite droplet arrays. Umemura [21] has reviewed the theoretical models available for predicting the degree of interaction in quasi-steady-state processes.

The degree of interactions in a transfer process (momentum, heat or mass transfer) can be defined in terms of an interaction parameter which is the ratio between the rate of a transfer process from a droplet in an array to that from a single isolated droplet. For mass transfer the interaction parameter is

$$\eta = \dot{m}_{array} \Big/ \dot{m}_{iso}$$

For linear droplet arrays generated by a VOAG the interaction parameter depends only on the nondimensional spacing between the droplets which is defined as $\varepsilon = l/a$, where

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a is the size and *l* the center-center spacing between successive droplets. Annamalai and Ryan [22] have reviewed the experimental and theoretical advances made in the study of interaction effects on droplet dynamics, heat and mass transfer, ignition and combustion of droplet arrays. Silverman and Dunn-Rankin [23] have studied the effect of interdroplet separation distance on vaporization and combustion rates of methanol and hexane droplets. Devarakonda [24] and Devarakonda and Ray [25] have studied the evaporation of single (ethanol + methanol) and multicomponent (ethanol + methanol, dibutyl pthalate + freon) droplets. From the observed evaporation rates, they found that the interdroplet interactions are significant ($\eta \sim 0.3$) for $\varepsilon < 7.0$ and are negligible for $\varepsilon > 20$.

2 Experimental

2.1 Experimental Setup

A schematic of the experimental setup is shown in Fig. 1. The components of the experimental setup were described earlier in detail [17]. A linear stream of monodisperse microdroplets is generated by a vibrating orifice aerosol generator [10], VOAG, which has been stabilized according to Lin *et al.* [11]. The droplet size is given by $d = (6Q/\pi f)^{1/3}$, where f is the frequency of the square wave from a synthesizer (HP 3325 B) applying to the PZT crystal with an amplitude of 10 V. The volumetric rate, Q, is monitored by continuously weighting the liquid reservoir (Sartorius, MC1, LC 3200D). It is kept constant by pressuring the liquid from a 50 l ballast gas tank. With a backing pressure of 1.5 bar, an orifice diameter of 20 µm and a frequency of 43.9 kHz one gets droplets with a diameter of 62 µm and a droplet spacing of about 362 µm.

The droplets consist of acetylene dissolved in acetone with a concentration of 0.7 mol/l. These droplets are injected with an initial velocity of 10 m/s in an air atmosphere of 1 bar. The droplets were observed 5 mm below the generator exit. This corresponds to a droplet residence time of 0.39 ms.

The droplet chain was illuminated by a cw Ar^+ laser (Spectra Physics, 2030) operating in single mode ($\lambda = 514.5$ nm, P = 5 W). Plasma emission from laser was filtered by a combination of prism and field stop. The polarization of the laser beam is set to be perpendicular to the scattering plane. A 35 mm focal length achromat focussed the laser beam to a waist diameter of about 30 µm onto the droplet chain. The light collecting optics was arranged under 90° to the droplet chain and the direction of laser beam. A high-quality, low-f-number objective imaged the scattered light onto the entrance slit (600 µm) of a double monochromator (Spex 1403). This instrument was equipped with two 600 groves/mm gratings and a holographic band-pass filter (POC, RHE 514.1D) to reject Mie-scattering. Images and spectra from the CCD camera (Wright Instr. 1) were processed with a PC-based imaging software (Wright Instr., AT1) and software developed in-house.

2.2 Gated Detection

To increase the spatial resolution, an image intensifier (PCO, Model IRO) was mounted in front of the CCD camera (Fig. 1) and gated synchronously with the droplet generator as described above. A gate pulse length of 1 µs was used for appropriate space resolution. The delay time (0–25 µs) between the gate pulse and the trigger pulse from the droplet generator was varied in steps of 1 µs. This made it possible to shift the observation region relative to the droplet position. A shift of the delay time by 1 µs corresponded to a shift of the observation region by 24 µm relative to the droplet position. The gas composition could be analyzed between the droplets at different locations by this technique.

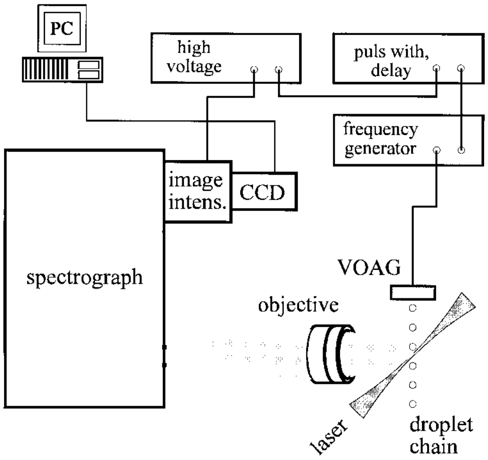

Figure 1. Sketch of the experimental setup.

The total observation time at each step was 10 s. Typical results are shown in Fig. 2, which shows a sequence of Raman spectra. Spectra with high intensities indicate the presence of a droplet. Between the droplets only the acetylene signal of the gas phase (1973 cm^{-1}) is visible. The vibrational Raman line of nitrogen of the surrounding air is visible at 2331 cm^{-1}. From these measurements the concentration of the evaporated acetylene can be determined.

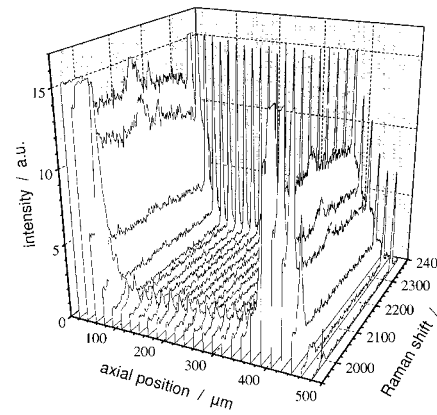

Figure 2. Raman spectra of the acetone/acetylene-droplet chain at various axial positions. Spectra with high intensities indicate the presence of a droplet. Between the droplets only acetylene signal of the gas phase (1973 cm^{-1}) is visible. At 2331 cm^{-1} lies the line of the air nitrogen.

3 Results and Discussion

3.1 2-D Spectroscopy

The concept of 2-D Raman spectroscopy [17,26] is illustrated in Fig. 3. As mentioned earlier, a laser beam is passed perpendicular to the droplet chain. The laser beam is imaged onto the entrance slit of the spectrograph in such a way that the laser axis is parallel to the slit height. With this optical setup, the diameter of the laser beam and the height of the entrance slit define the observation volume. The CCD image recorded in the exit plain of the spectrograph contains spectral and local information. In the exit plain of the spectrograph the light from the observation volume is dispersed spectroscopically in the horizontal direction, whereas the spatial information is preserved in the vertical direction. The horizontal spectral information allows the identification of the chemical components in the observation volume. The vertical direction gives information about the spatial distribution of a species in the observation volume, i.e., the direction of the laser beam. The acetylene concentration perpendicular to the droplet chain axis was determined by reading out the CCD camera without binning. This is shown in Fig. 3. The horizontal direction is the direction of spectroscopic dispersion.

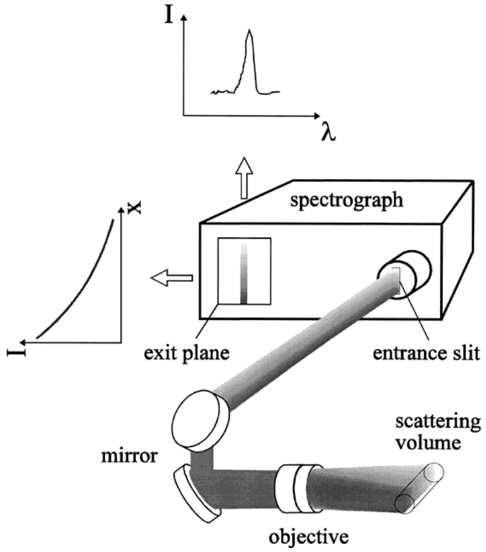

Figure 3. Sketch of the 2-dimensional spectroscopy.

A grey scale representation of a Raman image at a specific position between the droplets is given in Fig. 4. The length of the vertical side of the image defines the length of the scattering volume. Each line of the image corresponds to the concentration distribution along the laser beam of a specific chemical component in the observation volume at one specific position. The Raman signal of the liquid phase (dissolved acetylene and acetone) appears only as a relatively small band in the center of the image. This band corresponds to the region where the droplets crossed the laser beam. Fig. 4 shows that the nitrogen signal is present throughout the scattering volume (vertical band over the full height of the image). It is much more intense than the signal of the gas-phase acetylene. Therefore, the nitrogen signal was used as an internal reference to determine the concentration of the acetylene vapor concentration as a function of distance perpendicular to the droplet chain axis.

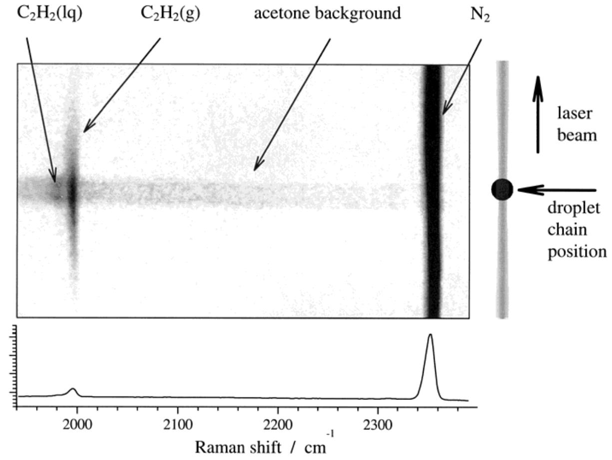

Figure 4. Grey scale representation of a Raman image at a position between the droplets. The horizontal direction is the direction of spectroscopic dispersion as indicated with the spectrum below. The vertical direction is parallel to the direction of the laser beam and gives information about the spatial distribution of the species in the scattering volume.

3.2 Data Analysis

In the horizontal direction, the data corresponding to the 2-dimensional images were evaluated line by line. Each line represents a spectrum at a specific position in the droplet chain. The spatial resolution is defined by the height of the pixel of the CCD camera and the magnification of the imaging system (5.3 μm in this case). The spatial resolution perpendicular to the laser beam is defined by the diameter of the laser beam and was approximately 37 μm. For a quantitative evaluation of the obtained spectra, the line intensities of single-component spectra (acetylene (g), acetylene (l), acetone and nitrogen) were fit to the measurements. Normalization of the acetylene signal to the nitrogen signal leads to the absolute concentration distribution of the acetylene in the gas phase at a specific position between the droplets.

3.3 Data Interpretation

Measurements were made at 23 equidistant axial positions in steps along the direction of the droplet chain. The spatial resolution for each step was increased by the particle movement to about 20 μm. The evaluation procedure described above was used to determine the gas-phase concentrations at each position with a spatial resolution of ≈ 40 µm. From this, the 2-dimensional concentration distribution shown in Fig. 5 were constructed. The position of the droplets is indicated by the grey ellipse. White areas in the vicinity of the droplets indicate the region where concentration measurements were impossible (droplet influence zone). In these regions, no gas concentrations could be measured, due to fluctuations in the droplet position. The droplet propagation in this representation is from top to bottom. The direction of the laser beam is from left to right. The apparent high acetylene concentration at the right side of the droplets of Fig. 5 is caused by distortion of the laser beam by the droplets.

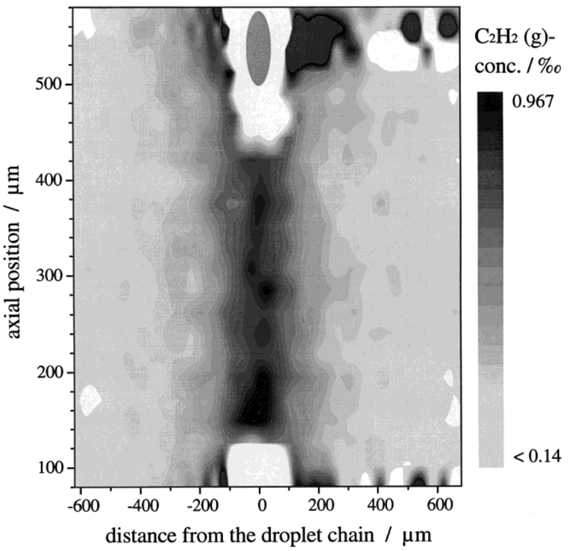

Figure 5. A grey scale representation of the 2-dimensional concentration field of the released acetylene between the droplets in an acetone/acetylene-droplet chain. The presence of the droplets is indicated by the white areas where no gas exists. The droplet propagation in this representation is from top to the bottom. The direction of the exciting laser beam is from left to right side.

It can be seen that the concentration of gaseous acetylene decreases with increasing distance from the droplet chain axis, as expected. Furthermore, the highest acetylene volume concentration of approximately one per thousand is in the wake behind the droplet. The acetylene concentration seems to decrease near the droplet influence position. This is an artifact caused by the fitting procedure and the contour plot calculation.

The pulsed 2-dimensional Raman spectroscopy yields not only the gas phase concentration but also information on the liquid phase. This can be used for testing the measurements because only at the position of the particles the liquid phase should be visible. In fact, Raman signals of the liquid acetylene and acetone are only visible at the particle position. The data shown in Fig. 6 represents the concentration of liquid of the specific component in arbitrary units within the scattering volume. The decrease in signal intensity at the boundary of the droplet has the following reason. The Raman-scattered intensity is proportional to the number of molecules in the observation volume. If part of the observation volume is occupied by the liquid droplet, the number of gas molecules in the scattering volume is reduced and a lower intensity is measured although the concentration of the gas phase has not changed. Fig. 6, therefore, represents the mole fraction of liquid acetone and acetylene, respectively, within the scattering volume.

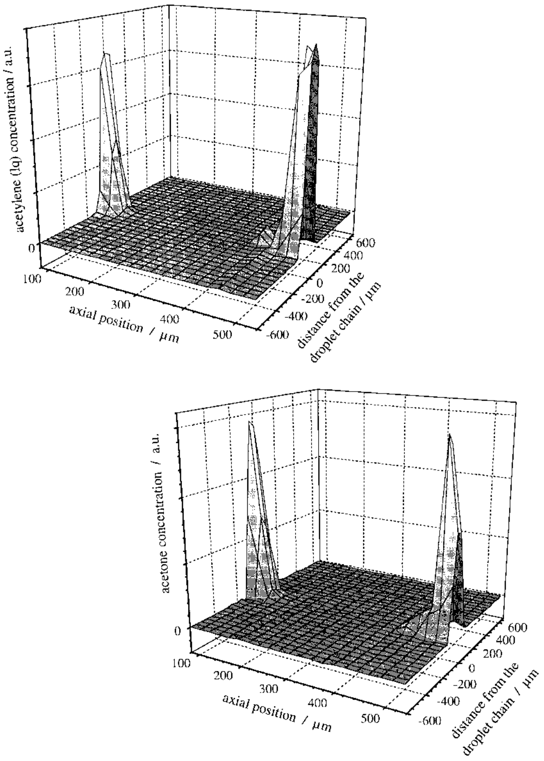

Figure 6. The concentrations of the particle phase in arbitary units vs. the distances from the droplet chain and in direction of the droplet propagation: the concentrations of the released acetylene (left) and the acetone (right).

4 Summary and Conclusions

It has been shown that the pulsed 2-dimensional Raman spectroscopy can be applied for the determination of average concentration in the liquid phase and concentration profiles in the gas phase surrounding fast-moving linear streams of microdroplets. This technique was applied on the binary system acetylene dissolved in acetone. The 2-dimensional concentration field of the desorbed acetylene could be determined with a spatial resolution of approximately 40 µm in direction of the droplet propagation and perpendicular to the droplet chain. The time resolution was about 1 µs. The detection limit of the pulsed 2-dimensional Raman spectroscopy for gaseous components in these experiments was about 100 ppm. The detection limit for the determination of average concentration in the liquid phase was about 1 mmol/l.

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