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SIMULTANEOUS IMAGING OF VAPOR AND LIQUID SPRAY CONCENTRATION USING COMBINED ACETONE FLUORESCENCE AND PHOSPHORESCENCE

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ABSTRACT

This study aims to improve a technique for measuring fuel distributions, e.g. mixture fraction and droplet sizes, in evaporating and mixing (two-phase) fuel sprays. The technique is based on planar laser-induced fluorescence of acetone, used as a surrogate fuel. Previous work investigated the use of signal level to discriminate against liquid acetone droplets bigger than a critical size. However, droplet streaks were observed. To determine the cause of the streaks, time decay experiments of the signal were conducted and. indicate that acetone phosphorescence is the cause. The phosphorescence lifetime and the phosphorescence to fluorescence ratio for the spray were determined and are similar to that of the vapor (in the absence of oxygen). Further measurements of bulk liquid acetone found widely different values for the phosphorescence lifetime and P/F ratio based on the exposure of the liquid acetone to oxygen. A method is suggested for simultaneous droplet size and vapor mixture fraction measurements. It utilizes two images acquired with a short delay. The first (short exposure) image captures the vapor and liquid fluorescence, and the second (long exposure) image measures the liquid phosphorescence. There is also some difference in the spectral content of the liquid fluorescence and phosphorescence The phosphorescence streaks also have the potential to provide some droplet velocity information.

INTRODUCTION

Quantitative two-phase mixture fraction measurements are important for understanding mixing in two-phase systems typical of modern combustion systems. This understanding can lead to the reduction of pollutants, improved combustor efficiency, reduced combustor size, longer combustor lifetimes and greater combustor stability. Thus there is a great need for the development of appropriate measurement techniques. This study aims to develop quantitative, spatially and temporally resolved measurements in two-phase flow using planar laser-induced fluorescence (PLIF) of acetone to measure both liquid and vapor concentrations with one technique.

Planar laser-induced fluorescence (PLIF) is well suited to the task of measuring mixing because it yields two-dimensional images of the flowfield and is a proven approach for non-invasive measurements.[1] A laser beam at a properly chosen wavelength is optically converted to a thin laser sheet that causes molecules in the flowfield to fluoresce. The resulting fluorescence is proportional to the amount of the absorbing species in the measurement volume. The concentration field of the absorber can be converted to mixture fraction, a measure of local mixing.

For fuel-air mixing measurements, acetone fluorescence is especially attractive.[2] It has many advantages over other fluorescing alternatives. Most importantly, acetone fluorescence in isobaric, isothermal flows is known to be linear with concentration and laser power,[3] which is not true for many fluorescing molecules. Additionally, acetone fluorescence works well in the presence of oxygen.

The fluorescence yield of acetone is limited by rapid intersystem crossing from the first excited singlet state (S1), which fluoresces, to the first excited triplet state (T1), which phosphoresces. The phosphorescence is strongly quenched by oxygen, leaving a strong fluorescence signal. Also, acetone absorbs ultraviolet light (225 - 320 nm) but fluoresces in the blue[3] (350 - 550 nm). The phosphorescence is also in the blue, but

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red-shifted somewhat compared to the fluorescence. Elastically scattered light is easily filtered out by simple glass optics since the absorption and emission spectra do not overlap.

Numerous studies have examined acetone (and other ketones) for measuring fuel vapor concentration in gaseous systems. However, little quantitative work has been performed in two-phase flows, i.e., evaporating sprays, to simultaneous measure the vapor concentration and droplet size using the simplicity of a single laser and single camera. One of the challenges in making such measurements is an understanding of the signal coming from the liquid acetone, which is a combination of fluorescence and phosphorescence depending on the O_2 level in the liquid and the environment. This is the focus of the current effort.

BACKGROUND

A key to making quantitative LIF measurements in multiphase flows is distinguishing between the signal coming from the different phases. While droplets sufficiently larger than a pixel can be resolved geometrically, phase discrimination is an issue for subpixel sized droplets. This is typically the situation since pixel resolutions in practical flows are usually limited to 100 μm or greater, and droplet sizes are often below 100 μm.

Since both phases of acetone fluoresce over essentially the same spectrum, the phases cannot be readily distinguished spectrally. However, the large density difference between the phases leads to a possible solution. The higher density of liquid acetone (~750× the vapor density at standard conditions) results in much larger signals from droplets compared to vapor of the same volume. Thus, signal strength can be used to separate liquid from vapor acetone. [4]

However, simple discrimination is possible only for droplets larger than some minimum critical diameter, i.e., when the fluorescence from the droplet exceeds the fluorescence from a pixel filled with saturated acetone vapor. In previous work,[5] a model was developed for distinguishing between the fluorescence from droplets and from vapor. The model included laser extinction within the droplet, as well as reflection and refraction effects. The model results were used to determine the cutoff diameter (Figure 1).

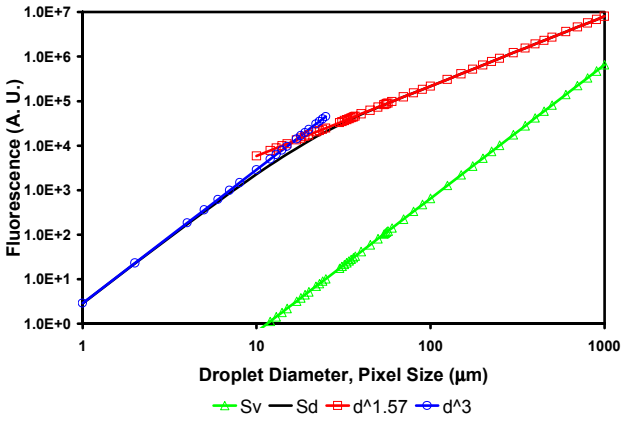

Figure 1. Fluorescence power versus droplet diameter for liquid acetone and versus pixel size for saturated vapor at room temperature. Fluorescence power scales like d3 for small droplets and like d3-n for large droplets. Calculations use 266 nm laser light, square pixels, and standard temperature and pressure.

For the experimental parameters, such as laser wavelength (266 nm) and pixel size (170 μm) used in that work, the critical diameter was 20 μm. In addition, the model was used to develop an algorithm for obtaining, simultaneously, droplet size and vapor concentration using two pieces of information: the pixel intensity and the laser extinction (absorption and scattering combined) across the pixel. However, it is difficult to determine the extinction across a single pixel in experiments.

Experimental results in an acetone spray, however, provided another potential approach. Droplets that were found to be approximately 100 μm in diameter, based on the model results, appeared as nonspherical images with long dimension of 1-2 mm (Figure 2). In addition, the droplet images were pointed radially outward, with the (radially) inner side of the image brighter than the outer side. Essentially, the images acquired with the unintensified CCD camera (exposure time ~10 ms) appeared to be droplet streaks, suggesting a signal lifetime greater than the expected fluorescence decay.

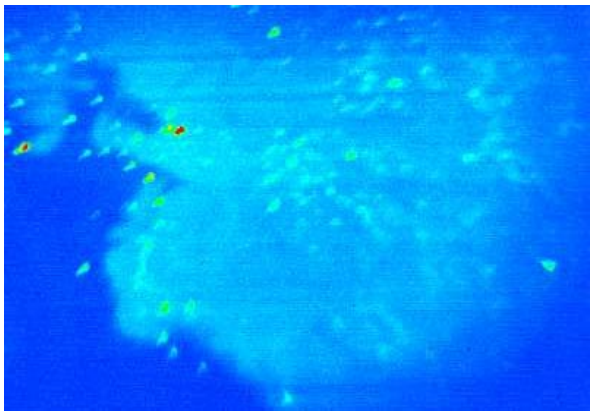

Figure 2. Image of evaporating spray 10 inches downstream shows streaks for individual droplets.

This long-lived signal could be useful for the technique, but first several questions must be answered. It must be determined if this is acetone phosphorescence and if it is, what phase is emitting the signal. If it is the droplets, then the phosphorescence lifetime and a ratio of phosphorescence to fluorescence for liquid acetone need to be measured. Also, the ratio of liquid to vapor fluorescence for the same number of acetone molecules will determine if the quantum efficiency is the same for the two phases (the model assumes it to be the same). A search in the literature found a reference to a study that established the liquid acetone phosphorescence lifetime as 30 μs.[6] The study used five freeze-thaw-pump cycles at 10^{-5} Torr to degas the liquid acetone and then sealed the sample under vacuum. A nitrogen laser was used to excite the sample at 337 nm. Because oxygen quenches acetone phosphorescence so strongly, it is unclear what the emission behavior of small droplets in air should be due to surface contact with oxygen even if no oxygen is present in the liquid.

The first signal lifetime measurements used an intensified CCD camera attached to a spectrometer to acquire images of a spray created with a pressure-atomizing nozzle using N_2 to provide the back pressure. These measurements yielded a signal lifetime of 185 μs, quite similar to the vapor phosphorescence lifetime of 200 μs. The ratio of total phosphorescence to total fluorescence was 7.5, also similar to the vapor value of 9. Subsequent measurements with air providing the back pressure failed to produce long-lived signals, demonstrating the quenching effect of oxygen on phosphorescence. This was compelling evidence of phosphorescence, but without definitive evidence of which phase was producing the signal. Since the literature value for the liquid acetone lifetime is significantly shorter, this led to the conclusion that either the long-lived signal was vapor phosphorescence or droplets behaved differently than bulk liquid acetone. Even if the longer lifetime was due to vapor fluorescence from acetone molecules surrounded by nitrogen from the spray, liquid phosphorescence may have been present as well. It was decided that measurements of bulk liquid acetone using an ICCD were needed to establish a lifetime for liquid phosphorescence under similar experimental conditions to help explain the spray results.

The first measurements of the liquid signal lifetime used a beaker of liquid acetone open to the atmosphere and with no attempt to remove any oxygen from the acetone. The next set of measurements used de-oxygenated acetone. Degassing was rejected as an impractical approach to removing oxygen for a practical spray measurement technique, but pressurizing the liquid acetone with nitrogen is both simple and applicable to a spray setup. The next step was to use a prolonged pressurization to remove most of the oxygen and then used a sealed cuvette to slow the diffusion of oxygen from the air into the liquid.

EXPERIMENTAL SETUPS

Beaker Measurements

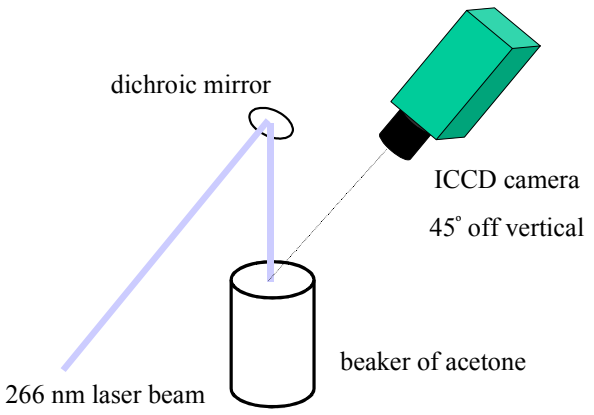

Figure 3. The experimental setup for beaker measurements of liquid acetone properties.

The imaging setup for the beaker measurements (Figure 3) employs a frequency-quadrupled Nd:YAG laser (266 nm) beam. The circular output beam of the Nd:YAG laser, with a spatial full-width at half-maximum of 7 mm, is reflected from a mirror vertically down into a beaker full of liquid acetone. The laser energy is approximately 75 mJ per pulse and the temporal full-width at half-maximum value of the pulse is 7 ns. The surface of the beaker is imaged with an ICCD camera held at 45 degrees off vertical. For a quick attempt at reducing the oxygen content for a

second set of experiments, the liquid acetone was pressurized in a vessel with nitrogen for approximately 30 minutes before being poured into the beaker. A small jet of nitrogen was directed over the surface of the beaker to provide a buffer from the atmosphere.

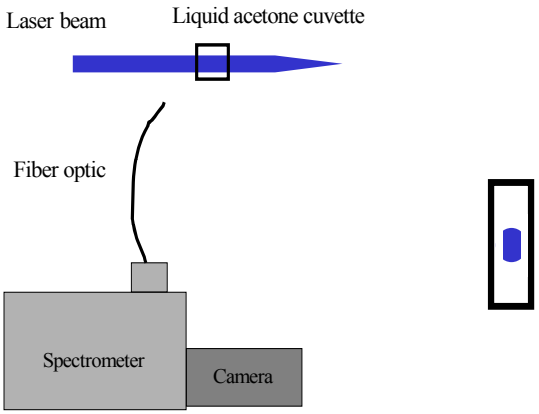

Figure 4. Top (left) and side (right) views of the experimental setup. The top view shows the optical setup used to acquire light emission at different time delays relative to the laser pulse. The laser hitting the cuvette filled with liquid acetone is shown in the side view.

Cuvette Measurements

The imaging setup for the cuvette measurements (Figure 4) employs the same frequency-quadrupled Nd:YAG laser (266 nm) beam. The laser energy is approximately 25 mJ per pulse to avoid saturating the measurement system. The circular output beam of the laser passes through an aperture to prevent the edges of the beam from hitting the metal cell holder, which has an 8 mm wide opening. The holder contains a fused silica cuvette with internal dimensions of 10 x 10 x 45 mm and a Teflon stopper in the top. To reduce the oxygen content, the liquid acetone was held at 15 psig with nitrogen for 14 hours. The acetone was quickly placed into a bottle and an eyedropper was used to fill the cuvette, but the acetone was exposed to the air for about five minutes during this process. The measurements were performed immediately afterwards, but there is still an inherent uncertainty about the level of oxygen in the liquid acetone and how much quenching occurs.

Light is collected into a spectrometer using a fiber optic and a 500 µm wide entrance slit, which is greater than the width of the fiber. The spectrometer grating used has 600 grooves/mm, with a resulting resolution of approximately 2 nm. An electronically cooled, ICCD camera is attached to the spectrometer to record the emissions spectrum from 379 to 520 nm (avoids the second laser harmonic at 532 nm). The 1024 x 256 pixel CCD was binned to become 1024 x 4 with one row for each possible fiber. One fiber was used and the next one was capped to provide a reference background. The images acquired here were taken with a range of gate widths from 50 ns to 10 µs, and with a series of time delays relative to the laser.

RESULTS

Liquid Acetone Measurements

The first measurements acquired were of liquid acetone in a beaker being hit directly by the laser beam. Very little phosphorescence was measured when the beaker was sitting in the quiescent environment (P/F = 0.12) and the measured lifetime was 244 ns (Figure 5). Clearly O_2 was quenching the phosphorescence, so efforts were made to reduce the effect. The acetone was placed in a pressurized nitrogen environment for 30 minutes before being put in the beaker, and a jet of nitrogen was directed over the beaker to reduce the ambient oxygen level. This resulted in only about a twofold increase in lifetime, which was not nearly enough. It was determined that a closed container was needed to eliminate the effect of ambient oxygen. This led to the use of the cuvette described previously.

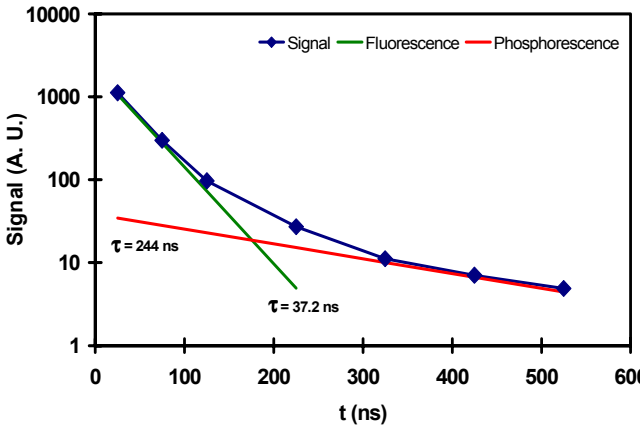

Figure 5. Time decay of the liquid acetone emission, with exponential fits for the shorter (37.2 ns) and longer (244 ns) lifetime components.

For measurements in the cuvette, it was filled entirely with liquid acetone and then sealed to keep out the air. The first measurements were taken with acetone that had not been pressurized in nitrogen, and again very little phosphorescence was seen. This indicated that dissolved oxygen in the acetone was indeed an important quencher. The next measurements used acetone that had been held in a 15 psig nitrogen environment for 14 hours before being placed in the cuvette. Images were acquired at time delays from 0 to 200 µs, and the gate of the ICCD changed from 100 ns

for shorter delays, to 1 µs and then to 10 µs for the longer delays (with an overlap at each gate width change). Non-delayed images were taken with 50 and 100 ns gates to better separate fluorescence from phosphorescence. Long exposure images (200 µs) were taken with delays of 0 and 100 ns to capture the entire signal.

The signal across the entire wavelength range acquired by the spectrometer/camera system was background corrected and summed. This was also done for a capped fiber, and the value from the capped fiber was subtracted from the open fiber value as a further correction. An exponential decay was fitted to the data points delayed at least 2 µs from the laser, as shown in Figure 6. The resulting lifetime was 39.5 µs, which is similar to the published value of 30 µs for degassed liquid acetone. Because a significantly different excitation wavelength is used for the two results (266 nm versus 337 nm), it is possible the difference in lifetime is a result of the shorter excitation wavelength used here.

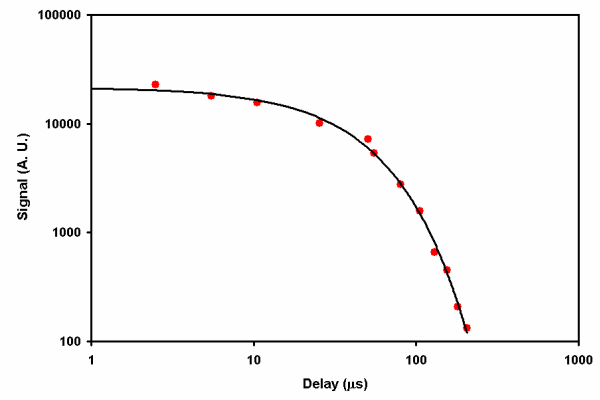

Figure 6. The best-fit exponential curve to the data points of laser-induced emission at different time delays, which yields a signal lifetime of 39.5 µs.

The total fluorescence signal (F) is contained in the 50 ns gate image taken with no time delay. However, the amount of phosphorescence during this time must be subtracted. Because the phosphorescence decays so slowly relative to the time gate, the phosphorescence signal generated from t = 50 ns to t = 100 ns should be virtually identical to the signal from t = 0 to t = 50 ns. Subtracting this value from the total signal in the 50 ns gate images yields the total fluorescence. The total phosphorescence signal (P) was calculated using the total corrected signal from the non-delayed, long exposure images and subtracting the total fluorescence signal. The resulting total phosphorescence to fluorescence ratio (P/F) for the liquid acetone is 2.7. For comparison, acetone vapor has a total phosphorescence to fluorescence ratio of 9,[7] and the droplets measured 7.5 as mentioned previously.

An important point to note is that the spectrometer system is not measuring the entire emission range, as seen in the emission spectra in Figure 7. Because the second harmonic of the YAG laser occurs at 532 nm, the spectrometer was set up to stop measuring short of this wavelength to protect the ICCD from saturating due to laser emission. Further tests with a sufficiently effective filter would allow the entire spectrum to be captured, which could increase the P/F ratio significantly since the phosphorescence is stronger than the fluorescence at the longer wavelengths.

Further measurements in the cuvette were done with a layer of liquid acetone below the height of the laser beam producing saturated acetone vapor in the remainder of the cuvette. The total fluorescence signal from acetone vapor was measured and compared to the value for liquid acetone. After accounting for the density difference and absorption effect on path length, the preliminary result was that the liquid signal was 3.5 times the vapor signal on a per molecule basis.

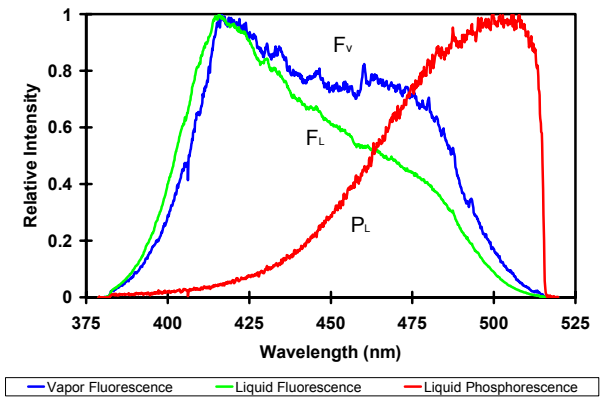

Figure 7. Measured spectra for acetone vapor fluorescence (leftmost curve), liquid acetone fluorescence (curve highest in the middle) and liquid acetone phosphorescence (rightmost curve).

Droplet Image Analysis

Images from the same spray used to measure the 185 µs lifetime for the long-lived signal were analyzed in greater depth. Streaks that represented 48 individual droplets were hand selected based on visual examination of the images (Figure 8), with an intentional avoidance of any very large droplets in the images. The large droplets were avoided because they were not representative of the "typical" droplets, but two were measured earlier to have diameters of roughly 100 µm. Since visual inspection was used, the analysis is also biased against very small droplets that are difficult to discern by eye.

Prior analysis had shown that the streak length converted to reasonable droplet velocities when using the 185 µs signal lifetime. Now the total signal contained within an individual streak was summed, and the 7.5 ratio of phosphorescence to fluorescence was used to separate the signals. The total fluorescence signal was then converted to a droplet diameter using the droplet fluorescence model. In addition, the same droplets were converted using the 2.7 ratio found with the cuvette. The resulting droplet size distributions are shown in Figure 9. All the droplets chosen by eye had diameters of between 12 and 28 µm, with a peak value of 11 droplets of diameters 12 and 13 µm for the 7.5 case. The lower ratio resulted in larger droplets, with a peak at 19 µm. While these seemed to be reasonable sizes considering the methodology, a basis for comparison was needed.

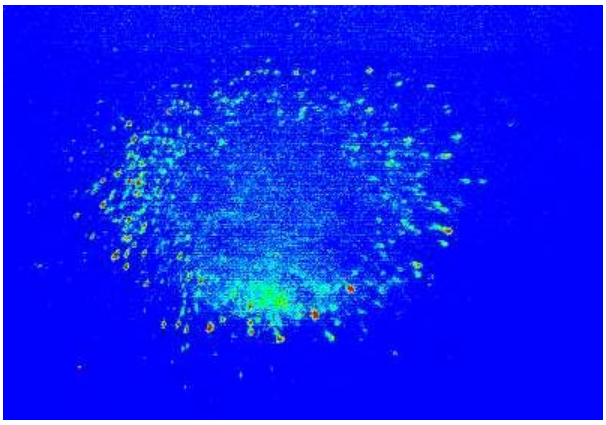

Figure 8. Spray image acquired 1 inch downstream showing typical droplets analyzed for diameter.

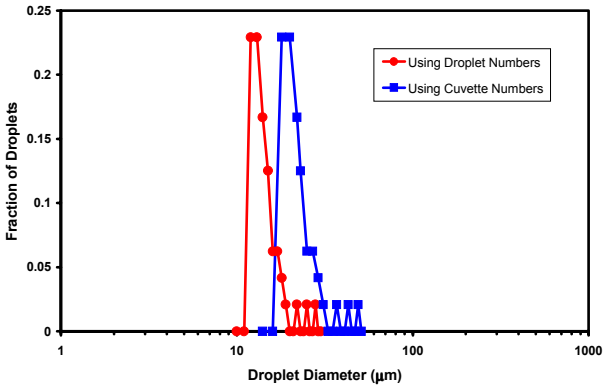

Figure 9. Droplet size distributions for droplets selected from images using the P/F ratio from the droplet measurements (leftmost curve) and from the cuvette measurements (rightmost curve).

The same spray conditions were measured using a phase-Doppler particle anemometer (PDPA) to provide a separate measure of the droplet size. Measurements were taken with 1 mm spacing using 5000 droplets at each location. Distributions at several radial locations are shown in Figure 10. The distribution gets broader and the droplets larger, on average, farther from the center of the spray. Most of the droplets picked by hand were contained in the outer half of the spray. It is clear from comparing the distributions that the image analysis consistently undersized the droplets, which should have yielded a peak droplet diameter of between 30 and 40 µm based on the PDPA data.

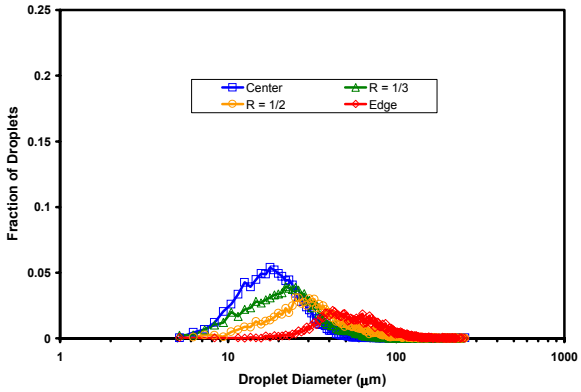

Figure 10. Droplet size distributions from the PDPA for the same spray conditions as the images.

CONCLUSIONS

The values of the liquid acetone P/F ratio and a phosphorescence lifetime were previously measured in a spray to be 7.5 and 185 µs respectively. However, the lifetime conflicts with the published value of 30 µs for degassed liquid acetone, implicating acetone vapor phosphorescence in the spray measurements. Apparently nitrogen from the liquid acetone formed a buffer layer to prevent oxygen from quenching the vapor phosphorescence. Measurements of bulk liquid were subsequently performed both in an open container with no attempt to purge the oxygen from the liquid acetone, and in a closed container with lengthy nitrogen pressurization of the liquid acetone to remove the oxygen. While the open container led to values of 0.12 and 244 ns, the closed container gave values of 2.7 and 39.5 µs. The closed container values cannot be taken as the absolute values for pure liquid acetone for two reasons. First, the possibility of oxygen contamination in the liquid acetone provides an uncertainty. Second, only part of the phosphorescence spectrum could be captured by the spectrometer system due to the second harmonic of the YAG laser (532 nm) saturating the system if it spectrometer measured that far in

wavelength. Clearly the total phosphorescence signal is larger than what was measured, which would increase the P/F ratio. The process of finding values for the signal lifetime and P/F ratio for liquid acetone has several implications for the future of this technique.

Knowing that the P/F ratio was overstated before, the droplet sizes calculated from the spray were re-examined. A lower P/F ratio indicates that more of the signal is fluorescence, and thus the droplet sizes would be significantly bigger. The 2.7 ratio moves the peak of the droplet size distribution from 12.5 μm to 19 μm and stretches the distribution out so it is more similar to the values from the PDPA at the center of the spray. These sizes are still too small, indicating that some form of calibration is needed to get a quantitative result for droplet diameter unless a more exacting model is developed.

The measurements reported here demonstrate that it is possible to deduce droplet size and vapor concentration from one spray image. It is clear that this technique will be very sensitive to the oxygen levels in the liquid and the environment, though. It would be best to make measurements in a non-oxygenated environment if quantitative droplet size measurements are required, but this will necessitate dealing with vapor phosphorescence. The increased vapor signal will increase the droplet cutoff size beyond which the technique cannot distinguish the phases. While the dissolved oxygen can be removed from liquid acetone, there is always the uncertainty of how much oxygen might be left or if some has leaked in since the removal process. This is less of a concern if qualitative droplet sizing is the goal, so the technique would be easier to apply in that case. It would also be possible to calibrate the technique for the system of interest as long as the liquid acetone is equally oxygenated for all the measurements. The ability to get rough droplet sizing simultaneously with quantitative vapor concentration measurements is still an exciting prospect, however.

A second, potentially more quantitative method would employ an interline camera which can acquire two images with very little delay between them (~ 1 μs). The first, short-exposure image would capture the fluorescence, while the long-exposure, slightly delayed image would capture the liquid phosphorescence. This second image would be used to calculate droplet sizes, and then the droplet fluorescence could be subtracted out of the first image to produce a vapor-only fluorescence image. The end result is a one laser, one camera system that produces quantitative measurements of droplet size and vapor concentration. The streaks from the droplets also provide potential velocity information.

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