

Measurements of Acetone Fluorescence and Phosphorescence at High Pressures and Temperatures

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Laser-induced fluorescence and phosphorescence signals of liquid acetone at pressures from 1 to 15 atm were measured and analyzed. Liquid acetone, which was preprocessed to minimize any dissolved oxygen, was injected as a low velocity jet into a pressurized chamber with either an air or nitrogen co-flow. The acetone was excited at 266 nm. The laser-induced fluorescence intensity from the liquid was found to be invariant with pressure and co-flow conditions. The measured phosphorescence lifetimes were also found to be independent of pressure, for both nitrogen and air environments. The phosphorescence lifetime for the liquid was measured to be $\sim 1 \mu\text{s}$, which is significantly smaller than the lifetime for acetone vapor ($200 \mu\text{s}$). This is likely due to self-quenching by acetone. The effect is further seen in the phosphorescence to fluorescence (P/F) ratio comparison between the liquid and vapor. The P/F ratio for liquid is 0.012, which is much smaller than the vapor value of 9.0. The overall phosphorescence intensities, however, were seen to decrease in the air co-flow cases compared to the nitrogen co-flow. Diffusion of oxygen into the liquid jet was observed, and the estimated concentration was found to be a few orders of magnitude less than the saturated concentration.

I. Introduction

Planar Laser-Induced Fluorescence (PLIF) is a non-invasive measurement technique that can provide qualitative as well as quantitative characterization of flowfields. A laser source is used to excite a tracer molecules to higher energy state, thereby causing these molecules to fluoresce. The fluorescence intensity can be related to the concentration of the tracer species. One application is characterization of mixing in a flowfield.¹ The spatial and temporal resolution provided by PLIF makes it an important tool among researchers; PLIF can provide measurements under a large range of operating conditions and has been widely used to measure the mixing properties in jets and sprays at various conditions.

Acetone is advantageous for gas mixing measurements with PLIF because of the linear relationship between the fluorescence intensity, acetone concentration, and laser power in an isobaric and isothermal environment.² Many studies have focused on PLIF of acetone vapor,^{1,3,6} but less attention has been given to the liquid phase. In the vapor phase, the majority of the signal in acetone-air mixing studies comes from fluorescence, since the phosphorescence is efficiently quenched by the presence of oxygen. This property of phosphorescence has been used to determine mixing efficiency, as demonstrated in a room temperature and pressure gaseous flowfield.⁴

In many practical combustion devices, however, fuel enters as a liquid. To study liquid fuel processes with acetone (or other ketones surrogates), it is important to understand the photophysics of their liquid phase. In the liquid phase, the acetone signal is a combination of fluorescence and phosphorescence. Also, depending on the droplet size, the signal is no longer a linear function of concentration above a critical size.⁵

Many mixing studies in combustion chambers have been performed at temperatures and pressures much lower than the actual operating conditions. For better understanding of breakup and mixing of liquid fuels, it can be important to properly simulate the higher pressure and temperature conditions. In many cases, these conditions can correspond to transcritical and supercritical states of the fuel. For example at supercritical pressures, heating the fuel does not produce a distinct transition from liquid to gas, rather the fuel behaves as a single homogeneous supercritical fluid that exhibits properties of both gas and liquid phases. The changes in the behavior of the fluid significantly affect the physical and chemical interactions of the fluid.

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Thus application of laser-induced emissions from acetone to study the mixing characteristics of a fuel and oxidizer under supercritical conditions requires characterization of the fluorescence and phosphorescence signal from acetone. Our long term goals, therefore, are to characterize the variation of the lifetime and intensity of phosphorescence and fluorescence from subcritical liquid to supercritical acetone at appropriate conditions of temperature and pressure. In the present paper, we examine subcritical liquid acetone photophysics, including lifetimes and phosphorescence-to-fluorescence ratio (P/F).

II. Background

A simplified model of acetone photophysics is illustrated in Figure 1. Laser excitation at a wavelength within the absorption band of acetone can excite molecules from the ground electronic configuration (S_0) to the first excited singlet state (S_1). From the specific excited energy level in S_1 , the acetone molecules can be de-excited either through radiative or non-radiative processes.⁶ The radiative process is denoted fluorescence. The non-radiative processes include: vibration relaxation (VR), internal conversion (IC), intersystem crossing (ISC), and collisional quenching (Q).

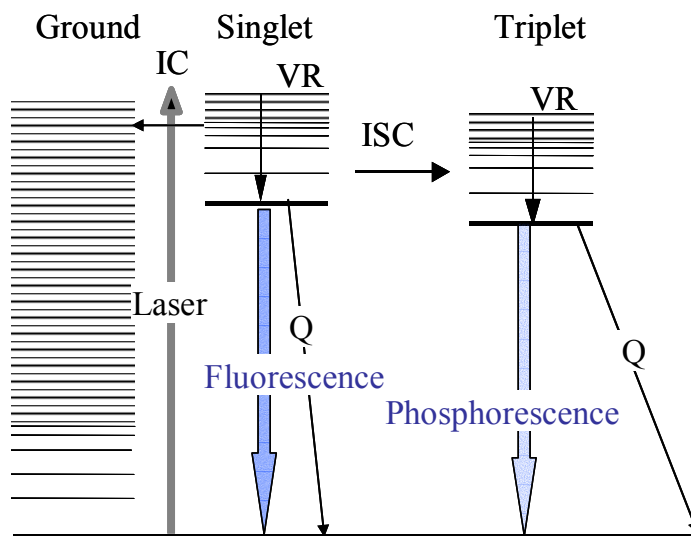


Figure 1. *Simplified model for acetone PLIF*

Internal conversion and intersystem crossing are both intramolecular energy transfer processes. Internal conversion occurs when the excited singlet relaxes back to S_0 through an intramolecular (non-collisional) energy transfer. This process is very slow since the energy difference between the singlet and ground states is very high and requires a large change in rotational and vibrational energy. Intersystem crossing involves transfer of energy from S_1 to the first excited triplet state (T_1). Thus ISC requires a change of spin, but not a large change in electronic energy. Vibration relaxation is the reduction in the vibrational energy of the excited molecules due to collisions with other molecules. Collisional quenching occurs when the excited acetone molecules relax to the S_0 due to collisions with quenching molecules such as oxygen.⁶ The molecules that are in the triplet state can be de-excited by a similar set of processes. The radiative de-excitation of the triplet state is called phosphorescence and is characterized by its longer lifetime compared to that of fluorescence.

In general the fluorescence and phosphorescence signal can be represented by Eq. 1:

$$S = n_{\text{optic}} \left(\frac{E}{hc/\lambda} \right) V_c n_{\text{acetone}} (P, T) \sigma(\lambda, T) \phi(\lambda, T, p, c_i) \quad \text{Equation 1}$$

where η_{optic} is the collection optics efficiency, E is the energy fluence of the laser, hc/λ is the energy per photon of the exciting laser, V_c is the collection volume, n_{acetone} is the number density of acetone, σ is the absorption cross-

section of acetone, and ϕ is the fluorescence or phosphorescence yield. η_{optic} , E , hc/λ and V_c are experimental setup variables and are not a function of flow conditions.

In general the number density for liquid acetone is dependent on both temperature and pressure, although it is more sensitive to changes in temperature than pressure. The number density decreases with increasing temperature. As the acetone reaches supercritical conditions, the variation with pressure and temperature is more pronounced. The absorption cross-section (σ) is a function of temperature and the excitation wavelength. Previous studies for vapor acetone indicate σ has a weak dependence on temperature for wavelength shorter than 285 nm.³

The fluorescence yield represents the fraction of excited molecules that get de-excited through fluorescence. It is equivalent to the ratio of the fluorescence rate to the total rate of the processes that remove molecules from the S_1 state. The fluorescence yield is dependent upon the temperature, pressure, excitation wavelength and concentration (c_i) of the quenching species. A general formula for the fluorescence yield is given in Eq. 2:

$$\phi_f = \frac{k_f}{k_f + k_{ISC} + k_{IC} + k_Q} \quad \text{Equation 2}$$

where k_f is the fluorescence rate, k_{ISC} is the intersystem crossing rate, k_{IC} is the internal conversion rate and k_Q is the quenching rate.⁶

From previous acetone vapor studies, k_{IC} is generally small compared to other rates and can be neglected.⁶ The intersystem crossing rate is directly proportional to the vibrational energy level of the molecules. Therefore, the higher the S_1 vibrational energy level, the faster the intersystem crossing rate. Vibrational relaxation moves molecules to lower vibrational energy levels. So, the overall ISC rate is inversely dependent on the vibrational relaxation rate of the molecules. Therefore, a change in k_{coll} will indirectly affect k_{ISC} in the opposite manner. For the vapor phase, k_{coll} increases with pressure. This is because the vibration relaxation rate is approximately equal to the collision rate between molecules since this is an intermolecular process. Thus the effective k_{ISC} (averaged over all the excited states) would decrease with pressure. For subcritical liquid acetone, however, k_{coll} should not vary significantly with pressure, since density is nearly pressure independent. At high pressures and elevated temperatures, k_{coll} may increase significantly with pressure. Since k_{ISC} is reduced due to the increase in k_{coll} , phosphorescence yield would likely decrease. The fluorescence yield could increase or decrease depending on the relative change in k_{ISC} and k_Q , which could also be pressure dependent under near critical or supercritical conditions. k_{ISC} is expected to increase with temperature, because it will raise the vibrational energy of the absorbing molecules, and therefore could result in excited molecules being deposited in higher vibrational energy levels than at low temperatures. This would tend to increase the effective ISC rate, decrease the fluorescence yield,^{3,6} and increase the phosphorescence yield. However, the increase in phosphorescence yield could be opposed by enhanced quenching in an oxygen environment due to increased diffusion of gaseous oxygen into the acetone. While quenching of fluorescence by oxygen has been shown by many to be negligible at low pressures, oxygen diffusion may also effect the fluorescence yield at higher pressures due to oxygen-assisted intersystem crossing.^{6,7} Phosphorescence, however, has shown a much higher sensitivity to collisional quenching by oxygen; its lifetime and signal is reduced dramatically even in the presence of minute quantities of oxygen.

III. Experimental Setup

The planar laser-induced fluorescence and phosphorescence measurements are performed in a high pressure chamber. The chamber is made from a $5 \times 5 \times 20$ cm stainless steel block with a hollow cylindrical chamber 3.8×20 cm. The chamber can be pressurized up to 100 bar. The acetone used for the experiments goes through pressurization/depressurization cycles in a nitrogen environment for at least 24 hours prior to its entry into the test chamber to remove any dissolved oxygen within the liquid. A small electric heating unit allows the acetone temperature to be heated up to 650 K before entering the test section. A thermocouple is placed at the top of the test section to monitor the temperature of the acetone near the inlet of the chamber. A pressure gauge positioned near the bottom of the test chamber is used to monitor the pressure inside the chamber. Three fused silica quartz windows on three sides of the chamber provide the required optical access. The bottom of the chamber is connected to another high pressure and high volume vessel to hold the acetone after it passed through the chamber. A ball valve at the bottom of vessel is used to drain the acetone after each experiment.

The acetone liquid jet enters the chamber through a small opening, approximately 300 μm in diameter and is excited by a frequency-quadrupled Nd:YAG laser (266 nm). The maximum laser output power used here is approximately 25 mJ per pulse. The unfocused Nd:YAG laser beam first passes through three dichroic mirrors (see Figure 1) in order to decrease the amount of 532 nm light reaching the chamber. After the mirrors, the beam is

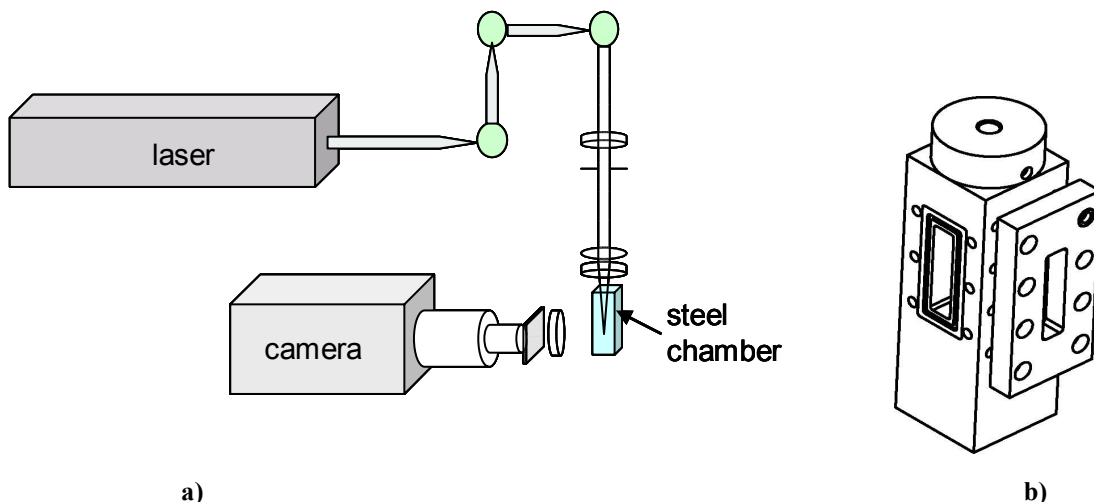


Figure 2. Experimental setup for acquiring liquid acetone PLIF imaging. a) full view of setup b) test section chamber.

collimated into a thin laser sheet with two cylindrical lenses and one spherical lenses. A set of knife edges are placed after the first cylindrical lens to further reduce the excess 532 nm light (which is slightly shifted in space from the 266 beam) and to remove the edges of the 266 nm beam, thus giving a more uniform energy profile in the laser sheet. The laser sheet is approximately 38 mm in height and 200 μm in thickness. The laser sheet passes through the windows of the steel chamber and is positioned so that it is parallel to the jet and intersects the center of the jet starting ~ 2 mm downstream of the jet exit and extending to ~ 40 mm downstream of the jet exit.

The laser-induced fluorescence and phosphorescence signal is collected by a UV-Nikkor (105 mm) lens and imaged onto an electronically cooled ICCD camera (Princeton PI-MAX ICCD). A Schott glass filter (WG 305) and a notch filter are used to remove light from wavelengths shorter than ~ 305 nm and from the 532 nm laser, respectively. Images are acquired with exposure times ranging from 50 ns to 100 μs and with time delays from zero (coincident with the laser pulse) to 300 ns. The data presented here are averages calculated from 100 images, which is intended to reduce the influence of any shot-to-shot fluctuations in the laser power or fluctuations in the jet.

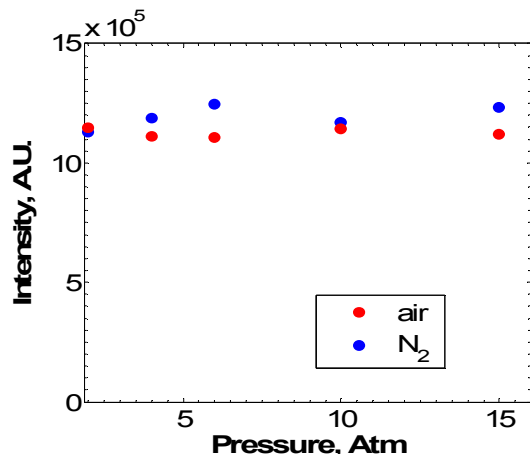


Figure 3. Intensity of liquid acetone fluorescence for varying pressure, with air and nitrogen co-flows.

IV. Results and Discussion

Acetone fluorescence and phosphorescence images were taken for pressures from 1 atm to 15 atm and with nitrogen and air co-flow at room temperature. The acetone fluorescence lifetime at varying pressure and co-flow was not measured due to the limited time-response of the intensifier; it could not gate fast enough to resolve the fluorescence decay, which in any case is less than the duration of the laser pulse. The intensity of the fluorescence signal was measured to determine the variation of the signal with respect to pressure (Figure 3). It can be concluded that the liquid acetone fluorescence signal is independent of pressure and flow conditions, as expected based on the model presented in the Background section.

The acetone phosphorescence average lifetimes and integrated intensity at varying pressure for both nitrogen and air co-flow are calculated and plotted in Figure 4 and Figure 5. Both values were calculated from a series of average images, each acquired with a 300 ns delay after the laser pulse and varying gate durations (with the maximum duration of 100 μs sufficient to temporally integrate all the phosphorescence emitted after a laser pulse). The intensity was then spatially averaged in each image over a region 2–3.5 mm from the jet exit. Finally, background acetone vapor phosphorescence, which becomes noticeable at long integration times for the nitrogen co-flow, was subtracted. The result, i.e., the temporally integrated signal as a function of integration time, is shown in Figure 6 for a pressure of 4 atm with an air co-flow. The phosphorescence lifetime is found by fitting the result to a single exponential decay equation. The phosphorescence lifetime in the nitrogen co-flow is approximately constant at 1 μs for the range of pressures tested. The liquid phosphorescence lifetime is much smaller than the value for acetone vapor, $\sim 200 \mu\text{s}$.⁸ A possible reason for the short lifetime of liquid phosphorescence is self-quenching.

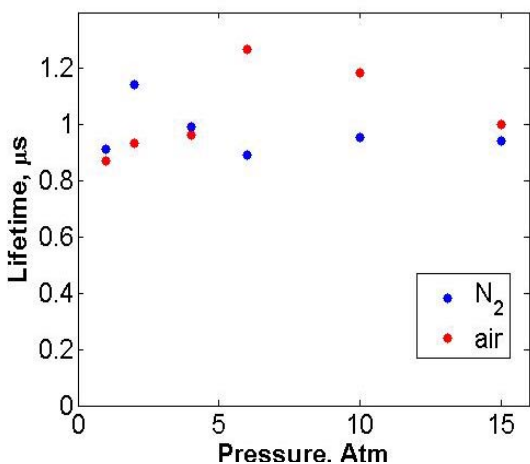


Figure 4. Liquid acetone phosphorescence lifetime for varying pressure, with air and nitrogen co-flows.

Lozano estimated that the phosphorescence self-quenching rate constant for acetone vapor as $1.2 \times 10^7 \text{ L}/(\text{mol s})$. For acetone at room temperature, the concentration of liquid acetone is approximately 0.013 mol/L. For the same self-quenching rate, the self-quenching lifetime for the liquid at its higher density would be 6.2 μs . This suggests either the self-quenching rate constant for liquid acetone is greater than for vapor, or it reflects the uncertainty in Lozano's estimate. The phosphorescence lifetimes measured with air co-flow are also constant at $\sim 1 \mu\text{s}$, however, there is a slightly higher variation in the values compare to the nitrogen co-flow cases. This fluctuation in the values could be due to differences in the co-flow velocities that result in changes in the jet steadiness or the lower signals observed in the air case (see below). The similar lifetimes for both N_2 and air environments suggest that little O_2 has had a chance to diffuse into the liquid jet at the region close to the jet exit (2-3.5 mm) used to determine the lifetime.

This variation in phosphorescence intensity between the nitrogen and air cases can be seen in Figure 5. The total intensity for the nitrogen seems invariant to the pressure. However, there is some fluctuation in the data. This could be caused variations in the liquid jet with pressure. The total phosphorescence intensity for the air co-flow seems to have a systematic variation with pressure. It is nearly constant from 1 atm to 4 atm, then drops to a new value for the 5-15 atm tests. Again, this behavior may be due to some systematic change in the facility as pressure is changed, rather than the photophysics of the acetone. The results also show the air phosphorescence to be consistently less than the N_2 results (by about 30-40%). While O_2 quenching of the phosphorescence is one possibility, the similarity of the lifetime measurements for air and N_2 co-flows makes this unlikely.

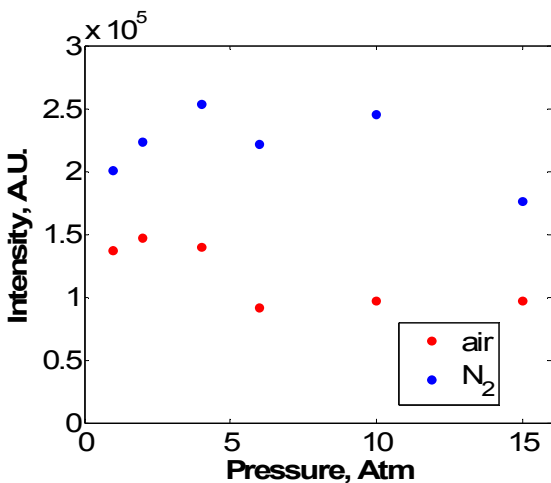


Figure 5. Total intensity of phosphorescence at different pressures.

Figure 7 shows phosphorescence images taken with a 10 μs gate 300 ns after the laser pulse. As seen in the two images, the signal from the nitrogen co-flow is higher and almost constant along the length of the stream, whereas, the signal from the air co-flow is less bright and is diminishing as it moves along the stream. A point to note, the signal for both the nitrogen and air co-flow is the same at the beginning of the jet. The reduction in the intensity of the air co-flow downstream is likely due to the presence of oxygen in the air. The effective quenching lifetime can be approximate from Eq. 3,^{9,10} where t_0 is the phosphorescence lifetime without oxygen, r_Q is the oxygen quenching rate constant [$\text{L}/(\text{mol s})$], and c_Q is the oxygen concentration [L/mol]. Assuming that the quenching rate is limited by the

diffusion of oxygen within the liquid, the Debye equation^{9,12} can be used to approximate the value for the quenching rate constant, r_Q . The Debye equation gives an approximate diffusion rate of a dilute solute within a solvent as a function of the temperature of the solution and the viscosity of the solvent. For example, the quenching rate calculated from the work of Bortolus *et al.*¹⁰ is found to be within 5 percent of the value calculated from the Debye equation.

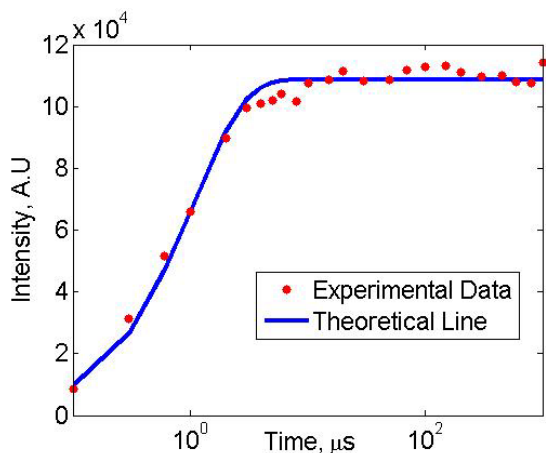


Figure 6. Phosphorescence lifetime calculation. The experimental data show a single exponential for the phosphorescence lifetime. Data are for 4 atm with air co-flow. Lifetime calculated is 0.965 μ s

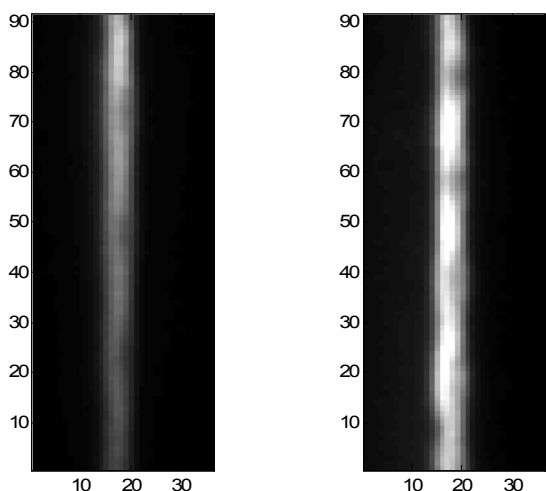


Figure 7. Phosphorescence intensity variation for air and nitrogen co-flow. Images of acetone phosphorescence for nitrogen (right) and air (left) co-flow taken with a 10 μ s gate and 300 ns after the laser pulse at 4 atm at 2mm after the jet exit. The size of the image is 4.5 mm \times 1.5 mm.

Preliminary data of laser-induced fluorescence was taken for preheated liquid acetone at 35° C and 1 atm. These initial result shows that the fluorescence intensity is approximately 20% lower than for liquid acetone at room temperature. However, questions remain about the effect of the temperature increase on the liquid jet (such as viscosity changes effecting jet stability).

$$\frac{1}{t} = \frac{1}{t_0} + r_Q C_Q \quad \text{Equation 3}$$

$$\frac{I_0}{I} = 1 + r_Q t_0 C_Q \quad \text{Equation 4}$$

The Stern-Volmer equation^{11,12} (Eq. 4) can be used to estimate the concentration of oxygen along the jet, given the ratio of the intensity I at any point to the intensity close to the jet exit (I_0). Figure 8 gives the estimated concentration of oxygen as a function of the distance downstream of the jet exit. The highest concentration of oxygen seen by the acetone jet in the location of interest is around 7×10^{-5} M. This concentration is smaller than the aerated concentration of oxygen (equilibrium/saturation in an air environment) in liquid acetone at room temperature, approximately 1×10^{-3} M.¹³ Thus the estimated values are at least two orders of magnitude less than the saturated levels expected at 4 atm.

The phosphorescence to fluorescence ratio (P/F) for liquid acetone was also calculated. It was found to be approximately 0.012 for the nitrogen co-flow. Comparing to the vapor value, approximately 9,⁸ the liquid ratio is 750 times smaller. Since the phosphorescence lifetime was roughly 200 times shorter for the liquid, most but not all of this change can be attributed to self-quenching of acetone phosphorescence.

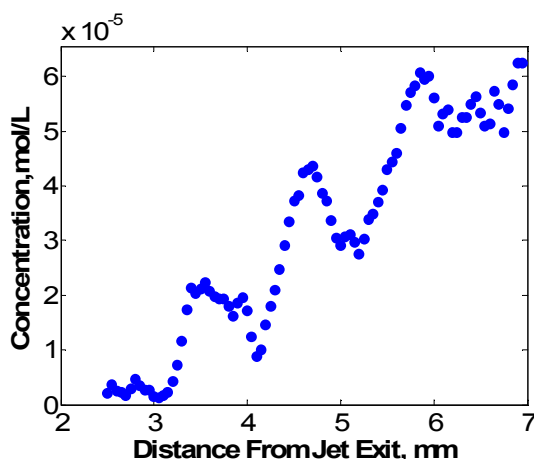


Figure 8. Concentration of oxygen as a function of distance downstream of the jet exit. Intensity is calculated from images taken with 10 μ s gate at 4 atm pressurization.

V. Summary

Planar laser-induced fluorescence and phosphorescence of liquid acetone at pressures of 1-15 atm and room temperature were characterized for both oxygen-free (nitrogen) and oxygenated (air) environments. It was found that the liquid fluorescence intensity was independent of pressure and oxygen environment as expected. In addition, the phosphorescence lifetime was shown to be invariant with pressure and flow conditions when O₂ is not present. The “oxygen-free” lifetime was found to be 1 μs. This is much less than the oxygen-free lifetime for acetone vapor, 200 μs, and is attributed to self-quenching by acetone. The total phosphorescence intensity was found to be lower for an air co-flow compared to a nitrogen co-flow, even though the lifetime remained the same. The reason for this is currently unclear. The diffusion of oxygen into the liquid was observed when air is present in the co-flow, but at a relatively low rate. The phosphorescence to fluorescence ratio for liquid acetone was measured to be 0.012. This is 750 times smaller than the ratio for vapor acetone. This reduction in ratio is not completely accounted for by the reduced phosphorescence lifetime, and suggests a difference in either the intersystem crossing rate for liquid versus vapor acetone, a difference in the vibrational relaxation rates, or possibly other transfer rates out of the S₁ state.

Acknowledgements

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