Measurements of Liquid Acetone Fluorescence and Phosphorescence for Two-Phase Fuel Imaging

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The fluorescence and phosphorescence from liquid acetone was studied to aid the development of quantitative mixing measurements in liquid-fueled systems. The time-resolved spectrum of the acetone fluorescence and phosphorescence was captured under typical operating conditions using two excitation wavelengths (266 and 285 nm). A chamber of liquid acetone was purged and pressurized with nitrogen gas for various durations before the measurements. The lifetime for phosphorescence from liquid acetone was found to vary from <175 ns to 3.5 µs, depending on the duration of the N₂ pressurization, the detection wavelength and the excitation wavelength. The N₂ pressurization presumably removes dissolved O₂ and shows little enhancement in the overall lifetime beyond 24 hours in the current setup. The measured phosphorescence lifetimes increased with detection wavelength, which is related to the observed red shift in the phosphorescence spectra with delay time after the laser pulse. The phosphorescence to fluorescence ratio was measured to be 0.035 for 266 nm excitation and 0.080 for 285 nm excitation. The overall short lifetimes and low phosphorescence signal are related to the vibrational distribution established in the triplet state for the different excitation wavelengths.

I. Motivation

Advances in quantitative, two-phase, fuel concentration measurements would greatly aid improvements in the design and performance of liquid-fueled combustors by increasing our understanding of fuel-air mixing. This in turn would lead to reductions in combustor size, decreases in harmful pollutant emissions and improvements in combustor stability. Planar laser induced fluorescence (PLIF) is a non-intrusive measurement technique that provides two-dimensional distributions of a large range of flowfield parameters. For example, PLIF has been successfully used to measure gaseous and liquid species concentrations, velocities, densities, pressure, and temperature.¹ For gaseous fuel-air mixing studies, PLIF of acetone vapor is well-documented.²⁻⁴ Acetone is advantageous for mixing measurements with PLIF because of its linear relationship between the fluorescence intensity, vapor acetone concentration and laser power in an isobaric and isothermal environment. It absorbs in the range of 225 nm to 320 nm and emits in the range 350 nm to 550 nm. Since the absorption spectrum and the emission spectrum do not overlap, it is easy to filter scattered laser light from the detector through use of a long pass filter. In addition, acetone can be purchases commercially and is inexpensive, and it is also relatively safe to work with, when compare to other illuminating tracers.¹⁻⁵

For liquid-fueled combustors, however, it is important to measure the distribution of both the liquid and evaporated fuel, and there is less information available about the laser-induced emissions from liquid acetone in combustion flows. Thus to extend the quantitative acetone PLIF technique to two-phase flows, basic studies of liquid acetone photophysics are required. For example, the signal in vapor acetone-air mixtures comes from fluorescence, since the acetone phosphorescence is efficiently quenched in the presence of oxygen.² From PLIF images of acetone sprays, however, there is evidence that phosphorescence can also contribute to the signal for liquid (droplets) under some conditions, e.g., when the liquid supply is pressurized by N₂.⁵ Also, depending on the droplet size, the signal may not be a linear function of fuel concentration above a critical size due to the high level of absorption by liquid acetone.⁶ Therefore the focus of this paper is basic characterization of acetone liquid photophysics.

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II. Background

In PLIF, a laser sheet is used to excite a specific chemical species, either naturally occurring or seeded in the flow. In most cases, the molecule is excited to a higher lying electronic state. Once it is in this higher energy state, the molecule can lose the excess electronic energy through a variety of possible processes, including dissociation, spontaneous emission, collisional quenching, and internal conversion (intersystem crossing). For acetone, spontaneous emission from the initially excited singlet electronic level is the source of the fluorescence signal, which is characterized by short lifetimes. The lifetime of the fluorescence depends primarily upon the efficiency of the intersystem crossing to the triplet state. The intensity of the fluorescence can be used to calculate the concentration of the acetone. Quantitative data is obtained by relating the signal from the fluorescence to the number density of the acetone molecules. A relation between the fluorescence intensity and the number density is given by Eq. (1),

\[ S_c(x, y) - S_b(x, y) = G \eta_{coll} f(T) N_{acetone} \eta_f I(x, y) \]

where \( S_c(x,y) \) is the measured signal intensity as a function of the individual pixel location and \( S_b(x,y) \) is the background signal, which has to be subtracted from the actual image to obtain the fluorescence signal. On the right of the equation are the factors that would determine the intensity of the fluorescence signal: \( G \) is the gain or responsivity of the imaging detector, \( \eta_{coll} \) is the efficiency of the collection optics, \( I(x,y) \) is the local laser intensity, \( f(T) \) is the population distribution function, which depends on temperature \( T \), \( \eta_f \) is the fluorescence quantum yield, and \( N_{acetone} \) is the acetone number density.

Acetone phosphorescence occurs when the excited molecule goes through a intersystem crossing to the triplet state. Once their, the electronic energy can be lost through most of the processes described above. Since transitions from the triplet state back to the ground (singlet) electronic state are dipole unallowed, the spontaneous emission from the triplet state has a much longer lifetime, and is therefore called phosphorescence. For acetone vapor, the phosphorescence signal is typically negligible, because it is efficiently quenched by even small amount of oxygen vapor. As noted above, however, phosphorescence from liquid acetone sprays in air has been observed.

There is some information in the literature concerning liquid acetone photophysics. For example, the lifetime of liquid acetone phosphorescence has been found by some researchers to be approximately 1 µs, while others give a much greater value of ~30 µs. (For comparison, the reported vapor acetone phosphorescence lifetime is roughly 200 µs.) These measurements were obtained for liquid acetone under conditions unlike those that would be expected in typical fuel-air mixing PLIF measurements. For example, the light sources used for one reference is a N₂ laser with emission wavelength of 337 nm, while another reference used a stroboscopic flashlamp. Also, the acetone was prepared using cycles of freeze-pump-thaw to degas the liquid in some studies. One previous study examined liquid acetone phosphorescence with 266 nm laser excitation; the liquid acetone was held in a quartz cuvette and a lifetime of ~39 µs was reported.

III. Experimental Details

Initially, the experimental setup of the previous 266 nm study was repeated. However, it was eventually determined that the long lived emissions were dominated by light from the cuvette itself, with a lifetime of ~35 µs measured even when nonemitting liquids were tested. Thus, a different experimental setup was chosen to measure the liquid acetone properties. This experimental arrangement is shown in Figure 1. A steady stream of acetone is formed by allowing it to flow out from a tube with an inner diameter of 1.0 mm. The acetone is purged and pressurized with nitrogen gas in a pressure vessel at ~790 kPa (100 psig) for various time intervals before the measurement. The pressure vessel is directly connected to the tube to prevent exposure to the atmosphere. The acetone flow rate is adjusted through a combination of valves, with a flow rate of ~1.5 ml/sec for the current measurements. This flow rate is slow enough to produces a continuous liquid jet, but fast enough to minimize diffusion of air into the liquid.

The acetone emission is excited by one of two laser sources. The first is a frequency-quadrupled Nd:YAG laser at 266 nm. The laser beam is first reflected from two 266 nm dichroic mirrors to reduce the 532 nm content within the beam. Subsequently, a set of cylindrical lenses is used to form the laser beam into a thin sheet approximately 300 µm thick and 20 mm tall. A double knife edge is positioned downstream to cut off the top and bottom edges of the sheet, thus reducing the fluence variation along the sheet. The nominal laser energy of the sheet after the aperture is approximately 7 mJ/pulse. The second laser source is a pulsed dye laser, pumped by a 532 nm beam from a Nd:YAG laser, and operating with rhodamine 6G dye at 570 nm. The output of the dye laser is then directed to a
frequency doubling crystal (BBO) to produce a 285 nm output beam. In this case, the two 532 nm dichroic mirrors are replaced by two broadband uv dichroic mirrors to reduce the intensity of the 570 nm radiation within the beam. The laser energy after the aperture for this laser is around 6 mJ/pulse. In order to compensate for the reduction in the energy within the sheet, the height of the sheet is reduced to 15 mm.

The laser-induced emission from the acetone stream is detected two ways: imaged directly onto an intensified CCD camera (PI-MAX ICCD) or indirectly on the same ICCD mounted on an imaging spectrometer. In both cases, a Schott glass filter (WG 305) is used to filter out any light from wavelengths shorter than ~305 nm. For the direct imaging experiments, the acetone emissions are collected by a UV-Nikkor (105 mm) lens mounted on the ICCD. For the spectrally resolved measurements, the light is collected with a fused-silica fiber optic probe. The fiber output is incident on the imaging spectrometer (Acton SP-300i), operating with a 300 grooves/mm grating. The relative spectral responsivity of the detection system (fiber optic, spectrometer, and ICCD) at a fixed grating angle was measured with a tungsten halogen lamp. In addition, the imaging spectrometer is subject to nonuniform response due to variations in effective solid angle across the ICCD. This alters the effective responsivity of the system as the grating angle is varied. This variation was determined by acquiring spectra from a monochromatic light source (HeNe laser) at various grating angles. Thus the relative spectral responsivity was determined for any grating angle and used to correct the acquired spectra.

For the results presented here, each spectrum is an accumulation of 300 laser shots. This is intended to reduce the influence of any shot-to-shot fluctuations in the laser power and to improve the signal-to-noise ratio of the measurements. To measure the time-dependent behavior of the acetone emission, the intensifier gate duration is varied from 300 ns to 10 µs, and the intensifier gate is delayed from 0-80 µs after the laser pulse. The minimum gate duration (300 ns) is limited by the ~100 ns time response of the 25 mm intensifier.

IV. Results and Discussion

Figure 2 shows a typical image of the liquid stream. The liquid acetone forms a continuous, stable jet under the chosen operating conditions. The laser-induced emission is primarily from a thin region at the edge of the stream where the laser sheet is incident (left side). The laser sheet energy is rapidly absorbed by the liquid acetone, which has an optical depth of tens of micrometers. Laser-excited images were initially acquired of the liquid stream with unprepared acetone, i.e., the acetone used was directly from the shipping container, with no nitrogen purging/pressurization. A strong prompt fluorescence signal was seen concurrent with the laser pulse. With a delay of 200 ns after the laser pulse, there is little signal from the acetone. Example images (acquired with a 300 ns gate) are shown in Figure 3. It also shows images of vapor acetone taken for comparison. The prompt fluorescence signal for the vapor can be seen very clearly but there is no long lived signal after the laser pulse. Two delayed images of the liquid jet are included: one for unprepared acetone and the other for acetone that was purged and pressurized for 24 hours before the experiment. The prepared acetone sample shows a much stronger delayed (phosphorescence) signal. The nitrogen preparation appears to remove dissolved oxygen from the liquid acetone, since oxygen efficiently de-excites the acetone triplet state.
Spectrally resolved measurements of the acetone emission were obtained with the gated spectrometer for different preparation times. Background images were also acquired and subtracted from the data. The spectrometer outputs was then corrected for the system’s spectral response, as indicated in the description of the experiment, and are presented below as relative spectral photon densities. Figure 4 presents results for 266 nm excitation and 24 hours of nitrogen purging/pressurization, while Figure 5 shows spectra for 285 nm excitation. For ease of comparison, all the results are normalized to have the same maximum peak intensity.

The (prompt) fluorescence with 266 nm excitation extends from 300 nm to ~600 nm (beyond the range of the current measurements), with a peak around 405 nm. This is the same as the reported value, which did not vary with the reported excitation wavelength.2,14 The fluorescence spectrum for 285 nm excitation has about the same range, though extending slightly farther in the red, and thus with a peak slightly higher, around 415 nm.

The longer lived phosphorescence spectra cover a range somewhat similar to the fluorescence. However, there is a noticeable red-shift in the spectrum over time. For short delays, the emission is blue-shifted with respect to the fluorescence, with a peak below 400 nm. For 266 nm excitation, the phosphorescence peaks shifts to 430 nm after ~2 µs. For 285 nm excitation, the peak shifts even farther, to ~460 nm. The peak wavelength for the longer delays is close to the previously reported value (440 nm) for liquid acetone phosphorescence.7 The fact that the phosphorescence develops over time has also been suggested.7 Figures 4 and Figure 5 clearly show the
difference in the short delay phosphorescence between 266 and 285 nm excitation, with more red content for 266 nm excitation. The effect of excitation wavelength on the fluorescence and long delay phosphorescence is more clearly seen in the direct comparison of Figure 6. The fluorescence distribution is nearly the same for the 266 and 285 nm excitation. There is a more noticeable shift in the phosphorescence, with more red content now for 285 nm excitation.

Figure 6. Excitation wavelength comparison of spectra. Spectrums for prompt and 2.3 µs delayed signals for two excitation wavelengths.

Long exposure (integrated) spectra were also taken to determine the relative intensity of the liquid acetone phosphorescence compared to the fluorescence for 266 nm excitation. The phosphorescence data were acquired with a 100 ns gate delay after the laser pulse to reject the fluorescence signal. The prompt signal was measured with a 300 ns intensifier gate width starting 100 ns before the laser pulse, effectively producing a 200 ns long gate. Thus the prompt signal contains both fluorescence and some fraction of the phosphorescence. Figure 7 shows the prompt and integrated phosphorescence spectra, with the phosphorescence accurately scaled with respect to the prompt signal. The prompt signal is clearly much larger. Integrating the two spectra results in a phosphorescence to fluorescence ratio for 266 nm excitation of 0.035. For 285 nm excitation, the ratio is 0.08. The relatively lower signal from the integrated phosphorescence would suggest that there is little phosphorescence contamination in the prompt signal. Assuming that the fluorescence lifetime is close to the reported value (<5 ns), the delayed signal is too strong be attributed in any part to fluorescence (the integrated fluorescence would be at least 7 orders of magnitude below the measured phosphorescence intensity over the delayed integration period). The increase in phosphorescence/fluorescence ratio with excitation wavelength is reasonable. Copeland and Crosley report that the vibrationally excited triplet emission has a maximum signal intensity when acetone is excited at ~313 nm, which is well above the peak of the absorption spectra (~280-290 nm).

The effect of nitrogen purging/pressurization on the acetone phosphorescence is shown in Figure 8. Results are shown for spectrally integrated signals for various preparation times and for the two excitation wavelengths. The data were obtained from direct
imaging, which provides higher signal levels than the spectrometer system. Thus these results have not been corrected for the spectral responsivity of the ICCD. The curves are calculated fits to the signals measured at different delays and gate durations. For no preparation (0 hrs), there is a very rapid decrease in the emission. When the preparation time is increased to 12 hours, there is a significant increase in the phosphorescence intensity, or equivalently a longer phosphorescence lifetime. Doubling the time to 24 hours of pressurization/purging continues to show a significant increase in the lifetime. Nearly doubling the time again (to 45 hours) produces only a minor increase in lifetime, suggesting we have nearly achieved the asymptotic (O2 free) phosphorescence lifetime. Comparing data between the two excitation wavelengths shows a small increase in the spectrally integrated, phosphorescence lifetime for longer wavelength excitation. Table 1 lists the lifetime calculated from curves of Figure 8; the maximum lifetime appears to be ~1 µs, with a 125 ns increase for 285 versus 266 nm excitation.

The lifetime reported here compares well with the values determined by Bogan and Lee,4 roughly 1 µs, and Wilkinson and Dubois,9 ~400 ns. It is quite different than the ~30 µs lifetime proposed by Bortolus et al.13 and Pischel and Nau.14 The difference between the current lifetime and the latter two studies may be attributable to the conditions under which the data were taken, e.g., acetone preparation, temperature or excitation wavelength. As noted previously, phosphorescence follows after the laser excited acetone undergoes an intersystem crossing from the first singlet state, S1, to the first triplet state, T1. There are many vibrational modes that can be accessed in the T1 state, and each would have a different lifetime.16,17 The previously measured 30 µs acetone phosphorescence lifetime was from a vibrationally hot triplet level measured using an excitation wavelength of 336 nm.12,16 For the much shorter laser wavelengths used here, it is reasonable to assume that the eventual distribution in the T1 state

### Table 1. Lifetime of acetone for various purging times at 266 nm and 285 nm excitation.

<table>
<thead>
<tr>
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<th>0 hours</th>
<th>12 hours</th>
<th>24 hours</th>
<th>45 hours</th>
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<tr>
<td>266 nm</td>
<td>&lt;175 ns</td>
<td>575 ±150 ns</td>
<td>900 ±150 ns</td>
<td>975 ±150 ns</td>
</tr>
<tr>
<td>285 nm</td>
<td></td>
<td>950 ±150 ns</td>
<td>1100 ±150 ns</td>
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Figure 9. Decay of individual wavelengths. Decay curve of specific wavelengths for 24 hours purging and both excitation wavelength.
would be different, leading to a change in the measured lifetime. This is partially substantiated by the difference in the 266 and 285 nm excitation lifetimes, and by the difference in the phosphorescence distributions (Figures 4-6) for the two cases. (For comparison, the accepted, oxygen-free phosphorescence lifetime of acetone vapor is ~200 µs,5,7 and is attributed to emission from the thermal, vibrationally relaxed triplet state.10,12)

The variation of the lifetime due to upper state distribution changes is also evidenced in the spectrally resolved phosphorescence decays, shown in Figure 9 for a few detection wavelengths and both excitation wavelengths. Also shown is a best fit (single) exponential curve for each data set. Note that the data for 266 nm excitation at early times appears to decay at a different rate. This multi-exponential behavior would be expected as the T1 vibrational population redistributes. The lifetimes (time constants) from these fits are listed in Table 2 for a few wavelengths, and plotted for a wide range of detection wavelengths in Figure 10. These results clearly show the dependence of the lifetime on detection wavelength. The lifetimes steadily increase from ~500-650 ns at 350 nm to ~1-3.5 µs at 520 nm. The lifetimes shown for wavelengths higher than 500 nm are less accurate due to the lower measured signals in this region and its proximity to the edge of the detector for the grating angle used. These values bracket the spectral lifetime shown in Table 1 (which were determined from the camera images). The short wavelength lifetimes are less than the integrated result, while long wavelength lifetimes are higher. Note, the lifetimes for 45 hour purging in Figure 10 are in many cases higher than the spectrally integrated values of Table 1. In part, this is because the integrated lifetime is weighted towards the peak region of the phosphorescence spectrum (400-415 nm). The results shown in Figure 10 also verify the earlier finding that the phosphorescence lifetime depends on the excitation wavelength. For most detection wavelengths, 266 nm excitation produces longer lifetimes compare to 285 nm excitation, though this inverts above ~500 nm. One reason for the red shift of the spectrum at long delays described above is quite noticeable in the 45 hour, 285 nm excitation case. The long lifetimes around 500 nm will eventually weight the spectrum to long wavelengths at long delay times.

<table>
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<tr>
<th>Detection Wavelength (nm)</th>
<th>Lifetime (ns)</th>
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<tr>
<td>350</td>
<td>450±70</td>
</tr>
<tr>
<td>400</td>
<td>1000±70</td>
</tr>
<tr>
<td>450</td>
<td>450±70</td>
</tr>
<tr>
<td>500</td>
<td>1100±70</td>
</tr>
</tbody>
</table>

Table 2. Phosphorescence lifetimes at selected detection wavelengths and both excitation wavelengths for acetone prepared for 24hrs.

Figure 10. Spectrally resolved phosphorescence lifetimes. Acetone lifetimes at different wavelengths for three cases: 24hr purging with 266 nm excitation, 24 hr purging at 285 nm, and 45 hr purging at 285 nm

V. Summary

Temporally and spectrally resolved measurements of laser-induced fluorescence and phosphorescence from liquid acetone were obtained at two laser excitation wavelengths. The experiments were performed in a stable jet of liquid acetone. The fluorescence spectra are in good agreement with previously published data. Unprepared liquid acetone shows little phosphorescence. Purging and then pressurizing with N$_2$ in a closed vessel for extended times increases the phosphorescence signal, presumably be removing dissolved O$_2$. After 24 hours of pressurization at 100 psig, there was little increase in the phosphorescence signal. While the time-integrated phosphorescence spectrum is quite similar (though slightly red-shifted) to the fluorescence spectrum, the time-resolved phosphorescence spectra show a gradual red-shift in time. In fact for short delays, the phosphorescence is blue shifted with respect to the fluorescence. The spectrally integrated, maximum lifetime for phosphorescence was found to be around 1 µs when sufficient time was allowed for N$_2$ pressurization, with a slight dependence on laser excitation wavelength (longer lifetimes for a longer excitation wavelength).

The phosphorescence lifetime also showed a dependence on detection wavelength, with longer lifetimes at longer wavelengths. This partly explains the red shift in the phosphorescence signal with time. These spectrally resolved lifetimes exhibit an interesting dependence on laser wavelength. For short detection wavelengths, 266 nm
excitation produces longer lifetimes, while 285 nm excitation produces longer lifetimes at long detection wavelengths. The phosphorescence to fluorescence ratio was measured to be 0.035 for 266 nm excitation and 0.080 for 285 nm excitation. The overall short lifetimes and low phosphorescence signal are related to the vibrational distribution established in the triplet state for the different excitation wavelengths. The lifetime, signal level and red-shift of the time-integrated phosphorescence are expected to increase with longer wavelength excitation. Thus if improved phosphorescence signals are desired from liquid acetone in fuel mixing studies, there may be an advantage to laser pumping at long wavelengths (e.g., 320-340 nm).

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References


