46th AIAA Aerospace Sciences Meeting and Exhibit
7 - 10 January 2008, Reno, Nevada

AIAA 2008-264

Acetone Photophysics at Near Critical to Supercritical Conditions

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The photophysics of vapor and liquid acetone are experimentally examined from subcritical to supercritical conditions with 266 nm excitation, motivated by an interest in using acetone to study transcritical fuel injection and mixing. The fluorescence quantum yield for acetone vapor is measured, and the values are compared to the models of Thurber and Braeuer. The measured fluorescence yields are found to be similar to the model predictions. In addition, the two models are found to converge as the excitation wavelength or pressure increases. For 266 nm excitation, the difference between the model predictions is approximately 2% for pressures above 30 atm. Liquid acetone fluorescence and phosphorescence data are obtained at various pressures and temperatures. The liquid fluorescence signals do not change with pressure and temperature. In addition, liquid fluorescence is not affected by oxygen quenching, as compared to vapor fluorescence. It was found that the oxygen saturation concentration in liquid acetone is extremely small compared to the concentration needed to affect the fluorescence signal. The liquid phosphorescence is also found to be invariant with pressure, but it decreases exponentially as the temperature of the liquid is raised. A corresponding decrease in the measured phosphorescence lifetimes indicates that the phosphorescence yield is reduced asymptotically with temperature, with little change above ~375 K. This is likely due to acetone-acetone quenching of the excited triplet state. Most of the liquid acetone photophysics can be explained as a high density limit of the vapor photophysics models.

I. Introduction

In many practical combustion devices, such as liquid rocket or aircraft engines, liquid (nonprevaporized) propellant is injected into the combustion chamber and mixed with oxidizer before burning. Most of these devices operate at high pressure and temperature conditions. To better understand the breakup and mixing mechanism of liquid fuels, it is important to properly simulate these conditions. For example, as the fluids approach their critical state, their properties changes greatly. Similarly at supercritical pressures, ambient heating of a fuel jet does not induce 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, e.g., jet breakup and eventual mixing of fuel and oxidizer.

The current research project is motivated by an interest in understanding the breakup and mixing properties of transcritical and supercritical fuel injectors. A technique is needed in order to visualize and quantify the mixing process, including the transition process from liquid-like to vapor-like behavior of a supercritical fluid. Planar laser-induced fluorescence (PLIF) is chosen because it is a non-invasive measurement technique that can provide qualitative as well as quantitative flowfield information.[1] In this approach, a laser beam is used to excite a specific species to a higher energy state, thereby causing these molecules to fluoresce. The fluorescence intensity is proportional to the concentration of the excited species, which can be interpreted, for example, as a measure of the mixing in the flowfield. The good spatial and temporal resolution provided by PLIF makes it an important tool among combustion 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 chosen as our fuel surrogate because it has been shown in the literature to be a good tracer for mixing measurements using PLIF; for vapor acetone, there is a linear relationship between the fluorescence intensity and acetone concentration in an isobaric and isothermal environment.[2] Vapor acetone photophysics at low pressure

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are reasonably well understood, allowing researchers to use acetone PLIF to measure properties such as concentration and temperature.[3,4] However, the photophysics of acetone vapor at high pressure, as well as liquid acetone photophysics, has not been sufficiently examined. Thus, this paper is aimed toward determining the photophysics of acetone under these conditions.

II. Acetone Photophysics Background

A simplified model of acetone photophysics, based on the low pressure studies, 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.[5] The radiative process is denoted fluorescence. The non-radiative processes include: vibration relaxation (VR), intersystem crossing (ISC), and collisional quenching (Q). Intersystem crossing involves transfer of energy from S_1 to the first excited triplet state (T_1). 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.

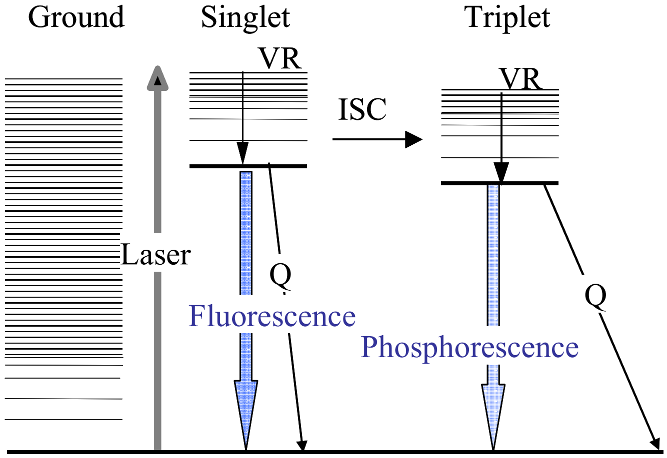


Figure 1. *Simplified model for acetone PLIF*

Many studies have focused on the vapor phase of acetone PLIF.[6-8] An important parameter for characterizing PLIF signals is the fluorescence yield (ϕ_{fl}). For example in the linear excitation regime,[1] the fluorescence signal S_{fl} is given by

$$S_{fl} = C_{\det}\alpha E_{las}\phi_{fl} \tag{1}$$

where C_{det} is a constant that depends on the detection system, α is the absorption coefficient, and E_{las} is the laser pulse energy. The fluorescence yield for acetone vapor has been modeled by Thurber and Hanson.[6] They validated the model for various excitation wavelengths up to 900 K at atmospheric pressure and up to 13 atm for room temperature acetone. The model was later modified by Braeuer *et al.*, who validated it for 248 nm excitation up to 20 atm and 700 K. In these models, the fluorescence yield is determined from eq. (2),

$$\begin{aligned}\phi_{fl} = \frac{k_f}{k_f + k_{coll} + k_{NR,1}} &+ \sum_{i=2}^{N-1}\left(\frac{k_f}{k_f + k_{coll} + k_{NR,i}}\prod_{j=1}^{i-1}\left[\frac{k_{coll}}{k_f + k_{coll} + k_{NR,j}}\right]\right) \\ &+ \frac{k_f}{k_f + k_{NR,N}}\prod_{j=1}^{N-1}\left[\frac{k_{coll}}{k_f + k_{coll} + k_{NR,j}}\right]\end{aligned} \tag{2}$$

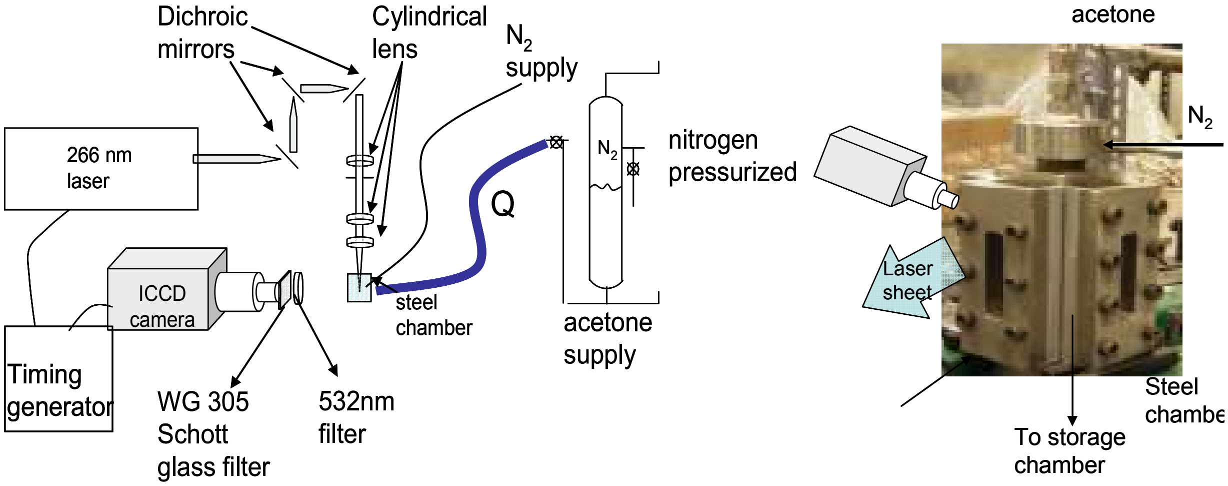
which is the summation of the fluorescence yield from each of the vibrational energy levels in the first excited singlet state. In the equation, k_f is the fluorescence rate, k_{coll} is the collision rate, and k_{NR} is the intersystem crossing rate. The collision rate is used to determine the vibration relaxation rate. The first term of the equation represents the fluorescence yield of the initially excited state. The second term is the fluorescence yield for the vibrational energy levels between the initially excited state and the thermalized state, e.g., the lowest vibrational energy level in the singlet state. It is the product of the probability that the molecule will fluoresce and the probability that the molecules will vibrationally decay to that level before undergoing intersystem crossing to the first excited triplet state. The last term is the fluorescence yield for the thermalized level. In the model, the fluorescence rate is assumed to be a known constant, while the collision and intersystem crossing rate are modeled. The model does not directly address acetone vapor phosphorescence, since it is quickly quenched when mixed with air.

Less attention has been given to the photophysics of the liquid phase**.** For liquid acetone, much like the vapor phase, the acetone signal is a combination of fluorescence and phosphorescence. It has been shown that the phosphorescence lifetime and signal of liquid acetone are reduced dramatically in the presence of even minute quantities of oxygen, while the fluorescence remains constant.[8,9] However unlike a vapor jet of acetone, a liquid acetone stream injected into an air environment can produce a phosphorescence signal, as the diffusion rate of oxygen into liquid acetone is much slower compare to vapor acetone. Thus, the phosphorescence signal or lack thereof can be used to delineate the interface between the “liquid-like” (less diffusive) fluid and the “vapor-like” (highly diffusive) fluid.

Therefore, 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 at those conditions. In the present paper, we examine near-critical liquid and critical vapor acetone photophysics, including intensity variation as a function of temperature and pressure and also how to differentiate between sub- and super-critical fluids.

III. Experimental Setup

The laser-induced fluorescence and phosphorescence measurements are performed in a high pressure chamber (Figure 2). It is made from a 5×5×20 cm^3 stainless steel block containing a hollow cylindrical chamber 3.8 cm in diameter and 20 cm long. The chamber can be pressurized up to 100 atm. The acetone used for the experiments goes through pressurization/depressurization cycles in a nitrogen environment prior to its entry into the chamber in order to remove any dissolved oxygen. A small electric heating unit allows the acetone temperature to be raised to as high as 650 K before it enters the test section. A thermocouple is placed at the top of the test section to monitor the temperature. A pressure gauge at the bottom of the test chamber monitors the pressure inside the chamber. Fused silica windows on three sides of the chamber provide the required optical access.



a) **b)**

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

For the liquid experiments, the acetone enters the test chamber through a 0.625 cm tube with a 300 µm orifice at the end of the tube. For the vapor experiments, an acetone-nitrogen mixture is injected through a 0.625 cm tube into a 0.8×0.8 cm^2 square quartz tube. The quartz tube is used to maintain a constant acetone concentration within the test chamber and prevents mixing with recirculating gases in order to measure the fluorescence yield. In both experiments, a nitrogen co-flow is used to reduce the excess vapor acetone surrounding the acetone stream, thereby minimizing any laser absorption between the incident window and the stream.

The acetone molecules are excited by a frequency-quadrupled Nd:YAG laser at 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 2) to decrease the amount of 532 nm light reaching the chamber. After the mirrors, the beam is collimated into a laser sheet with two cylindrical lenses and one spherical lenses, and it passes through the windows of the steel chamber to the stream of acetone. The laser-induced fluorescence and phosphorescence signal is collected by a 55mm Nikon lens and imaged onto an electronically cooled ICCD camera. A Schott glass filter (WG 305) removes any light from wavelengths shorter than ~305 nm, and a 532 nm holographic notch filter is used to remove any scattered 2nd harmonic laser light. Fluorescence images are acquired with an intensifier gate 50 ns long that is coincident with the laser pulse. Phosphorescence images are taken with intensifier gates of 300 ns to 600 μs and a delay time of 300 ns after the laser pulse.

V. Results and Discussion

Fluorescence data were acquired for vapor acetone at temperatures and pressures ranging from subcritical to supercritical. Relative fluorescence yields were determined as indicated by Eq. (1), i.e., by dividing the measured signals by the laser energy and absorption coefficient determined *in situ*. Figure 3 shows the measured fluorescence yields as a function of temperature, normalized to the fluorescence yield at 295 K, for various pressures ranging from ~1 to 60 atm. For a given pressure, the fluorescence yield decreases nearly linearly with increasing temperature. Figure 3 also shows the relative fluorescence yields as given by the models proposed by Thurber and Braeuer. The agreement is good, though the measured yields are slightly lower than the predicted values. The decrease in ϕ_{fl} with temperature occurs because the molecules are initially in a higher vibrational energy state when the acetone is hotter. So when they are excited by the laser, they begin in a higher vibrational energy state in the first excited singlet state. This leads to faster intersystem crossing, reducing the fluorescence yield. The same data are shown plotted as a function of pressure in Figure 4, where the data at a given temperature are normalized to the fluorescence yield value at 1 atm. The fluorescence yield is seen to increase with pressure, though above 30 atm there is little change. The fluorescence yield appears to asymptote to a value that is approximately twice the fluorescence yield at 1 atm. This is due to an increase in the vibrational (collisional) relaxation rate, thereby moving

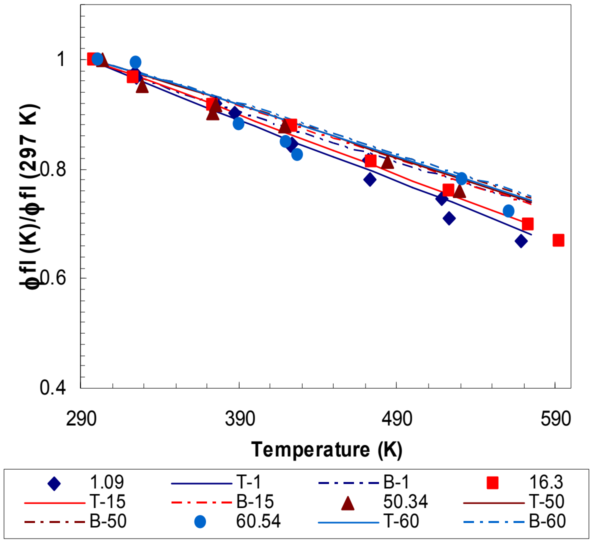


Figure 3. Normalized fluorescence yield (ϕ) of vapor acetone at varying pressures and temperatures in nitrogen co-flow. Data normalized to ϕ_{fl} at 295 K for each pressure set. Symbols- experimental data. Solid line-Thurber's model. Dash lines are Braeuer's model. The legends indicate the pressure in atm.

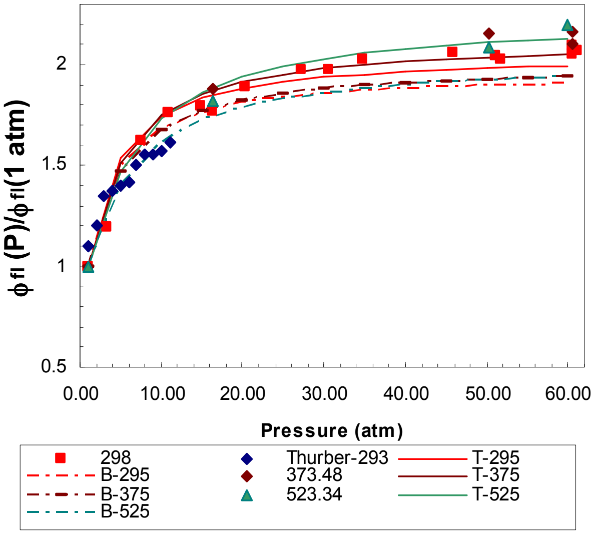


Figure 4. Normalized fluorescence yield of vapor acetone at varying pressures and temperatures in nitrogen co-flow. Data normalized to ϕ_{fl} at 1 atm for each temperature set. Symbols-experimental data. Solid lines-Thurber's model. Dash lines-Braeuer's model. Legends indicate the temperature in Kelvin.

molecules to lower vibrational energy levels with slower intersystem crossing rates. This increases the fraction of molecules that fluoresce. The increase in fluorescence yield is limited once the pressure is high enough that the vibrational relaxation rate dominates the intersystem crossing rate.

The data also indicate that the temperature and pressure effects are nearly independent of one another. As shown in Figure 3, the Braeuer model predicts a weaker temperature dependence of the fluorescence yield compared to either the experimental data or the Thurber model. The same is true for the pressure dependence (Figure 4); the Braeuer model has a weaker pressure dependence compared to the Thurber model and the experimental data. The fluorescence yield results for the two models also differ greatly for short excitation wavelengths. Figure 5 shows the fractional difference between the two models for different wavelengths at various temperatures. From the figure, it can be seen that the variation between the two models is highest for the combination of short excitation wavelength, low pressure and high temperature. For longer wavelengths, the difference between the models is greatly reduced, for example, to less than one percent at 308 nm for all temperatures and pressures. The two models use different intersystem crossing rates. The Thurber model for the intersystem crossing rate was based on experimental rate for vibrational energies up to 7000 cm^{-1}. Thus it was not able to correctly predict the intersystem crossing rate for higher energy levels, which are accessible for laser excitation at 248 nm. The Braeuer model has an increased intersystem crossing rate for vibrational energies above 7000 cm^{-1}. Therefore fewer molecules are able to fluoresce before transferring to the triplet state. For the wavelength used in the current study (266 nm), the difference between the models is only 2-3% for pressures above 30 atm, independent of temperature, as opposed to the 4-6% difference for 248 nm.

Experiments were also performed for liquid acetone injected at subcritical temperatures and subcritical to supercritical pressures. The data is shown in Figure 6 for two cases: a liquid stream flowing into a nitrogen environment and into an air (i.e., oxygen containing) environment. The fluorescence from the liquid acetone is essentially invariant to changes in pressure and temperature, at least in the range tested, for the nitrogen case (Figure 6a). The fluctuations in the signal, which have no consistent trend with pressure or temperature, are likely due to small laser energy variations and unsteadiness in the liquid jet.

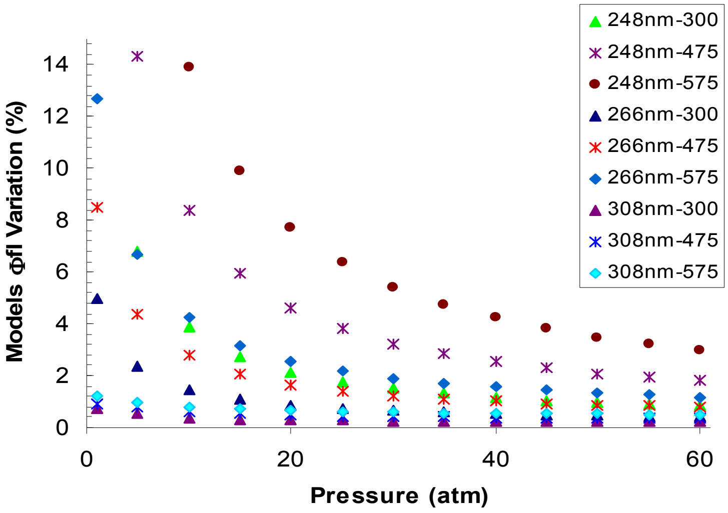


Figure 5. Fractional variation in ϕ_{fl} between the Thurber and Braeuer models for three excitation wavelengths and three temperatures for varying pressures (indicated in the legends).

The trend from the liquid acetone is similar to what the vapor models would predict at very high pressures, or equivalently at high densities. Since the molecules in the liquid essentially have low mean free paths or high collision rates, the vibrational relaxation rate would be expected to be much faster than the intersystem crossing rate. Also, since pressure and temperature have little influence on the liquid density, it is not surprising that the fluorescence changes little with pressure and temperature. Application of the vapor models to liquid acetone would also suggest that the liquid would have a higher fluorescence yield compared to acetone vapor, i.e., the high pressure fluorescence yield limit for vapor acetone would be the liquid acetone fluorescence yield.

The fluorescence signal of liquid acetone injected into an air co-flow at room temperature and elevated pressures is shown in Figure 6b. For pressures from 1 to 30 atm, there is no variation in the fluorescence signal. Also there is little change in the fluorescence for the air versus N_2 environment, in contrast to the behavior of the vapor fluorescence. The vapor fluorescence decreases in the presence of air compared to nitrogen for pressures above 2 atm. This is caused by oxygen-assisted intersystem crossing from the singlet state to triplet state.[6] Thus it is expected that the fluorescence signal should decrease in the presence of oxygen. A possible explanation for the similar fluorescence signal between the nitrogen and air co-flow for the liquid acetone is that the oxygen penetration into the jet is not fast enough so the oxygen concentration is very low. The concentration is high enough to affect the phosphorescence signal, as seen later in this paper, but insufficiently high to affect the fluorescence. The saturated concentration of oxygen inside liquid acetone is approximately 1×10^{-3} M, which is approximately 6.02×10^{20}

molecules/m^3 or 0.0244 atm.[10] This is about 12% of the oxygen concentration of air at atmospheric pressure. Oxygen only affects the vapor fluorescence signal at operating pressure of 2 atm or above. That would mean the oxygen concentration is 0.4 atm, much higher than the oxygen saturation concentration inside liquid acetone. Therefore, the minimum oxygen concentration required to reduce the fluorescence intensity is much higher than the saturation concentration within the liquid, thus oxygen will not affect liquid acetone fluorescence intensity.

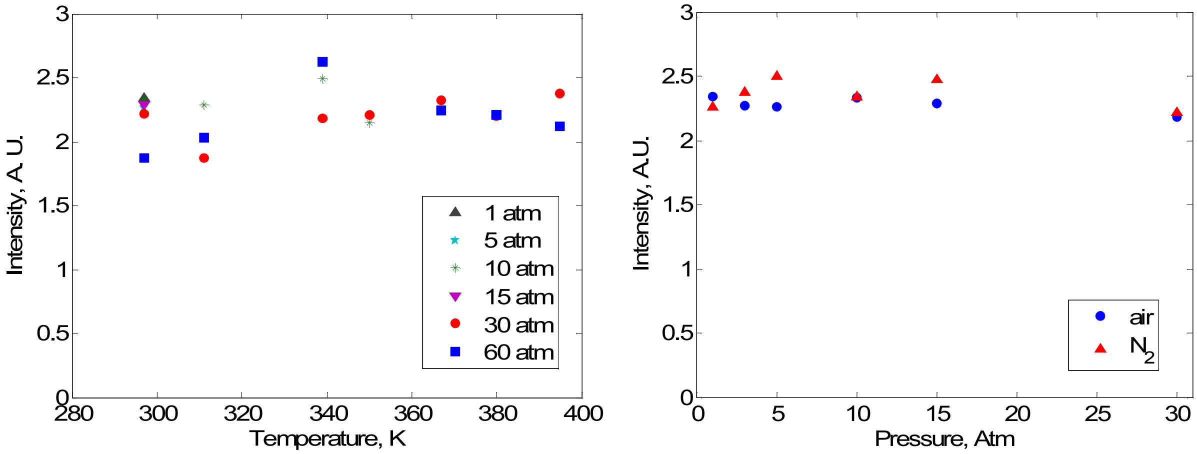


Figure 6. Fluorescence signal of liquid acetone. *a) Fluorescence signal at varying pressure and temperature in a nitrogen co-flow. b) Fluorescence signal at varying pressure in air and nitrogen co-flow at room temperature.*

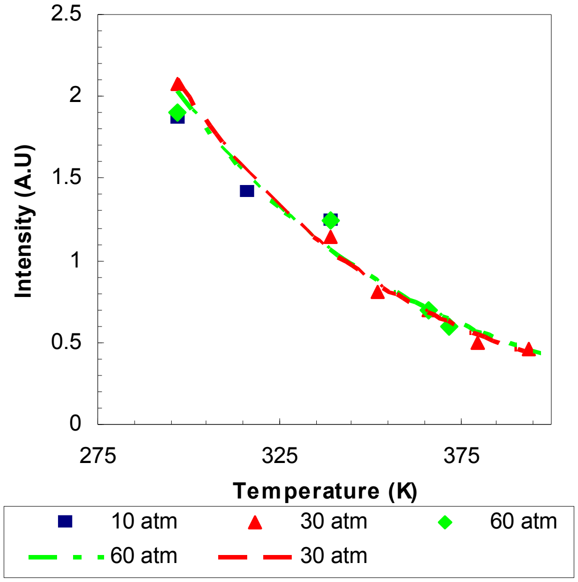


Figure 7. Phosphorescence signals of liquid acetone at varying temperatures from subcritical to supercritical pressure. *Lines are least-square-error exponential fits.*

The liquid acetone's phosphorescence signal at various pressures and temperatures in a nitrogen co-flow is shown in Figure 7. The liquid phosphorescence is invariant with pressure (from subcritical to supercritical pressures for our subcritical temperature). The phosphorescence exponentially drops as the temperature is increased. This is seen for all three pressures cases shown here. In addition, the phosphorescence signal is seen to approach a limit as the temperature increases. Based on the vapor photophysics models, again considering the liquid to be like a highly dense gas, the phosphorescence intensity trend can be interpreted as follows. From Figure 6, the liquid fluorescence signal in invariant for both temperature and pressure. This suggests that the fraction of excited molecules crossing from the first excited singlet state to the first excited triplet state is the same for all pressures and temperatures. Therefore, the phosphorescence intensity should only be influence by processes that occur after the intersystem crossing. From Figure 7, it can be inferred that temperature somehow reduces the phosphorescence yield. If this is so, then we should expect a corresponding decrease in the phosphorescence lifetime.

The decay of the phosphorescence signal with time was determined previously[11] for the same test conditions. The phosphorescence decay can be fitted to a double exponential decay, and these phosphorescence lifetimes are plotted in Figure 8. For the temperature and pressure range tested, both lifetimes are shown to decrease with increasing temperature. The first lifetime ranges drops from 1.10±0.1 μs by roughly a factor of two to 0.50±0.07 μs. The second, slower decay, lifetime decreases by nearly the same ratio from 7.0±0.5 μs to 4.0±0.5 μs. There is a much larger dependence of the phosphorescence signal upon the first lifetime; since approximately 85–90% of the phosphorescence occurs during the decay associated with the first lifetime. The phosphorescence lifetime also approaches a limit as the temperature increases, similar to the trend seen in the phosphorescence signal (Figure 7). Thus it can be concluded that the phosphorescence yield does decrease with temperature, likely due to acetone-acetone (collisional) interactions that nonradiatively relax the triplet state.

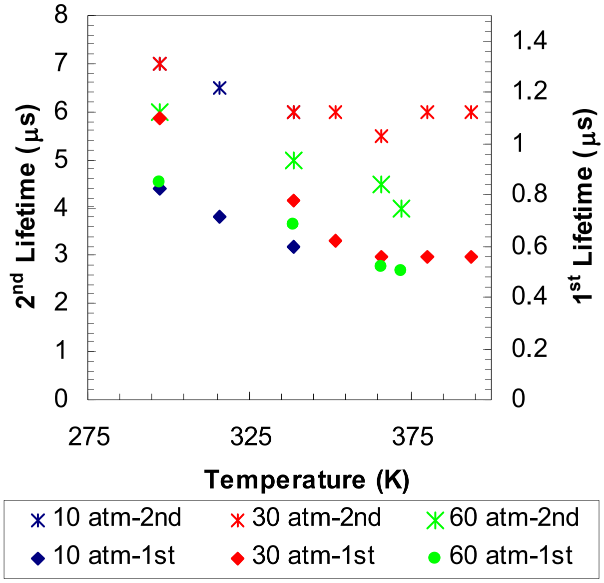


Figure 8. Phosphorescence lifetimes of liquid acetone at varying temperatures from subcritical to supercritical pressure.

V. Summary

Acetone photophysics for both vapor and liquid have been studied by measurements of fluorescence and phosphorescence quantum yields. It was found that the vapor fluorescence yield follows the models proposed by Thurber and Braeuer for pressures and temperatures from subcritical to supercritical values. The current results are in closer agreement with the Thurber model, though it should be noted that the two models essentially converge for high pressures or long excitation wavelengths. The liquid acetone fluorescence signal was shown to be invariant with pressure and temperature, at least over the range of conditions tested. The liquid phosphorescence yield is independent of pressures but decreases exponentially with increasing temperature, as verified by phosphorescence lifetime measurements. In general, the existing photophysics models for acetone vapor can be used, at least qualitatively, to explain the behavior of the liquid acetone fluorescence. To address the phosphorescence yield, an issue not addressed in the current models, requires modifications to the models. Still, the current models appear to be sufficiently accurate to be useful for interpreting acetone PLIF measurements in transcritical and supercritical jet breakup and mixing studies.

Acknowledgements

This work was supported by NASA grant NCC3-994 (through the Institute for Future Space Transport and the Constellation University Institutes Project).

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