PLIF imaging of naphthalene-ablation products in a Mach 5 turbulent boundary layer

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A new technique is currently under development that uses planar laser-induced fluorescence (PLIF) imaging of sublimated naphthalene to image the transport of ablation products in a hypersonic boundary layer. The primary motivation for this work is to understand scalar transport in hypersonic boundary layers and to develop a database for validation of computational models. The naphthalene is molded into a rectangular insert that is mounted flush with the floor of a Mach 5 wind tunnel. The distribution of naphthalene in the boundary layer is imaged by using PLIF, where the laser excitation is at 266 nm and the fluorescence is collected in the range of 320 to 380 nm. To investigate the use of naphthalene PLIF as a quantitative diagnostic technique, a series of experiments is conducted to determine the linearity of the fluorescence signal with laser fluence, as well as the temperature and pressure dependencies of the signal. The naphthalene fluorescence at 297 K is determined to be linear for laser fluence that is less than about 200 J/m². The temperature dependence of the naphthalene fluorescence signal is found at atmospheric pressure over the temperature range of 297K to 525K. A monotonic increase in the fluorescence is observed with increasing temperature. Naphthalene fluorescence lifetime measurements were also made in pure-air and nitrogen environments at 300 K over the range 3.3 kPa to 101.3 kPa. The results in air show the expected Stern-Volmer behavior with decreasing lifetimes at increasing pressure, whereas nitrogen exhibits the opposite trend. Preliminary PLIF images of the sublimated naphthalene are acquired in a Mach 5 turbulent boundary layer. Relatively low signal-to-noise-ratio images were obtained at a stagnation temperature of 345 K, but much higher quality images were obtained at a stagnation temperature of 375 K. Our results indicate that PLIF of sublimating naphthalene may be an effective tool for studying scalar transport in hypersonic flows.

Nomenclature

Symbols

\( c \) = speed of light
\( E_l \) = laser energy (J)
\( h \) = Plank’s constant
\( k_f \) = rate of spontaneous emission
\( k_{int} \) = rate of energy transfer from \( S_i \) not due to collisions
\( k_Q \) = collisional quenching rate
\( n \) = total number density
\( n_i \) = number density of colliding species \( i \)
\( M \) = Mach number
\( P \) = total pressure (Pa)
\( P_i \) = partial pressure of species \( i \) (Pa)

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S₀ = Singlet ground state
S₁ = Singlet 1st electronic excited state
S₂ = Singlet 2nd electronic excited state
Sᵣ = fluorescence signal
T = temperature (K)
⟨v⟩ᵢ–Na = mean relative speed between species i and naphthalene
ΔV = probe volume

Greek
χᵢ = mole fraction of species i
η_opt = collection optics collection efficiency
σᵢ = absorption cross-section
σᵣ = quenching cross section of species i
φ = fluorescence yield
λ = wavelength (nm)
δ₉₉ = 99% velocity boundary layer thickness (m)
τᵢ = time-decay constant
ν = wavenumber (cm⁻¹)

Subscripts
i = designates species i
ref = reference value (300 K)
₀ = stagnation value
∞ = free-stream value

I. Introduction

Ablation modeling has received renewed interest owing to NASA’s interest in planetary-atmosphere entry,¹ as well as the US Air Force’s interest in developing hypersonic long-range aircraft and missiles. The thermal protection systems of these devices experience a highly complex process that is characterized by several physical processes including high-temperature non-equilibrium chemistry, radiation, turbulence, mass/heat transfer, radiation, gas-solid reactions and mechanical erosion.² The coupled nature of these thermophysical processes make developing mathematical models of ablation particularly challenging.³ The large-eddy simulation (LES) technique is currently being applied to the ablation problem, but these efforts are limited by the lack of accurate subgrid-scale models that capture the details of the turbulent scalar transport. For this reason, the current study is aimed at considering a limited-physics problem, where a low-temperature sublimating ablator is used to capture the surface-gas transpiration and resulting transport of the ablation products in the turbulent boundary layer. The sublimating ablator used is naphthalene, which has the particularly useful property that it can be imaged using planar laser-induced fluorescence (PLIF). Naphthalene (C₁₀H₈) is a polycyclic aromatic hydrocarbon that absorbs light over a band extending from 250 nm to 350 nm. It emits fluorescence over the range 300 nm to 400 nm, depending on the pump wavelength. This sublimation technique shares some characteristics with techniques that transpire a non-reacting fluorescent gas such as nitric oxide into the heat-shield boundary layer,⁴ but it adds the complexity that the ablation products result from a true, albeit simplified, ablation process. A major goal of this work is the simultaneous acquisition of naphthalene PLIF and particle image velocimetry (PIV) to enable the computation of the scalar-velocity correlations that are used in LES model development.

Naphthalene is a solid in crystalline form at room temperature and has a melting temperature of 353 K. Relevant physical properties of naphthalene are given in Table 1. At temperatures lower than its melting point mass is removed by sublimation. Naphthalene can be readily formed into virtually any simple shape by either machining it from preformed blocks with a mill, coating surfaces by dipping/spraying, or by casting. In the past naphthalene has been extensively used in low-speed studies to determine the heat transfer rate by using the heat-mass transfer analogy. Essentially, the heat transfer rate is inferred from a measurement of the mass loss, either by weighing the ablated material or by measuring the recession depth.⁵ Furthermore, low-temperature sublimating ablators, such as camphor and naphthalene, have been used to determine nose-tip recession rates of supersonic projectiles.⁶ Camphor has a higher melting temperature and so is often preferred for shape-change studies in some higher-enthalpy supersonic wind tunnels.

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To date, naphthalene PLIF has not been used in supersonic flows, but it has seen some use as a fuel marker in low-speed reacting flows. In Ref. 10 the dependence of the naphthalene PLIF signal on temperature was used to image the temperature of the unreacted fuel in a jet flame. Furthermore, a few naphthalene fluorescence lifetime studies have been performed as well. Quenching rates for naphthalene fluorescence in N$_2$, O$_2$, and H$_2$O have been studied, and the effect of temperature on the lifetime of naphthalene fluorescence was also studied in oxygen free environments. A more detailed discussion of the spectroscopy of naphthalene is given in the following section. We note that a great deal of insight into needed measurements can be obtained by consulting studies that investigated the spectroscopy of other hydrocarbons, such as acetone and toluene.

The current paper reports on the development of the naphthalene sublimation technique for investigating scalar transport of ablation products in low-enthalpy hypersonic flows. The ablating surface is a solid naphthalene insert that is flush-mounted with the floor of a Mach 5 wind tunnel. Planar laser-induced fluorescence is used to image distribution of naphthalene vapor in the boundary layer. The overall objective of the work is to develop a quantitative diagnostic technique, and so the photo-physical properties of naphthalene were also investigated. In particular, studies of linearity of the LIF signal with laser fluence, and the temperature and pressure dependencies of the LIF signal, were conducted. The conditions investigated were intended to span the range of conditions experienced as the naphthalene is transported throughout the Mach 5 boundary layer. However, at this time, we have made measurements only at temperatures of 300 K and above, even though the more important temperature range is from 100 K to 300 K. The lower temperature measurements will be reported in a future paper.

<table>
<thead>
<tr>
<th>Table 1. Physical Properties of Naphthalene</th>
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<tr>
<td>Molecular formula</td>
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<tr>
<td>Molar Mass (kg/kg-mole)</td>
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<td>Melting temperature (K)</td>
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<tr>
<td>Vapor pressure at 300 K (Pa)$^{14}$</td>
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<td>Vapor pressure at 350 K (Pa)$^{14}$</td>
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II. Naphthalene Spectroscopy

The energy-level structure of the naphthalene molecule is complex because of the presence of different vibronic levels that are entangled with one another. Figure 1 shows a simplified illustration of the energy levels that are close to the photon energy of the fourth harmonic of the Nd:YAG laser ($\lambda=266 \text{ nm}$ or $\nu=37,600 \text{ cm}^{-1}$), since this is the excitation frequency that is used in the current work. The first and second excited singlet electronic states, denoted as S$_1$ and S$_2$ respectively, are located at an energy level of 32000 and 35000 cm$^{-1}$ above the ground electronic state (S$_0$). Each electronic state is associated with a manifold of closely-spaced vibrational energy levels. These vibrational levels are classified as either a “totally symmetric” (TS) or “non-totally-symmetric” (NTS), depending on the symmetry of the vibration. In general, the vibrational levels in the TS group have a shorter lifetime compared to the NTS group. In addition, since the energy level difference between the S$_1$ and the S$_2$ states are quite small, the vibrational manifolds of the two states overlap and form a larger entangled manifold. There also exist excited triplet vibronic states T$_1$ and T$_2$, whose energy level structure is very similar to the singlet levels S$_1$ and S$_2$. In Fig. 1, the excitation by a 266 nm photon is illustrated, which excites the naphthalene molecule from the ground state to the second excited state, S$_2$. Almost all of the excited molecules undergo an “internal conversion” to the vibrational levels of S$_1$. The internal conversion process takes place much faster than the fluorescence lifetime of the S$_2$$\rightarrow$S$_0$ transition. Most of the fluorescence, therefore, results from S$_1$$\rightarrow$S$_0$ vibronic transitions even though the S$_2$ state is pumped. A fraction of the molecules in the S$_1$ and S$_2$ states makes an “inter-system transfer” to triplet vibronic states T$_1$ and T$_2$. The rate of inter-system transfer increases with increasing excitation-photon energy and with increasing pressure. For example, the inter-system transfer is considerable for excitation wavelengths lower than 250 nm or pressure over 150 torr. The molecules in the triplet states T$_1$ and T$_2$ undergo both collisional de-excitation and radiative transition. The radiative transitions from the triplet to the ground (singlet) state represent long-lived phosphorescence with a lifetime of order milliseconds. The inter-system transfer, however, is small for 266 nm excitation, and so the dominant emission is S$_1$$\rightarrow$S$_0$. 

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Several studies have also investigated different aspects of naphthalene fluorescence. The fluorescence signal with units of photons, under the assumption of broadband detection and weak excitation, is given by:

\[
S_f(P,T) = \frac{E_l}{hc/\lambda} \eta_{opt} \Delta V \chi_{naph} n(P,T) \sigma_a(\lambda,T) \phi(\lambda,T,P,\chi) 
\]

where \(E_l\) is the laser fluence (J/m\(^2\)), \(h\) is Planck’s constant, \(c\) is the speed of light, \(\lambda\) is the wavelength of the laser, \(\eta_{opt}\) is the collection optics collection efficiency, \(\Delta V\) is the probe volume, \(\chi_{naph}\) is the naphthalene mole fraction, \(n\) is the total number density, \(\sigma\) is the absorption cross-section, \(\phi\) is the fluorescence yield, \(P\) is pressure and \(T\) is temperature. If we assume that the fluorescence results from the \(S_1\) state, and that the spontaneous emission rate and electronic quenching rates are the same for each state, then we can write the fluorescence yield as,

\[
\phi(\lambda,T,P,\chi) = \frac{k_f}{k_f + k_{int} + k_Q} 
\]

where \(k_f\) is the rate of spontaneous emission, \(k_{int}\) is the rate of de-excitation of \(S_1\) not due to collisions, and \(k_Q\) is the collisional quenching rate. Here we model the quenching rate as,

\[
k_Q = \sum_i n_i \sigma_i \langle v \rangle_{i-Na} 
\]

where \(n_i\) is the number density of colliding species \(i\), \(\sigma_i\) is the is quenching cross section of species \(i\), and \(\langle v \rangle_{i-Na}\) is the mean relative speed between species \(i\) and naphthalene. When naphthalene is seeded in air, oxygen is the dominant quencher and we have: \(k_Q = n_{O_2} \sigma_{O_2} \langle v \rangle_{O_2-Na}\).

When the species is excited by a short-pulse laser, the fluorescence decay typically follows an exponential form with time-decay constant,

\[
\tau_f = (k_f + k_{int} + k_Q)^{-1} 
\]

Figure 1. Vibrational-electronic energy level diagram of gas-phase naphthalene. There are two electronic systems, singlet and triplet, where each electronic state is associated with a manifold of closely-spaced vibrational levels.
The equations above are for an extended two-level model with broadband detection, and they are reasonable approximations under some conditions, but we caution that they can be highly inaccurate in others (e.g., low pressure). Some of the limitations are explored below and in the discussion of our results.

Several studies have focused on understanding the single vibrational level fluorescence at low pressure and at near absolute zero temperature, the fluorescence life times and quantum yields of the first and higher excited states, and the intersystem transfer to the triplet states and the corresponding phosphorescence. A detailed review of the studies on fluorescence and non-radiative lifetimes and the quantum yields for different vibronic states is given in Ref. 21. The fluorescence decay waveform was reported to be bi-exponential by several previous researchers. The bi-exponential trace is because of the simultaneous decay of two types of vibronic states. The timescale of the longer lifetime transitions was about 1 μs and the shorter lifetime ranged between 85 to 400 ns. The shorter duration decay corresponds to the fluorescence of the vibronic states of S_1 level. The range of lifetimes within the S_1 vibronic states is because of the differences in the lifetime of different groups of vibrational levels, which differ in their symmetry. For the present study, the fluorescence decay corresponds to the vibronic states of S_1 level only. Most of the above fluorescence decay measurements were performed in a vibrationally frozen condition (very low temperature) and at extremely low pressures. At these conditions, the effect of collisional de-excitation is not present. Suto et al. and Schlag et al. performed fluorescence decay measurements at a temperature of about 300 K. They reported a much smaller quantum yield and fluorescence lifetime compared to the single vibrational level measurements.

Only a few studies have focused on measuring electronic quenching rates of gas-phase naphthalene. For example, quenching measurements of oxygen, nitrogen, methane, noble gases and nitric oxide have been reported but only at a limited range of conditions. Oxygen is reported to be one of the major quenching agents of naphthalene and its quenching effect was studied by different workers. Kaiser and Long measured the quenching of naphthalene by oxygen and nitrogen at room temperature and above. They reported that oxygen dominates the quenching process. Similar conclusions were drawn by Martinez et al. who measured O_2 and N_2 quenching rates at standard conditions and found that the O_2 quenching cross-section is about an order of magnitude larger than that of N_2. A preliminary study of the quenching by oxygen and nitrogen at different pressures is made in the present work also. Our intention is to extend this work to include the full range of conditions experienced by the naphthalene vapor as it is transported throughout the Mach 5 boundary layer. Here we report our preliminary data, which spans only a fraction of the relevant temperature range, as mentioned above.

### III. Experimental Program

The wind tunnel experiments were conducted at the High-Speed Wind Tunnel Laboratory located at the Pickle Research Campus of the University of Texas at Austin. Complementary investigations of fluorescence linearity, and temperature/pressure dependence were conducted in a temperature-controlled jet of naphthalene exhausting into atmospheric conditions or a pressure-controlled cell.
The experimental setup for the experiments conducted in the Mach 5 wind tunnel is shown in Fig. 2. The Mach 5 tunnel is driven by a 2500 psi pressure tank that gives a stagnation pressure of 360 psi and exhausts to the atmosphere. The air is heated before the test section to give a variable stagnation temperature from 345 K to 375 K. The naphthalene plug is 101.6 mm long by 57.2 mm wide and is flush with the floor of the wind tunnel. The naphthalene plug, Fig. 3, can be imbedded with up to 15 thermocouple equally spaced in a 5 by 3 array 22.2 mm apart, with 5 installed length wise at three span wise positions. The optical access allows viewing of the ablation product 23.5 mm to 264.8 mm downstream of the downstream edge of the naphthalene plug. The naphthalene plug was formed by using a molding procedure. This procedure entailed heating solid naphthalene past its melting point, then pouring it into the naphthalene plug. A cover was placed over the plug during the cooling process. Once the naphthalene solidified the cover was removed, and the resulting surface was relatively flat and smooth. The thermocouples are installed before the molding procedure and become imbedded within the naphthalene after it has solidified. After the naphthalene solidified, the cover was removed and the plug was installed into the test section floor. The sublimation rate at standard conditions is quite slow and no noticeable mass is lost even if the insert sits for hours without flow. Only a small amount of ablation (less than a fraction of a millimeter) is observed over the course of a 1 minute wind tunnel run.

![Figure 2](image)

**Figure 2. Schematic diagram of the naphthalene PLIF setup in the Mach 5 wind tunnel.** *(a) Overall assembly and (b) inside the test section*
The naphthalene fluorescence was excited with a laser sheet from a quadrupled Nd:YAG laser (Spectra-Physics Model PIV 400) operating at 266 nm. Fused silica windows were downstream of the naphthalene insert to enable the laser sheet to pass through the test section and reduce reflections. A back-illuminated CCD camera (PixelVision SpectraVideo Model SV512V1) imaged the fluorescence through a fused silica window in the tunnel side wall. The camera was fitted with a 100 mm focal length, f/2.8 UV lens (Eads Sodern Circo) operated at full aperture. A Schott WG-295 filter and Schott UG-5 filter were used to pass the fluorescence (in the range 295nm to 400nm), while rejecting most of the elastically scattered light. The imaging field of view was 27 mm wide by 14mm tall.

A temperature-controlled jet of naphthalene-laden air exhausting into atmospheric conditions was used to study the saturation and temperature dependence of the naphthalene fluorescence. The schematic of the setup is shown in Fig. 4. Air (10 LPM) was passed through a cell filled with naphthalene crystals. This vapor-laden flow was then passed through an in-line heater capable of heating the air to 525 K. A jet was formed as the flow exits from a 12.7 mm tube. To avoid condensation of the naphthalene on the walls of a test cell, these measurements were made in a free jet. The fluorescence was excited with a quadrupled Nd:YAG laser operating at 266 nm. The beam was passed through a varying number of fused silica flats, which are used to change the energy of the beam. To obtain the lowest fluences, a 90 percent beam splitter was used along with the fused silica flats. The beam propagation direction was perpendicular to the axis of the jet. The back-illuminated CCD camera was used to image the naphthalene fluorescence in the potential core of the jet. The linearity of the LIF signal was studied by changing the energy of the beam while keeping the temperature constant.

In a related experiment the temperature dependence of the naphthalene fluorescence from 297 K to 525 K was investigated by varying the temperature while keeping the energy constant (and low enough to be within the linear regime). The jet issued into atmospheric pressure and the flow rate was maintained at 30 SLPM. The naphthalene concentration was saturated at a constant room temperature of 298 K.

The experiments to investigate the pressure dependence of the LIF signal were conducted in a temperature controlled jet of naphthalene-vapor-laden air exhausted into a pressure controlled cell. The experimental setup is the same as in Fig. 4 except instead of exhausting into atmospheric conditions the jet is exhausted into a vacuum cell, as shown in Fig. 5. The cell had fused silica windows on three sides to allow for the 266nm laser beam to pass through and for imaging the fluorescence. The cell was kept at a constant pressure (vacuum) by flowing the gas through a metering valve and then into a large vacuum chamber. To determine the pressure dependence of the naphthalene fluorescence decay, the pressure in the test cell was varied from 3.3 kPa to 101.3 kPa, while keeping the mass flow rate at 30 SPLM. The jet was kept at a constant temperature of 297 K and was monitored by a type T thermocouple. If not cleaned after every
run, the naphthalene would condense on the windows and would be burned by the absorption of the laser light. The fluorescence decay signal was measured using a 1P28 photomultiplier tube (PMT). The laser energy was set at few tens of microjoules to avoid saturating the PMT.

IV. Results

LIF Linearity with Laser Fluence

To determine the effect of laser fluence on the fluorescence signal, the fluorescence signal from the naphthalene jet was imaged on the CCD camera at varying laser energy. The frequency quadrupled Nd:YAG laser had a pulse duration of about 20 ns. Here, we are ignoring the effect of pulse duration since it is constant for this study. The laser energy was varied by passing the beam through a variable number of fused silica flats to reflect different fractions of the energy. For the lowest energy cases the fused silica flats were combined with a 90% beam splitter. The laser energy was measured with a Joule meter. The laser beam was passed through the potential core of the air-naphthalene jet and the resulting fluorescence was imaged. To obtain the area of the laser beam, intensity profiles were then extracted from the images. The fluence was then computed as the energy per pulse divided by the area of the laser beam. The use of fused silica flats and a beam splitter kept the beam profile consistent during each experiment. The results are shown in Figure 6. The error bars represent a 95 percent confidence interval determined from the standard error computed from six different sets of experimental results, and the pre-factor obtained from the student’s t distribution. Each data point of each set represents an average of 100 images over which the fluorescence signal was spatially-averaged over the jet potential core. The area of the beam was assumed to correspond to that of a disk with diameter equal to the full-width-at-quarter-maximum of the fluorescence signal profiles. Full width at quarter maximum was used instead of full width at half maximum due to a plateau region in the beam profile near the half maximum point, which made the width very sensitive to the exact value of maximum intensity used. Typically, the areas derived from the full-width-at-quarter-max points is about 1.56 times larger than those computed from the half-maximum points.

Figure 6 shows that there is a region where the fluorescence signal is linear with laser fluence but it levels off with increasing fluence. From the figure, the LIF signal diverges from linear for fluences that are greater than about 200 J/m². This value of fluence that maintains linear behavior is relatively low as compared to other popular tracers, such as acetone.

In PLIF imaging, we typically want to maintain linear behavior because this improves our ability to make accurate sheet corrections. So say we use a 5 cm wide and 500 μm thick laser sheet with a 10 ns pulse duration, then the maximum laser energy that can be used is only 5 mJ. Now, approximately linear behavior is achieved for fluence that is nearly twice this value, and the resultant bias error may be acceptable if achieving higher signals is critically important. The data in Fig. 6 were acquired at atmospheric pressure, but the fluorescence linear regime may not be the same at the conditions of interest in the Mach 5 wind tunnel (30 Torr), and so these measurements will be repeated at lower pressures.
pressure in future work.

**LIF Temperature Dependence at Atmospheric Pressure**

The temperature dependence of naphthalene was determined by imaging the fluorescence of a heated naphthalene-air jet. Here we normalize the fluorescence signal by the room temperature value \((T_{\text{ref}}=300 \text{ K})\), i.e.,

\[
\frac{S_f(T)}{S_f(T_{\text{ref}})} = \frac{T_{\text{ref}} \sigma_a(T) \phi(T)}{T \sigma_a(T_{\text{ref}}) \phi(T)}
\]

In the quenching dominated limit where we assume the quenching cross-section is constant over our temperature range then we have,

\[
\frac{\sigma_a(T)}{\sigma_a(T_{\text{ref}})} = \left( \frac{S_f(T)}{S_f(T_{\text{ref}})} \left( \frac{T}{T_{\text{ref}}} \right) \right)^{1/2}
\]

The temperature dependence of the fluorescence signal per unit-mole-fraction of naphthalene is shown in Fig. 7(a). These measurements represent the time- and spectrally-integrated fluorescence signal. Four sets of data were collected to determine the 95 percent confidence intervals. The large uncertainty results from day-to-day variations in the naphthalene vapor pressure. The data sets were collected by both increasing the temperature throughout the run and decreasing it. Each point in the data sets consisted of an average of 100 fluorescence images over which the fluorescence signal was spatially-averaged over the jet potential core. The energy per pulse was in the linear regime of naphthalene fluorescence at room temperature and verified at 525 K. The monitored energy per pulse was used to correct the fluorescence signal. The temperature of the naphthalene saturation cell was closely monitored, which was used to correct the fluorescence signal for changing naphthalene vapor pressure \(^{14}\), but there still seems to be some lack of precision in this process. Figure 7(a) shows that the fluorescence increases sharply at lower temperatures and levels off with higher temperatures, but this trend is not entirely trustworthy considering the uncertainty. Future work will be directed at reducing the uncertainty of these measurements. The normalized absorption cross-section is presented in Fig. 7(b). The cross-sections were obtained by multiplying the fluorescence signals by the temperature factor as shown in Eq. 6. Figure 7(b) shows that the cross-sections exhibit a more steady increase with temperature. Similar measurements of other complex organic molecules, such as acetone, show that the dependence of the signal on temperature will depend strongly on the excitation wavelength.\(^{13}\)

**Measurements of Naphthalene Lifetime: Quenching Effects**

The fluorescence lifetime of naphthalene vapor was measured at different pressures in a nitrogen environment and in a pure-air environment (ultra zero-air). Since nitrogen is not an efficient quencher of naphthalene fluorescence, the fluorescence decay in a nitrogen environment is due mainly to self-quenching (naphthalene-naphthalene collisions) and natural decay (spontaneous emission and non-radiative internal transfer). In contrast, the decay in an air environment is dominated by oxygen quenching, which is very efficient.\(^{18,9,25}\) The fluorescence lifetimes were determined by fitting an exponential to the PMT signal time-traces. It should be emphasized that the measured fluorescence decay is the average of the radiative decay from different vibrational levels; hence, fitting an exponential to the observed signal provides the measure of the average lifetime of the different vibrational levels that participate in the radiation.

Figure 8 shows a Stern-Volmer plot of the quenching of the naphthalene vapor by air. This plot is the variation of the reciprocal of the fluorescence decay time-constant with pressure. It can be seen that the variation of the reciprocal time-constant is linear with pressure for pressures greater than 2 kPa (40 torr). This linear variation indicates that the fluorescence is dominated by quenching at these pressures. A straight line was fitted in order to determine the slope and the y-intercept of the line. The quenching rate obtained from the slope of the Stern-Volmer plot was \(k_Q = 0.0096 \text{ (kPa ns)}^{-1}\). For this fit the last two points at the low-pressure end were omitted. Since air is composed of 21% O\(_2\), this gives a quenching rate of \(k_Q = 0.046 \text{ (kPa ns)}^{-1}\) for O\(_2\). This value is reasonably close to the value of 0.06 (kPa ns)\(^{-1}\) measured by Martinez et al.\(^{9}\) using 308 nm excitation. In Fig. 8 the y-intercept, which
gives the sum of the fluorescence decay and non-radiative non-collisional de-excitation, is estimated to give a lifetime of about 123 ns, although the actual lifetime at zero-pressure is lower than this as will be discussed below. The value of 123 ns can be considered an effective lifetime that is appropriate for higher pressure conditions where the trend is linear.

An interesting feature is the deviation from the linear trend at low pressures. In particular, it can be seen that the magnitude of the lifetime is less than that predicted by the Stern-Volmer variation (i.e., the reciprocal of time is larger than the linear trend would extrapolate to). This deviation indicates the role of internal de-excitation mechanisms ($k_{int}$) that becomes important as the collisional de-excitation rate ($k_Q$) approaches zero.

A preliminary study of the effect of nitrogen dilution on the fluorescence lifetime was also conducted. Since $N_2$ is a relatively weak quencher, the internal transfer mechanisms on the fluorescence lifetime are revealed. Figure 9 shows the variation of the fluorescence lifetime with pressure in a nitrogen environment, and for reference, the air environment is also shown. The variation is strikingly different from that in the pure-air environment. In the case of nitrogen, the fluorescence lifetime actually increases with increasing pressure. A qualitatively similar increase in lifetime with increasing pressure was also reported by Ref. 18 and 27, who excited naphthalene vapor in an argon environment using 268 nm and 265 nm irradiation, respectively. Fig. 10 compares the lifetimes measured in the current nitrogen environment and those of Ref. 18 who used an argon environment. It is seen that the trends are similar but the lifetime in Ref. 18 reaches a plateau above about 8 kPa (70 torr), but such a plateau is not reached even at the highest pressures of the current study. Beddard et al.18 proposed that the increase in fluorescence lifetime with increasing pressure is because the vibrational levels are not in equilibrium at low pressures, but they attain equilibrium at high pressure. An estimate of the lifetime at high pressures (equilibrium distribution) using previously measured quenching constants was also made in Ref. 18. They estimated a lifetime of 180 ns at a pressure of about 80 torr, which is very similar to the value that we obtain in our measurement. The differences observed in Fig. 10 may be due to the weak quenching effects of the nitrogen as compared to argon, or possibly to self-quenching of naphthalene. Naphthalene is a weak quencher but is present at a mole fraction of about 1%.

The collisional stabilization model of Beddard et al.15 is not clearly established at the pressures tested for the case of nitrogen since a plateau has not yet been reached. Other researchers have also reported non-equilibrium of the vibrational levels at low pressures.15,17,21 Behlen et al.15 studied the variation of lifetime with increasing photon energy (increasing the frequency of irradiation), and found that the fluorescent lifetimes at low pressure decreased with increasing photon energy. They attributed it to an increase in population in higher vibrational levels with increasing photon energy. This view was further corroborated by Schlag et al.28, who showed that the fluorescent lifetime decreases with increasing vibrational levels. Avouris et al.29 or Schlag et al.28 present a detailed discussion of the lifetimes of different vibronic states. The trend in the fluorescence lifetime found in the present experiments can be explained with the above results. At low pressures, the laser pulse excites the molecules to the $S_1$ vibronic states, and the molecules undergo a rapid internal transfer to the $S_0$ vibronic states (at rates of $10^{10}$ s$^{-1}$). At low pressures, lack of collisions locks the population in these upper vibrational states, whose fluorescent decay times are short (on the order of 50 ns). However, at higher pressure, the upper states are more thermalized and so the lower

![Figure 7. Temperature dependence of: (a) naphthalene LIF signal at atmospheric pressure, and (b) absorption cross-section (T_{ref}=300 K).](image)
vibrational states are more highly populated. These lower vibrational states have a longer decay time constant compared to the higher states, which is seen as the increased fluorescence time constant at higher pressures. Figure 9 also shows that the lifetimes measured in the nitrogen environment and in pure-air environment as \( P \rightarrow 0 \), are very similar to one another. This of course is expected, and provides some validation of the experimental technique employed.

_Ablation in a Mach 5 Turbulent Boundary Layer_

A set of experiments were conducted to determine the feasibility of using PLIF of sublimating naphthalene to visualize the dispersion of ablation products in a Mach 4.95 turbulent boundary layer. The boundary layer developed naturally on the wall of the wind tunnel and had the following properties: 99% velocity thickness \( \delta_{99} = 19.3 \text{ mm} \), momentum thickness \( \theta = 0.76 \text{ mm} \), shape factor \( H = 12 \), momentum thickness Reynolds number \( \text{Re}_\theta = U_\infty \theta / \nu_\infty = 3.8 \times 10^4 \), and skin friction coefficient \( C_f = 7.6 \times 10^{-4} \).

Tests were conducted in two campaigns; the first was very preliminary and had several conditions that were improved in the second campaign. For example, in these initial studies the naphthalene insert was small, only 2.5 cm long by 5 cm wide. Furthermore, the stagnation temperature of the tunnel was 345 K and the camera used was an intensified CCD camera (Princeton Instruments PI-Max). The laser energy delivered to the test section was about 50 mJ and the sheet width and thickness were 150 mm and 1 mm, respectively. This gave a fluence of about 330 J/m^2, which is somewhat outside of the linear region. An example PLIF image is shown in Fig. 11. The field of view for this image is 22.9 mm wide by 15.7 mm high, and is 50 mm downstream of the naphthalene insert. This figure shows that the naphthalene ablation technique is quite promising for visualizing the transport of ablation products, but we see the signal-to-noise ratios are quite low (less than 5).

The second campaign was focused on improving the PLIF signal levels. Since the fluorescence saturates at relatively low laser energy, it is not possible to significantly improve the SNR by increasing the laser energy in a given pulse. Instead, two laser pulses of laser light were used, separated in time by 100ns, so that more energy could be delivered to the flow, but without increasing the laser intensity. Each laser pulse had energy of 30 mJ per pulse delivered to the flow. The laser sheet was about 150 mm wide and 1 mm thick. The resulting fluence was about 200 J/m^2, which is within the linear regime. Note that since the cameras integrate over the two pulses, the images are slightly blurred due to flow motion. However, this blurring effect is negligible because the flow convects a maximum of .08 mm, which is about one pixel width, between pulses.
The double-pulsing enabled us to obtain about a factor-of-two increase in signal, but the main means of improving SNR was to increase the naphthalene concentration in the boundary layer. The main improvements were to increase the size of the ablating surface and to raise the stagnation temperature of the wind tunnel. The size of the insert was increased by about a factor of six and this design was described in the experimental program section above. The largest improvement was obtained by increasing the stagnation temperature of the tunnel from about 345 K to 375 K. The saturation pressure of naphthalene increases by about a factor of 3 for each 10°C increase in temperature, and so heating is potentially very effective at increasing the signal. Note, however, that the surface of the naphthalene is not the same as the stagnation temperature since the sublimation process cools the surface, which is purpose of an ablator. The temperatures of the naphthalene 1 mm, 5.1 mm, and 8.9 mm below the surface were measured during each run at the center of the naphthalene plug with type T thermocouples and were found to be steadily increasing. It was noted that as the stagnation temperature increased to its steady state value at the beginning of each run, the fluorescence signal was seen to increase. This simply reflected the increase in naphthalene vapor pressure with temperature. It took about 30 seconds for the temperature to reach a steady state, and typically images were captured for about 30 seconds during this steady state period.

Figure 12 shows instantaneous naphthalene PLIF images after the stagnation temperature had reached a steady state. In this case the field of view started 105 mm (x/δ99=5.4) downstream of the downstream edge of the naphthalene insert. The size of the field of view was 27 mm wide by 14 mm high. The images show that the fluorescence signal-to-noise ratio is approximately 20, which represents a major improvement over the images obtained in the first campaign. The ablation products are seen to be confined to be quite close to the wall of the wind tunnel. It appears though, that the scalar is transported out into the boundary layer in bursts in accordance with known transport mechanisms in turbulent boundary layers.

To show the development of the scalar transport over a wider field of view, Fig. 13 shows a composite of two instantaneous (but uncorrelated) naphthalene PLIF images. The total field of view spans 2.8δ99 in the streamwise direction. The first image starts 78 mm (x/δ99=3.98) downstream of the downstream edge of the naphthalene insert. In future work a wider range of downstream locations will be explored.

The mean fluorescence profile was computed from a set of 18 images like Fig. 12. To improve the statistics, the pixel-columns were averaged; i.e., the images were averaged in the streamwise direction as well as time. Figure 14 shows a plot of the normalized mean LIF signal through the boundary layer. The naphthalene PLIF signal is seen to peak at the wall and exhibit a gradual decrease in magnitude with increasing distance from the wall.

The objective of the previously described spectroscopic studies is to enable us to correct the measured naphthalene LIF signals to obtain quantitative measurements of naphthalene mole fraction. The dominant effect on the fluorescence signals will be the temperature effect, since the mean pressure across the boundary layer is approximately constant. For example, as the naphthalene is transported from the wall to say the midpoint of the boundary layer it may cool from say 370 K at the wall to 100 K. Although we currently do not have spectroscopic data at temperatures below 300 K, we can go through a correction process that will be used once the data are available. For example, we currently have data on the temperature dependence of the fluorescence signal and absorption cross-section at atmospheric pressure, for which the fluorescence is quenching dominated. In this case we have,

\[
\frac{S_f(T)}{S_f(T_{ref})} = \frac{T_{ref} \sigma_s(T) k_f(T) k_q(T_{ref})}{T \sigma_s(T_{ref}) k_f(T_{ref}) k_q(T)}
\]  

Figure 10. Fluorescence lifetime measurements for naphthalene diluted in nitrogen (current work) and argon (Beddard et al.18).
If we assume that the spontaneous emission rate and quenching cross-section for oxygen are temperature independent, then we have,

\[
\frac{S_f(T)}{S_f(T_{ref})} = \frac{\sigma_v(T)}{\sigma_v(T_{ref})} \left( \frac{T_{ref}}{T} \right)^{1/2},
\]

which we can use to obtain the temperature dependence of the cross-sections. Now, at the conditions of the Mach 5 boundary layer, the pressure is 30 Torr and the fluorescence is not quenching dominated. In this case, for the same assumptions as above, we can write,

\[
\frac{S_f(P,T)}{S_{f_{max}}} = \frac{\chi_{naph}}{(\chi_{naph})_{max}} \frac{(T/T_{ref})_{max}}{(T/T_{ref})} \frac{\sigma_v(T) / \sigma_v(T_{ref})}{\sigma_v(T_{ref})_{max}} (k_f + k_{int} + k_Q(P,T_{max}))
\]

This equation can be used to obtain the normalized mole-fraction of naphthalene vapor from the normalized fluorescence signal. Here we obtain the temperature profile in the boundary layer from the Crocco-Busemann formula and the known mean velocity profile. Since we do not have absorption cross-section data at lower temperatures, we simply extrapolate the data in Fig. 7(b) to low temperature. Obviously, this is a very coarse assumption that will be checked in our future studies. Finally, we take the quenching rate from the quenching measurements and the assumed form as given in Eq. 3. The corrected mean is shown in Fig. 14. We caution that this is only a proof-of-concept exercise to show how the fluorescence data can be corrected to obtain quantitative results, provided the absorption data can be measured at low-temperatures. In future work, our intention is to make the required LIF temperature-dependence measurements. In addition we plan to measure simultaneous velocity and naphthalene PLIF by the PIV technique. The simultaneous PIV data will enable us to obtain estimates of the instantaneous temperature by using the Crocco-Busemann formula.

It is clear that if this technique is to be made quantitative, it will be necessary to have some idea of the local conditions, because the fluorescence signal is strongly dependent on them. It is clear that having a simultaneous measurement of temperature is critical. In the case of a boundary layer, this information can be achieved with a separate velocity measurement (and Crocco-Busemann), but in cases where measuring velocity is not possible then it may be possible to use a dual-line excitation method to infer the temperature, as has been done with acetone.\(^{13}\) This possibility will also be explored in future studies. In cases where the free-stream pressure varies widely, such as over the shoulder of a blunt re-entry vehicle, it may be necessary to use simultaneously-acquired data from pressure taps, or perhaps a numerical simulation, to obtain a first-order estimate for the local pressure.
Planar laser-induced fluorescence has been used to image the ablation products given off by a sublimating ablator in the presence of a Mach 5 boundary layer. Naphthalene is used as the ablator because its vapor is readily detected by the laser-induced fluorescence technique with 266 nm excitation. The results show that excellent signal-to-noise-ratio PLIF images can be obtained with this technique. Furthermore, it is an objective of this work to conduct targeted spectroscopic studies to enable the quantitative interpretation of the PLIF signal in terms of naphthalene mole fraction. To date, test-cell measurements have been made to determine the fluorescence signal and absorption cross-section dependence on temperature, over temperature range of 297 K to 525 K. On a per-mole basis, the temperature dependence of naphthalene fluorescence increases sharply at lower temperatures and levels off with higher temperatures, whereas the absorption cross-section exhibits a more gradual increase with

V. Conclusion

Planar laser-induced fluorescence has been used to image the ablation products given off by a sublimating ablator in the presence of a Mach 5 boundary layer. Naphthalene is used as the ablator because its vapor is readily detected by the laser-induced fluorescence technique with 266 nm excitation. The results show that excellent signal-to-noise-ratio PLIF images can be obtained with this technique. Furthermore, it is an objective of this work to conduct targeted spectroscopic studies to enable the quantitative interpretation of the PLIF signal in terms of naphthalene mole fraction. To date, test-cell measurements have been made to determine the fluorescence signal and absorption cross-section dependence on temperature, over temperature range of 297 K to 525 K. On a per-mole basis, the temperature dependence of naphthalene fluorescence increases sharply at lower temperatures and levels off with higher temperatures, whereas the absorption cross-section exhibits a more gradual increase with

Figure 12. Instantaneous naphthalene PLIF images in a Mach 5 turbulent boundary layer.
temperature. Stern-Volmer plots show a linear variation of the inverse lifetime with pressure, which indicates the fluorescence follows a conventional quenching model at pressures greater than 2 kPa (40 torr). It was further found that for the fluorescence to remain linear with laser fluence, the laser fluence should be less than about 200 J/m².

To obtain quantitative concentration information in the Mach 5 turbulent boundary layer, the naphthalene PLIF images will need to be corrected for temperature effects since the boundary layer temperature can vary considerably with distance from the wall. A correction procedure was demonstrated that used velocity data to obtain the needed temperature information. However, a limitation of this process was the lack of absorption cross-section data at the lowest temperatures encountered in the boundary layer. Obtaining this needed data will be a major focus of our future efforts.

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