

## 2D THICKNESS AND TEMPERATURE MAPPING OF FLUIDS BY MEANS OF A TWO-DYE LASER INDUCED FLUORESCENCE RATIOMETRIC SCHEME

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*This paper presents the principles behind the use of a two-dye Laser Induced Fluorescence (LIF) technique for two-dimensional film thickness and temperature mapping of fluids. The need for two fluorescent emissions arises as a consequence of the fluorescence dependence on excitation light intensity. A ratiometric scheme that normalizes the fluorescent emission of one dye against the fluorescent emission of a second dye is used in order to eliminate undesirable effects due to illumination intensity fluctuations, in both space and time, and optical distortions. The same ratiometric scheme is applied for both film thickness and temperature measurements, but the required spectral characteristics of the dyes used and the optical conditions differ significantly between the two measurements. The concepts of emission reabsorption and optical thickness are discussed in light of the requirements for each particular measurement. Experimental validation of the technique in measuring the thickness and temperature of a film of lubricating oil is also presented.*

### INTRODUCTION

Laser Induced Fluorescence (LIF) has been extensively used as a general-purpose visualization tool in 1D, 2D, and 3D applications. However, it is mainly employed as a tracer for qualitative purposes, and has seen very limited use as a quantitative tool. This stems primarily from the fact that fluorescent intensity is dependent on exciting light intensity; thus, variations in exciting light intensity make fluorescence-based correlations (fluorescence calibrations) very impractical if not obsolete. By using two different fluorescent dyes and ratiometric their emissions it is possible to get rid of the exciting light intensity information, while preserving the information of interest. Presented herein is the application of this ratiometric approach in the measurement and 2D mapping of thickness and temperature in fluid films.

In a fluorescence process, an external light source (incandescent lamp or laser, in the present case) is used to excite a fluorescent substance (fluorophore or fluorescent dye). The external source supplies photons of energy  $h\nu_{EX}$ , which are absorbed by the fluorophore. Consequently, the fluorophore molecules go from a ground electronic state ( $S_0$ ) to a higher excited electronic singlet state ( $S_1'$ ) (Fig. 1). This excited

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## NOMENCLATURE

$A$	area of one pixel	$t$	film thickness
$C$	dye molar concentration, effective two-dye molar concentration	$T$	temperature
$C_1$	dye 1 molar concentration	$T_{avg}$	average temperature in the direction perpendicular to plane of observation
$C_2$	dye 2 molar concentration	$W$	film sample width
$D$	collecting lens diameter	$x$	coordinate perpendicular to plane of observation
$df_f$	differential fluorescent intensity	$y$	coordinate parallel to plane of observation
$df_{f,1}$	dye 1 differential fluorescent intensity, without reabsorption	$\epsilon(\lambda)$	molar absorption (extinction) coefficient at a given wavelength (absorption spectrum); effective two-dye molar absorption (extinction) coefficient
$df'_{f,1}$	dye 1 differential fluorescent intensity, with reabsorption	$\epsilon_1(\lambda)$	dye 1 molar absorption (extinction) coefficient at a given wavelength (absorption spectrum)
$dV$	differential volume element	$\epsilon_{1,0}(\lambda)$	dye 1 molar absorption (extinction) coefficient zero temperature reference value at a given wavelength
$dx$	differential length in $x$ -direction	$\epsilon_2(\lambda)$	dye 2 molar absorption (extinction) coefficient at a given wavelength (absorption spectrum)
$F$	fluorescence power	$\Phi$	quantum efficiency
$h$	Planck's constant	$\Phi_1$	dye 1 quantum efficiency
$I_e$	exciting light intensity	$\Phi_2$	dye 2 quantum efficiency
$I_f$	total fluorescent intensity	$\eta_1(\lambda)$	dye 1 relative emission at a given wavelength (emission spectrum)
$I_{f,1}$	dye 1 total fluorescent intensity, without reabsorption	$\eta_2(\lambda)$	dye 2 relative emission at a given wavelength (emission spectrum)
$I'_{f,1}$	dye 1 total fluorescent intensity, with reabsorption	$\nu_{EM}$	light wave frequency of emission
$I_{f,2}$	dye 2 total fluorescent intensity	$\nu_{EX}$	light wave frequency of excitation
$I_0$	exciting light intensity at $x = 0$	$\lambda_{laser}$	laser wavelength
$k$	molar absorption (extinction) coefficient temperature dependence proportionality constant	$\lambda_{filter1}$	narrow band filter 1 wavelength
$L$	distance from sample to collecting lens	$\lambda_{filter2}$	narrow band filter 2 wavelength
$S_0$	ground state	$\tau$	time
$S_1$	relaxed singlet excited state	$\xi$	monitoring efficiency
$S'_1$	singlet excited state		

state only exists for a very short period of time (typically  $1-10 \times 10^{-9}$  seconds). During this time, the molecules undergo conformational changes and interactions with other molecules, lowering the excited energy state to a lower relaxed singlet excited state ( $S_1$ ), from which fluorescence originates. For some of the excited mole-

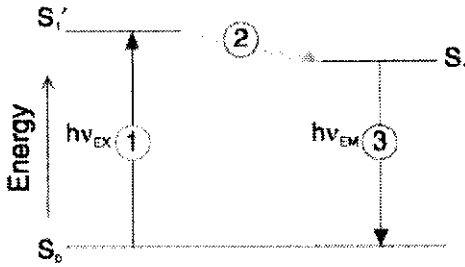


Fig. 1 Fluorescence principle (from [1]).

cules the interactions might be so severe and strong that the drop in energy returns them to the ground state ( $S_0$ ), giving up heat in the process instead of fluorescent emission. The ratio of the number of molecules returning to the ground state by fluorescent emission over the total number of molecules excited is termed the fluorescence quantum yield. Because of the energy drop from  $S_1'$  to  $S_1$ , those molecules returning to the ground state via fluorescent emission will give up a photon of energy  $h\nu_{EM}$ , lower than the exciting photon energy  $h\nu_{EX}$ . This difference in energy is called the Stoke's shift and it allows separation of the excitation light from the fluorescent emission (different wavelengths) [1].

From this description it is apparent that the fluorescent intensity, aside from being dependent on the molecular characteristics and concentration of the fluorophore, is directly related to the number of exciting photons available, that is, to the exciting light intensity. In general, one would try to measure a scalar quantity that affects the fluorescent intensity, via a molecular characteristic dependence, as in the case of temperature, or through the number of molecules (dye amount) present at a particular location, as in the case of film thickness. The problem lies in the intensity fluctuations, both in space and time, of the light source. This is especially true for lasers. Most laser beams are not uniform. They fluctuate in intensity in space and time. Pulsed Nd:YAG lasers are particularly prone to exhibit this behavior. Use of pulsed Nd:YAG lasers is desirable though, because of their short pulse duration (consequently short fluorescent emission), which allows for nearly instantaneous measurements of the desired scalar, their high power output, and their visible spectrum when frequency doubled (532 nanometer wavelength).

In order to correlate the instantaneous two-dimensional fluorescent intensity to the scalar of interest, temporal and spatial variations in illumination intensity must be determined and accounted for. This can be accomplished by using a ratiometric technique where the fluorescent intensity containing the desired scalar information is

divided by the laser intensity eliminating the fluorescence dependence on excitation intensity. One way to achieve this is by using two dyes, simultaneously recording their fluorescent emissions, and observing their ratio. The emissions contain the desired scalar information as well as information on the excitation light source intensity. By observing the ratio of the emissions of each dye, variations in excitation intensity can be minimized. This technique has been extensively used for measuring pH and temperature and is known as Dual Emission Laser Induced Fluorescence (DELIF) [2, 3] and Two Color LIF [4], respectively. The current work extends this technique to measure film thickness by using emission reabsorption as a means of embedding the thickness information in the fluorescence. Presented herein are the principles and optical conditions necessary to achieve film thickness and temperature measurements using a two-dye ratiometric approach.

## 1. LIF BACKGROUND

### Optically Thin versus Optically Thick

Consider a rectangular differential volume element of fluid mixed with a fluorescent dye with cross-sectional area  $A$  and length  $dx$  irradiated by light (normal to the area  $A$ ) with uniform intensity  $I_e$  (Fig. 2). The total fluorescence,  $F$ , emitted by this differential volume is given by:

$$F = I_e \epsilon(\lambda_{laser}) C \Phi dV \quad (1)$$

From Eq. (1), it is evident that fluorescence is dependent on:

- (1) the amount of exciting light available to produce molecular transitions to higher, excited levels;
- (2) molar absorptivity, which determines how much of the incident light per molecule produces actual molecular transitions;

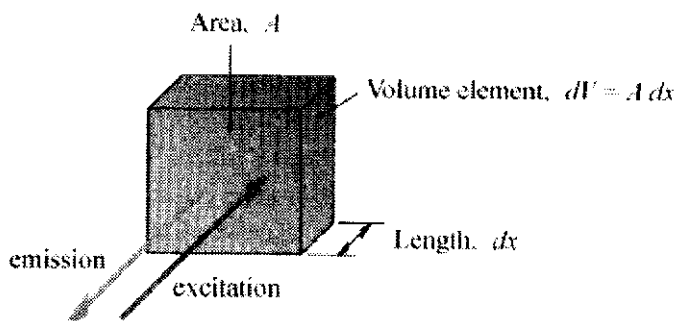


Fig. 2 Fluorescence of fluid element.

- (3) dye concentration, which is a measure of the number of molecules present;
- (4) quantum efficiency, which is the ratio of the energy emitted by the energy absorbed, and is a measure of how much of the energy stored in the higher electronic states is emitted as fluorescent light, when the molecules return to their ground state; and,
- (5) the volume of the element, which is the control volume over which excitation and fluorescence takes place.

If the area  $A$  is assumed to be the projected area of a single pixel, the intensity collected by a CCD pixel from this differential fluorescent element is given by:

$$I_f = I_e \epsilon(\lambda_{laser}) C \Phi dx \quad (2)$$

The previous analysis assumes that all the fluorescent light emitted by the differential volume element is collected by the imaging system. In reality, since the fluorescent light is pointed in all directions, only a fraction of the total fluorescence emitted by a differential volume element is collected by the CCD detector. This is referred to as the "monitoring efficiency" of the system [5], and is a function of the size of the aperture of the collecting system (lens diameter in this case) and the distance from the emission location to the aperture (Fig. 3). For such an arrangement, the monitoring efficiency is given by:

$$\xi(x, y) = \frac{1}{2} \left[ 1 - \frac{x+L}{\sqrt{(x+L)^2 + (D/2)^2}} \right] \left[ \frac{x+L}{\sqrt{(x+L)^2 + y^2}} \right]^4 \quad (3)$$

If the thickness and sample half-width over which fluorescence takes place are much smaller than the distance from the fluorescent sample to the collecting system aperture, the "monitoring efficiency" can be approximated as:

$$\xi \cong \frac{1}{2} \left[ 1 - \frac{L}{\sqrt{L^2 + (D/2)^2}} \right] = \text{const.} \quad (4)$$

which is a constant (between 0 and 1) over the entire thickness of the sample. Both of the previous conditions are achieved with the use of a long working distance lens. Therefore, the only modification required on the analysis is a multiplication of Eq. (2) by this constant. This constant, as it will become clear later, is eliminated in the ratio of dye emission intensities and is, thus, inconsequential. Because of this, this constant does not appear in the following analysis.

It is apparent that pixel intensity is proportional to the excitation intensity, dye characteristics, concentration, and thickness of the fluid element. For very thin film thickness, this representation is accurate. If the excitation intensity is known and dye

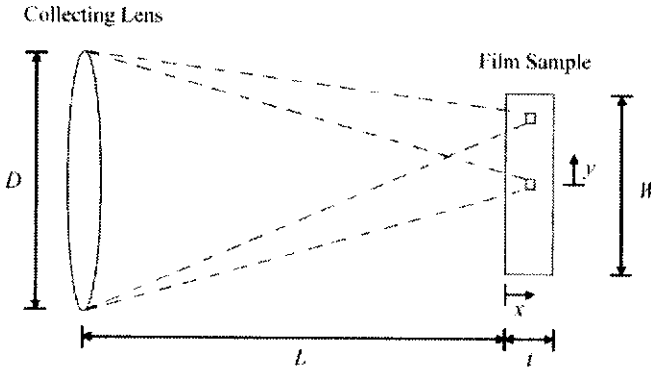


Fig. 3 Monitoring efficiency.

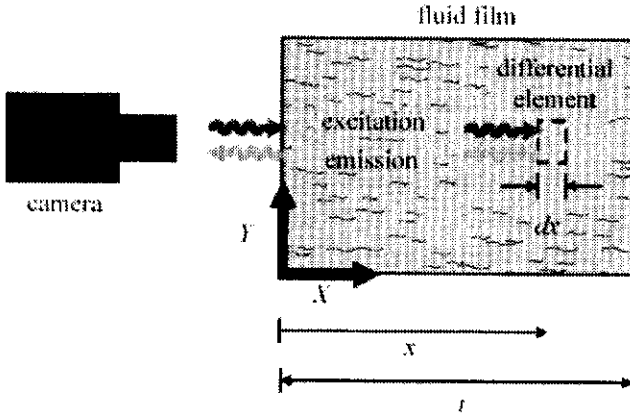


Fig. 4 Fluorescence through a thick fluid film.

characteristics and concentration are constants, the fluid film thickness can be directly inferred from the fluorescence. A more accurate representation of the fluorescence phenomena can be obtained from Beer-Lambert's Law of Absorption [6], which takes into account the absorption of the exciting light by the finite fluid through which it travels:

$$I_e(x) = I_0 \exp [-\epsilon(\lambda_{laser})Cx] \tag{5}$$

Consider the differential element shown in Fig. 4 within a region of finite film thickness. The fluorescent intensity collected by the CCD from this fluid element is:

$$dI_f = I_e \epsilon(\lambda_{laser})C\Phi dx \tag{6}$$

Thus, from Eqs. (5) and (6):

$$dI_f = I_o \exp[-\varepsilon(\lambda_{laser})Cx] \varepsilon(\lambda_{laser}) C \Phi dx \quad (7)$$

For a given fluid thickness,  $t$ , the total intensity collected by the CCD is:

$$I_f(t) = \int_0^t dI_f = \int_0^t I_o \exp[-\varepsilon(\lambda_{laser})Cx] \varepsilon(\lambda_{laser}) C \Phi dx \quad (8)$$

such that

$$I_f(t) = I_o \Phi \left[ 1 - \exp[-\varepsilon(\lambda_{laser})Ct] \right] \quad (9)$$

For small values of  $t$  (thin films), Eq. (9) can be approximated as:

$$I_f(t) \approx I_o \varepsilon(\lambda_{laser}) C \Phi t \quad (10)$$

This is identical to Eq. (2) and is the basis for the concepts of optically thin and optically thick systems. The fluorescence's dependence on film thickness is linear (or more properly, quasi-linear) for optically thin systems, while it is exponential for optically thick systems. What is considered a thin or thick film thickness depends on the product  $\varepsilon(\lambda_{laser})C$ .

## Reabsorption

Emission reabsorption is often encountered in fluorescent techniques and is generally regarded as problematic. Fluorescent dyes are characterized by their absorption and emission spectrums (Fig. 5). When the emission spectrum of one dye overlaps the absorption spectrum of another or with its own absorption spectrum, reabsorption of the dye fluorescence occurs (Fig. 6). This has two effects: (1) it increases the fluorescent emission of the second dye as, in addition to the external light source excitation, it is being excited by the fluorescence of the first dye; more importantly, (2) the fluorescent emission of the first dye is reduced since it is being reabsorbed by the second dye. In LIF, the external illumination intensity is generally much greater than dye fluorescent emission. Consequently, the increase in fluorescent emission due to excitation by the fluorescence of one dye by another can be neglected. This is not the case for the reduction in fluorescence of a dye due to reabsorption by a second dye since this reduction can be substantial in comparison with the total emission of the dye when there is no reabsorption. From the differential element of Fig. 4, it is apparent that the differential fluorescent emission produced by any single element must travel back through the medium before reaching the CCD.

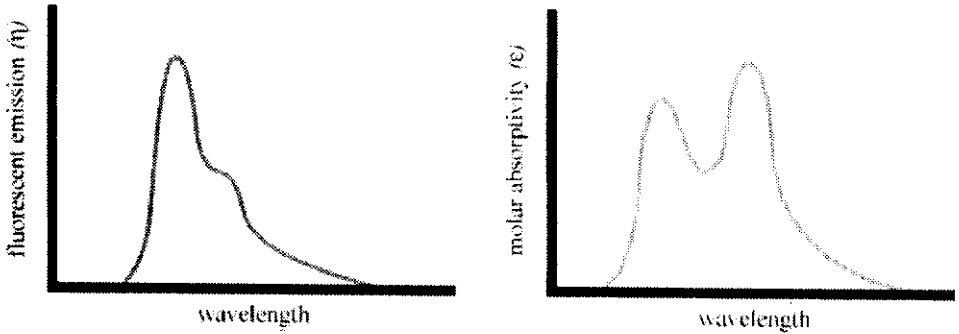


Fig. 5 Emission and absorption spectra.

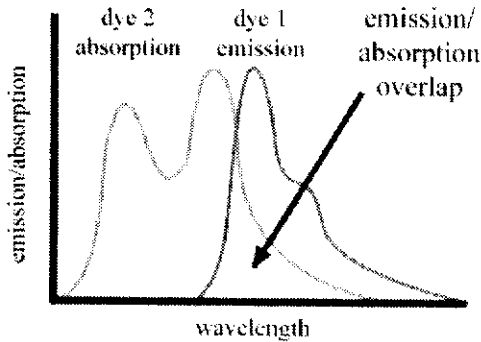


Fig. 6 Reabsorption schematic.

If there is reabsorption of the differential element fluorescence, Lambert's law must be applied to the differential fluorescent emission in order to compute the actual fluorescence collected by the CCD. Thus, assuming the situation represented in Fig. 6 occurs:

$$dI_{f,1} = I_o \exp[-\varepsilon(\lambda_{laser})C_1x] \varepsilon_1(\lambda_{laser}) C_1 \Phi_1 \eta_1(\lambda) dx d\lambda \quad (11)$$

$$dI_{f,1}' = dI_{f,1} \exp[-\varepsilon_2(\lambda)C_2x] \quad (12)$$

$$dI_{f,1}' = I_o \exp[-\varepsilon(\lambda_{laser})C_1x] \varepsilon_1(\lambda_{laser}) C_1 \Phi_1 \eta_1(\lambda) \exp[-\varepsilon_2(\lambda)C_2x] dx d\lambda \quad (13)$$



Equation (7) has been modified in Eq. (11) to reflect the fact that the fluorescent emission occurs over a wide range of wavelengths that constitute the emission spectrum. In the same way, Eqs. (12) and (13) portray a reabsorption that occurs over a wide range of wavelengths. If the emission spectrum of dye 1 and the absorption spectrum of dye 2 are known, Eq. (13) can be integrated over varying film thickness and wavelengths in order to compute the total intensity collected by the CCD. If a very narrow interference filter is used to filter all wavelengths except for the one of interest, Eq. (13) can be simplified by removing the dependence of the differential intensity on the emission and absorption spectrums. Thus, the total intensity collected on the CCD can be calculated as [7]:

$$I_{f1}(t, \lambda_{filter1}) = \int_0^l I_o \exp[-\varepsilon(\lambda_{laser})C_1 x] \varepsilon_1(\lambda_{laser}) C_1 \Phi_1 \eta_1(\lambda_{filter1}) \exp[-\varepsilon_2(\lambda_{filter1})C_2 x] dx \quad (14)$$

$$I_{f1}(t, \lambda_{filter1}) = \frac{I_o \varepsilon_1(\lambda_{laser}) C_1 \Phi_1 \eta_1(\lambda_{filter1}) (1 - \exp\{-[\varepsilon(\lambda_{laser})C_1 + \varepsilon_2(\lambda_{filter1})C_2]t\})}{\varepsilon(\lambda_{laser})C_1 + \varepsilon_2(\lambda_{filter1})C_2} \quad (15)$$

For reabsorption to play a significant role on the fluorescence, the system must be optically thick and  $\varepsilon_2(\lambda_{filter1})C_2 \gg O[\varepsilon(\lambda_{laser})C_1]$ .

## 2. TWO-DYE RATIO-METRIC TECHNIQUE

### Principle

In the previous analysis, based on Fig. 4, and in Eqs. (1) through (15), the non-uniformities of the exciting light intensity over the plane of observation and in time are not taken into consideration. In reality, illumination intensity is a function of both position and time:

$$I_o = I_o(y, \tau) \quad (16)$$

Therefore,

$$I_f = I_f(t, \lambda, y, \tau) \quad \text{or} \quad I_f = I_f(T, \lambda, y, \tau) \quad (17)$$

depending on whether or not there is a fluorescence dependence with temperature. Consequently, the scalar of interest (in this case film thickness and/or temperature)

cannot be inferred from fluorescent intensity unless illumination intensity at a particular location and time is known. The ratio of the fluorescent intensity and the illumination intensity, however, is independent of spatial and temporal variations in excitation light intensity:

$$\frac{I_f}{I_o} \equiv R = R(t, \lambda) \quad \text{or} \quad \frac{I_f}{I_o} \equiv R = R(T, \lambda) \quad (18)$$

Notice that in the case of film thickness measurements, the ratio is still dependent on thickness, while for temperature measurements this is not the case. As it will become clear later, this can be achieved by using an optically thick system with reabsorption for film thickness measurements and an optically thin system for temperature measurements.

Obtaining illumination intensity is not trivial. A two-dimensional instantaneous illumination map, however, can be inferred from the fluorescence of a second dye. This is the principle behind the two-dye fluorescence scheme:

- (1) the fluorescence of dye 1 in a two-dye system contains the desired information (film thickness, temperature, which will be discussed later), along with exciting light intensity information;
- (2) the fluorescence of dye 2 also contains the exciting light intensity information but behaves differently than dye 1 to the scalar of interest;
- (3) by rationing the fluorescence of dye 1 with the fluorescence of dye 2, the excitation light information is canceled out, giving a ratio that contains only the desired scalar information.

## Film Thickness

Film thickness measurements are achieved using an optically thick system that takes advantage of reabsorption. Film thickness information is contained in both fluorescent emissions due to the absorption of the exciting light (laser in this case). But in addition to this, film thickness information is also embedded in the emission of dye 1 due to the reabsorption of the fluorescence of dye 1 by dye 2. The excitation light intensity information is contained both in the fluorescence of dye 1 and dye 2. If two narrow-band interference filters are used to capture the two distinctive fluorescent emissions, we can compute their intensities using the analysis that led to Eqs. (9) and (15). Since there is reabsorption of dye 1 by dye 2, the reduced fluorescent emission of dye 1 is given by [7]:

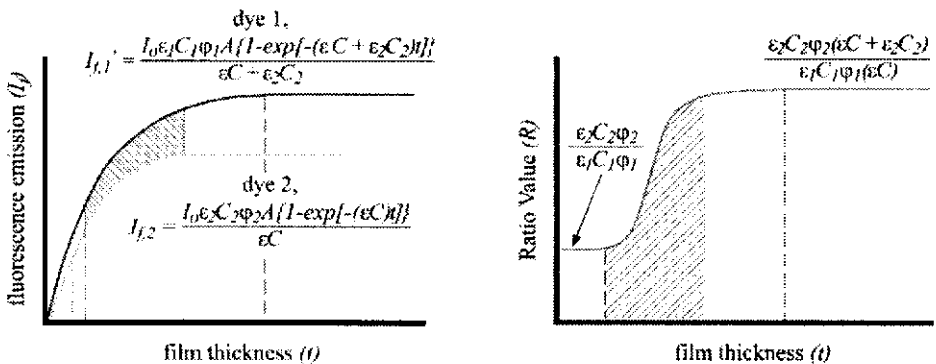
$$I_{f1}(t, \lambda_{filter1}, y, \tau) = \frac{I_0(y, \tau) \epsilon_1(\lambda_{laser}) C_1 \Phi_1 \eta_1(\lambda_{filter1}) (1 - \exp\{-[\epsilon(\lambda_{laser}) C + \epsilon_2(\lambda_{filter1}) C_2] t\})}{\epsilon(\lambda_{laser}) C + \epsilon_2(\lambda_{filter1}) C_2} \tag{19}$$

As mentioned before, the reabsorption of dye 1 by dye 2 introduces a boosting element to the fluorescent emission of dye 2, due to an increase of the exciting light. However, this increase in excitation intensity is minimal compared to the laser intensity and can thus be neglected. Therefore, the fluorescent intensity of dye 2 is given by:

$$I_{f2}(t, \lambda_{filter2}, y, \tau) = \frac{I_0(y, \tau) \epsilon_2(\lambda_{laser}) C_2 \Phi_2 \eta_2(\lambda_{filter2}) (1 - \exp\{-[\epsilon(\lambda_{laser}) C] t\})}{\epsilon(\lambda_{laser}) C} \tag{20}$$

Taking the ratio of these intensities we get:

$$R(t, \lambda_{filter1}, \lambda_{filter2}) = \frac{I_{f1}}{I_{f2}} = \frac{\epsilon_1(\lambda_{laser}) C_1 \Phi_1 \eta_1(\lambda_{filter1}) \epsilon(\lambda_{laser}) C (1 - \exp\{-[\epsilon(\lambda_{laser}) C + \epsilon_2(\lambda_{filter1}) C_2] t\})}{\epsilon_2(\lambda_{laser}) C_2 \Phi_2 \eta_2(\lambda_{filter2}) [\epsilon(\lambda_{laser}) C] (1 - \exp\{-[\epsilon(\lambda_{laser}) C] t\})} \tag{21}$$



$$R(t) = \frac{I_{f2}}{I_{f1}'} = \frac{\epsilon_2 C_2 \Phi_2 (\epsilon C + \epsilon_2 C_2) \{1 - \exp[-(\epsilon C)t]\}}{\epsilon_1 C_1 \Phi_1 (\epsilon C) \{1 - \exp[-(\epsilon C + \epsilon_2 C_2)t]\}}$$

Fig. 7 Film thickness ratio.

By taking the ratio of the emission of the two dyes, the excitation light intensity dependence is cancelled leaving a ratio that is only dependent on film thickness. As film thickness information is contained in the reabsorption of the fluorescence of dye 1 by dye 2, the system must be optically thick, in order for the reabsorption to be substantial and measurable (Fig. 7). We have labeled this film thickness measurement technique with the name *Emission Reabsorption Laser Induced Fluorescence (ERLIF)* [7].

## Temperature

It is possible to use LIF as a temperature indicator when there is a dependence of either the molar absorption (extinction) or quantum efficiency coefficients on temperature:

$$\epsilon = \epsilon(T) \quad (22)$$

and/or

$$\Phi = \Phi(T) \quad (23)$$

The problem of separating the temperature information from the exciting light intensity contained in the fluorescence still exists. This is further complicated by the film thickness information that is also imbedded in the fluorescence. The same two-dye fluorescence ratiometric approach used to separate the film thickness information from the exciting light intensity information can be used for temperature measurement. However, the optical conditions for proper temperature measurement are quite different from those of film thickness measurement. Reabsorption of one dye fluorescence by the other must be avoided as it adds film thickness information to the fluorescence making it difficult to separate the temperature information contained in the fluorescence. In addition, the system must be optically thin. There are two reasons for this: (1) even if there is reabsorption (it is hard to control whether a system will have reabsorption or not, and in most practical situations reabsorption is present), an optically thin system will ensure that the reabsorption effects are minimal as the fluorescence is approximately linear with film thickness; more importantly, (2) it is easier to deal with temperature variations in the direction of observation (i.e.,  $x$  direction in Fig. 4). Let us explore the last point in more detail. The goal in using fluorescence for temperature measurement is to obtain a two-dimensional map of temperature, that is, temperature variations in the plane of observation. It, however, is very likely that the temperature field also varies in the direction of observation. If this is the case and if, in particular, Eq. (22) holds, one can rewrite Eq. (8) as:

$$I_f(t, T) = \int_0^t dI_f = \int_0^t I_o \exp[-\varepsilon(\lambda_{laser}, T)Cx] \varepsilon(\lambda_{laser}, T)C\Phi dx \quad (24)$$

However, since  $T = T(x)$ , Eq. (24) cannot be integrated unless the temperature field as a function of  $x$  is known. This implies that, in order to correlate fluorescence to temperature, an *a priori* knowledge of the temperature field in the direction of observation is needed, defeating the purpose of the technique. Thus, the two-dimensional temperature map cannot be easily inferred from the fluorescence for optically thick films if the fluorescence temperature dependence is contained in the molar absorption (or extinction) coefficient. In general, it is difficult to correlate fluorescence with temperature if there are temperature variations in the direction of observation. However, if the temperature dependence is contained in the quantum efficiency coefficient and/or the system is optically thin, the effects of temperature variation in the direction of observation on the fluorescence are not as substantial and a more accurate two-dimensional map of the temperature can be obtained [8]. In the limit of optically thin systems, the fluorescence will correlate to the average temperature of the film in the direction of observation, provided that Eq. (22) or (23) is linear with respect to temperature.

In order to see this, let's assume that the absorptivity of dye 1 is a function of temperature and is given by:

$$\varepsilon_1(\lambda_1, T) = \varepsilon_{1,o}(\lambda_{laser}) - kT \quad (25)$$

Equation (25) implies a decrease of the absorptivity (and therefore the fluorescence) with temperature. Generally, temperature dependent dyes portray a decrease in emission with temperature, as is the case in Eq. (25). The behavior of dye 2 would be independent of temperature.

Since the system would be considered optically thin for both dyes, we can neglect the absorption of the exciting light, and use equation (2) in the computation of the total fluorescent emissions. Thus, we have:

$$I_{f1}(t, T, \lambda_{filter1}) = \int_0^t I_o \varepsilon_1(\lambda_{laser}, T)C_1 \Phi_1 \eta_1(\lambda_{filter1}) dx \quad (26)$$

$$I_{f2}(t, \lambda_{filter2}) = \int_0^t I_o \varepsilon_2(\lambda_{laser})C_2 \Phi_2 \eta_2(\lambda_{filter2}) dx \quad (27)$$

Now, taking their ratio and remembering that  $T = T(x)$ :

$$R(T, \lambda_{filter1}, \lambda_{filter2}) = \frac{I_{f1}}{I_{f2}} = \frac{\varepsilon_{1,o}(\lambda_{laser})C_1 \Phi_1 \eta_1(\lambda_{filter1})}{\varepsilon_2(\lambda_{laser})C_2 \Phi_2 \eta_2(\lambda_{filter2})} - \frac{kC_1 \Phi_1 \eta_1(\lambda_{filter1})}{\varepsilon_2(\lambda_{laser})C_2 \Phi_2 \eta_2(\lambda_{filter2})} \frac{\int_0^t T(x) dx}{t} \quad (28)$$

where

$$\frac{\varepsilon_{1,o}(\lambda_{laser})C_1\Phi_1\eta_1(\lambda_{filter1})}{\varepsilon_2(\lambda_{laser})C_2\Phi_2\eta_2(\lambda_{filter2})} = const. = a \quad (29)$$

$$\frac{kC_1\Phi_1\eta_1(\lambda_{filter1})}{\varepsilon_2(\lambda_{laser})C_2\Phi_2\eta_2(\lambda_{filter2})} = const. = b \quad (30)$$

and

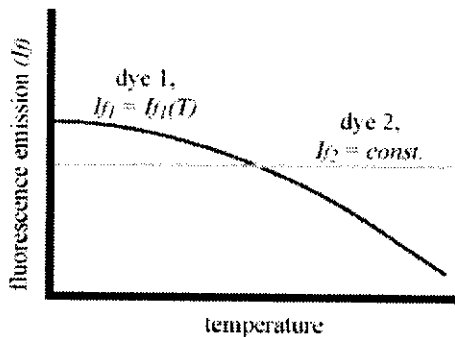
$$\frac{\int_0^t T(x) dx}{t} = T_{avg} \quad (31)$$

Therefore, we can rewrite Eq. (28) as:

$$R(T_{avg}, \lambda_{filter1}, \lambda_{filter2}) = a - bT_{avg} \quad (32)$$

Equation (32) reflects the fact that the ratio would be a function of the interference filters used (that is, on the portion of the emission spectrums recorded) by way of  $a$  and  $b$ , but in addition, it would be a function of the average temperature along the direction of observation. The same analysis and results would be obtained if it were the quantum efficiency, instead of the absorptivity, that bears the temperature dependence (as long as this dependence is also linear).

The dependence of fluorescence on excitation light intensity and film thickness cancels when the ratio of the two fluorescent emissions is used. By using this radiometric approach on optically thin systems, temperature variations in the direction



$$R = \frac{I_{f1}}{I_{f2}} = R(T)$$

Fig. 8 Temperature ratio.

of observation are averaged over the film thickness and the fluorescence ratio can be correlated to an average temperature in the direction of observation (Fig. 8).

### 3. EXPERIMENTAL SETUP AND RESULTS

A two-camera system was developed in order to simultaneously capture the two fluorescent intensities (Fig. 9). The system consists of two 12-bit Princeton Instrument CCD cameras mounted on a single lens, optical-path-splitting module. The use of a single lens simplifies alignment and minimizes distortion between the two cameras. Two dichroic mirrors are used in order to separate the laser and fluorescent emissions. The first dichroic is located outside the module and is used to simultaneously steer and separate the laser from the fluorescent emissions. The second dichroic is located inside the module and serves two functions: (1) to separate and (2) to steer the low and high wavelength fluorescent emissions. Interference filters are used just before the CCD cameras in order to isolate a particular wavelength emission. The module also contains adjustment optics that allow for mechanical alignment of the two images captured by the respective CCD cameras. Further alignment is accomplished by computer processing of the two images. A piece of sandpaper is placed in front of the module and imaged by both CCD cameras. A cross correlation Particle Image Velocimetry (PIV) algorithm [9] is then used to locally correlate the two images in order to find the displacement vectors (at the sub-pixel level) for each pixel position, which will subsequently be used on all other images when computing the ratio.

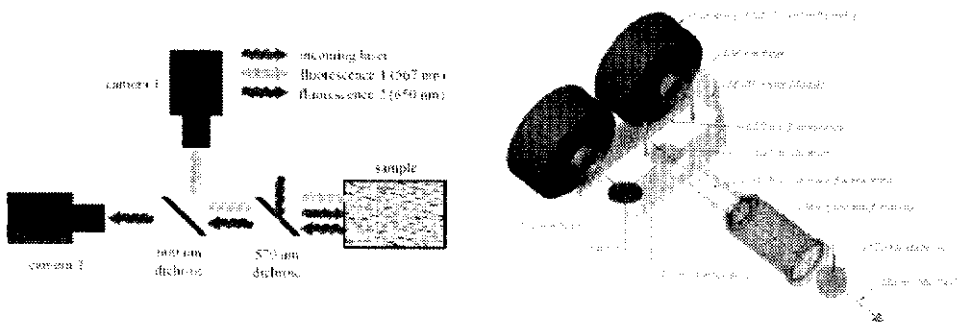
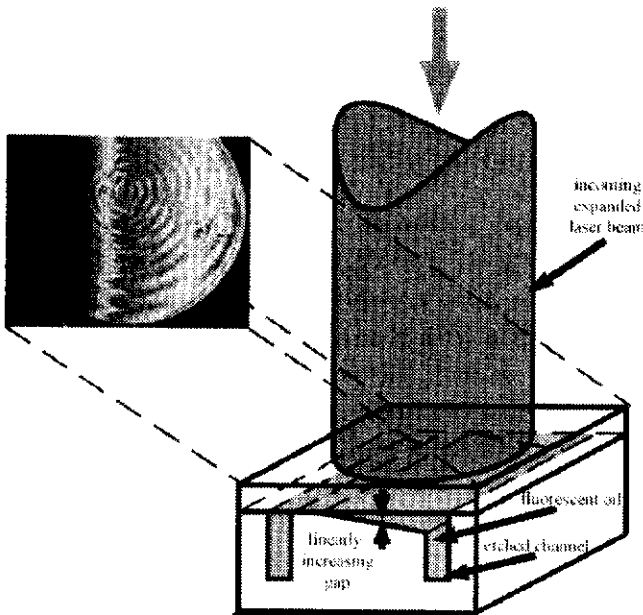


Fig. 9 Experimental setup.



**Fig. 10** Calibration fixture.

The system was originally developed for tribological studies, in particular in the study of lubrication of rotating shaft seals. Therefore, in the validation of the technique oil was used as the fluid medium of interest. For oil film thickness measurements, the two dyes selected were Pyrromethene 567 and Pyrromethene 650. These dyes were selected because: (1) both are excitable by the 532 nm line of the Nd:YAG; (2) wide separation exists between the primary emission peak of each dye; (3) both dyes have high quantum efficiencies; (4) the emission peak of Pyrromethene 567 is highly absorbed by Pyrromethene 650; and (5) both are non hazardous. For temperature measurements, the combination of Pyrromethene 567 and Rhodamine 640 was implemented. The same selection criteria were used in choosing these two dyes, with the added decisive factor that the Rhodamine 640 emission is very sensitive to temperature changes. The fact that Rhodamine 640 absorbs the Pyrromethene 567 emission is actually detrimental to the temperature measurement scheme. However, as mentioned before, by using an optically thin system, this effect can be minimized.

A calibration fixture was fabricated in order to provide a linearly increasing film thickness against which the technique could be tested. The fixture consisted of a quartz optical flat that formed the top and a quartz flat set at an angle with an inside reservoir channel etched around it (Fig. 10). When joined together, the optical flats produced a linearly increasing gap that was filled with liquid in order to pro-



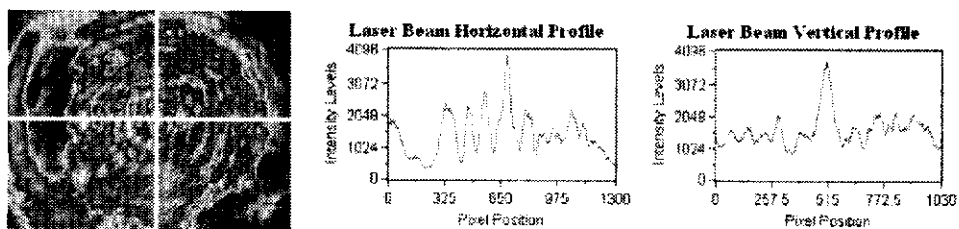


Fig. 11 Laser beam profile.

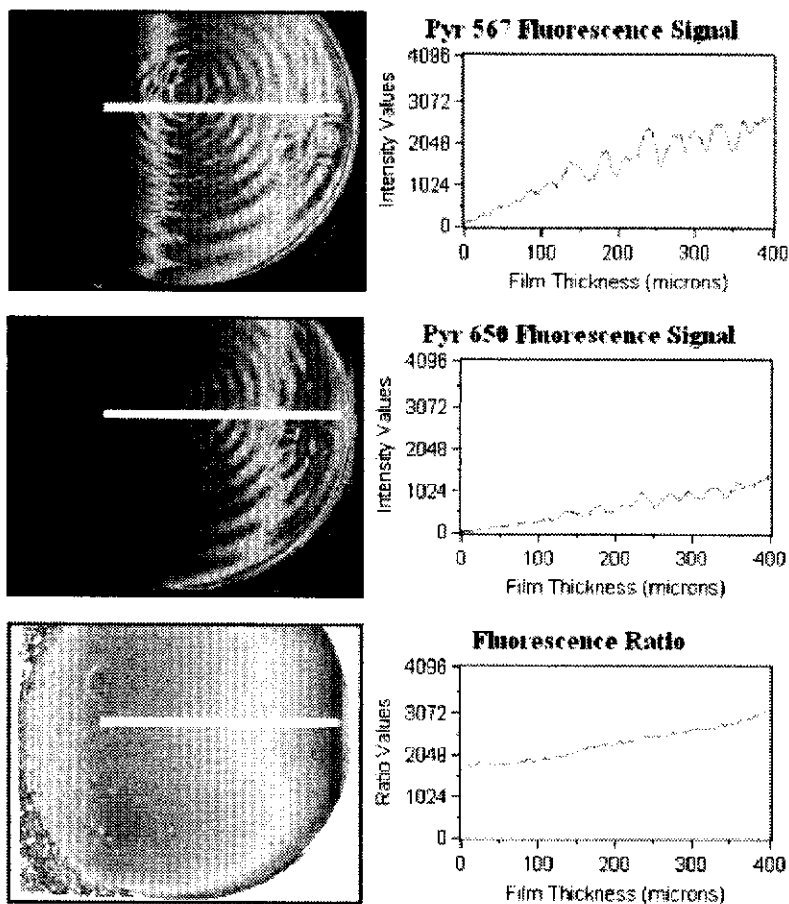
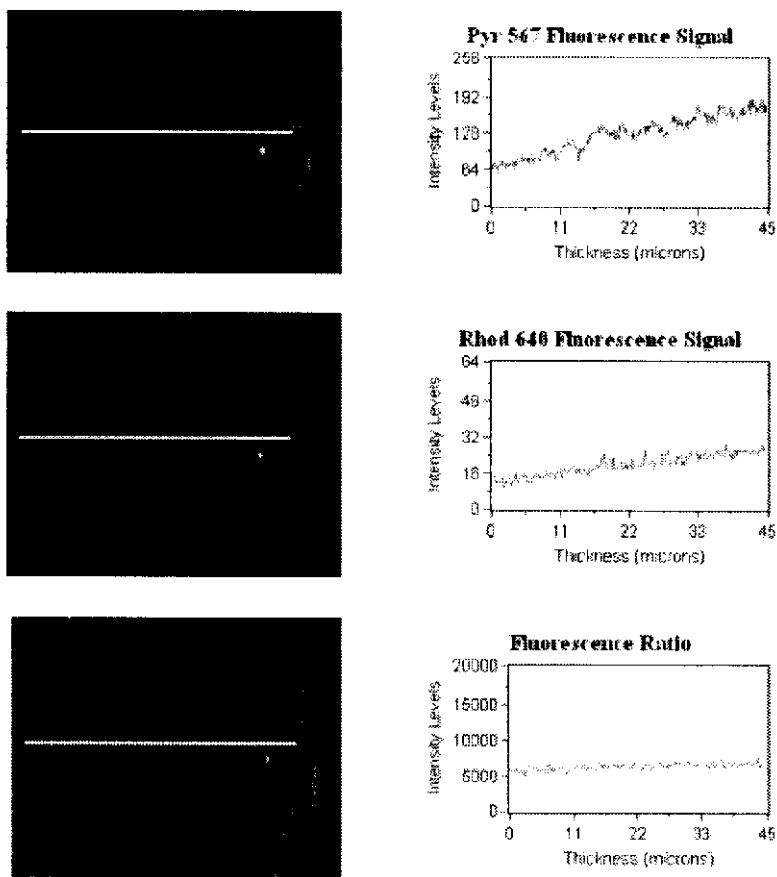


Fig. 12 Comparison of the film thickness LIF signal for Pyromethene 567 and Pyromethene 650 versus their ratio (optically thick system with strong reabsorption).

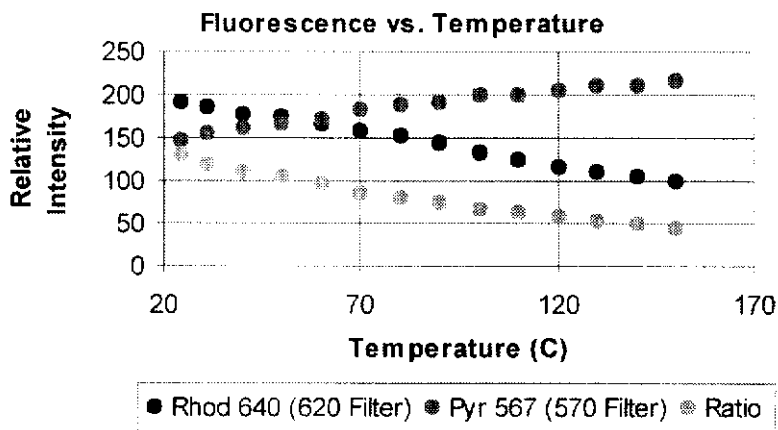
duce a known film thickness. The fixture was measured using a CMM to verify the thickness of the gap within the calibration area.

Figure 11 depicts the laser beam intensity profile. Strong spatial intensity variations can be observed with fluctuations of as much as 400% between the highest and lowest intensity regions of the beam. Since the technique was originally developed for lubrication and tribological purposes, the system was initially tested on its ability to measure oil films. A dye concentration of  $8 \times 10^{-4}$  mol/liter of oil was used for both dyes. Figure 12 shows the fluorescence's dependence on film thickness for Pyrromethene 567 and Pyrromethene 650. There is a noticeable increase in fluorescence with film thickness that becomes non-linear as the film thickness increases (optically thick system). It is apparent, however, that the laser intensity fluctuations are embedded within the film thickness information making it difficult to separate the two. The bottom of Fig. 12 shows the ratio of the two fluorescent emissions. Note the disappearance of the laser intensity fluctuations illustrating that the laser intensity information is canceled in the ratio. Note also that the ratio has a nearly linear dependence on film thickness. As explained earlier, this is a consequence of reabsorption within the optically thick system. For the dye combination used, it was possible to resolve film thickness from 5 to 400  $\mu\text{m}$  with 1% accuracy. Accuracy can be greatly improved over a specific range of film thickness through careful dye selection and adjustment of dye concentrations.

For oil film temperature measurements, an optically thin system must be used, in order for the ratio to suppress film thickness information. A dye combination consisting of  $8 \times 10^{-5}$  mol/liter Pyrromethene 567 and  $2.4 \times 10^{-4}$  mol/liter Rhodamine 640 dissolved in oil was used. Since the emission spectrum of Rhodamine 640 overlaps the absorption spectrum of Pyrromethene 567, this two-dye system exhibits reabsorption. However, due to the low concentrations used for both dyes and the fact that only thickness up to 45 micrometers were considered, an optically thin behavior with minimal reabsorption is achieved. Consequently, the fluorescence dependence of both dyes over the film thickness range of the calibration fixture is linear. This results in a constant value for the ratio over the thickness range. Figure 13 shows the fluorescence's dependence on film thickness for Pyrromethene 567 and Rhodamine 640. Again, a noticeable increase in fluorescence with film thickness is observed for both dyes, and laser intensity fluctuations are evident within the film thickness information. The bottom of Fig. 13 shows the ratio of the two emissions. As before, the laser intensity fluctuations disappear with the ratio. However, in this case, the ratio remains constant over the film thickness range. There is no dependence of the ratio on film thickness because the system is optically thin and reabsorption has minimal influence. This is appropriate when a ratiometric approach is to be used to measure scalar quantities such as temperature, pH, and pressure.



**Fig. 13** Film thickness LIF signal for Pyromethene 567, Rhodamine 640 and their ratio (optically thin system with negligible reabsorption).



**Fig. 14** Fluorescence versus temperature.

Once an optically thin system was achieved, the calibration fixture was set on top of a heating plate. Changing the heating plate settings varied the temperature, which was monitored through the use of thermocouples in the calibration fixture. Fig. 14 depicts the change in fluorescent intensity with temperature for both Pyromethene 567 and Rhodamine 640 and their ratio.

#### 4. SUMMARY AND CONCLUSIONS

The bases for a two-dye Laser Induced Fluorescence ratiometric technique for 2D mapping of film thickness and temperature were presented. The core of the technique lies in the use of a ratiometric approach for the purpose of suppressing excitation intensity information from the fluorescent emission. Two fluorescent emissions are required to accomplish this; one is used as the carrier of the desired scalar information (film thickness or temperature) and the other is used as the carrier of the excitation intensity information. The basic principles and equations behind photofluorescence, optically thin and thick systems, and reabsorption were introduced in light of the technique and in order to develop a theoretical framework on which to base the technique. It is shown that the non-linearity resulting from emission reabsorption, while detrimental to the measurement of most scalars, can be used to accurately quantify film thickness when a ratiometric approach is used. On the other hand, when the ratiometric approach is used to measure temperature, an optically thin system, where reabsorption is negligible, is required. Besides canceling film thickness information in the ratio, the use of an optically thin system allows for temperature variations in the direction of observation to be averaged out in the measurement. Implementation of the technique using a two-camera system and a calibration fixture demonstrated the feasibility of this unique technique and its ability to accurately determine film thickness and temperature despite variations in illumination intensity.

#### REFERENCES

1. R. P. Haugland, *Handbook of Fluorescent Probes and Research Chemicals*, Seventh Edition, Molecular Probes, 1999.
2. J. Coppeta and C. Rogers, Dual Emission Laser Induced Fluorescence for Direct Planar Scalar Behavior Measurements, *Experiments in Fluids*, vol. 25, no. 1, pp. 1-15, 1998.
3. J. Coppeta, C. Rogers, A. Philipossian, and F. B. Kaufman, Characterizing Slurry Flow During CMP Using Laser Induced Fluorescence, Second International Chemical Mechanical Polish Planarization for ULSI Multilevel Interconnection Conference, Santa Clara, CA, February 1997.

4. J. Sakakibara and R. J. Adrian, Whole Field Measurement of Temperature in Water Using Two-Color Laser Induced Fluorescence, *Experiments in Fluids*, vol. 26, no. 1/2, pp. 7–15, 1999.
5. N. S. Wang, P. J. B. Rinaudo, and T. J. McAvoy, Laser-Induced Fluorescence Monitoring of Multicomponent Aromatic Amino Acids, Presented at 196th National ACS Meeting, Los Angeles, CA, September 1988.
6. G. Poll, A. Gabelli, P. G. Binnington, and J. Qu, Dynamic Mapping of Rotary Lip Seal Lubricant Films by Fluorescent Image Processing, in B. S. Nau (ed.), *Proceedings, 13th International Conference on Fluid Sealing* (Brugge, Belgium), BHRA, 1992.
7. C. H. Hidrovo and D. P. Hart, Emission Reabsorption Laser Induced Fluorescence (ERLIF) Film Thickness Measurement, *Measurement Science and Technology*, vol. 12, no. 4, pp. 467–477, 2001.
8. C. H. Hidrovo and D. P. Hart, Dual Emission Laser Induced Fluorescence Technique (DELIF) for Oil Film Thickness and Temperature Measurement, Proceedings of ASME FEDSM'00, ASME 2000 Fluids Engineering Division Summer Meeting, Boston, MA, June 2000.
9. D. P. Hart, Super-resolution PIV by Recursive Local-correlation, *Journal of Visualization*, vol. 3, no. 2, pp.187–194, 2000.