

PLANAR LIQUID AND GAS VISUALIZATION*

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INTRODUCTION

Over the past decade, a variety of fluorescent diagnostic systems, based on the photophysics of organic molecules and intended for use in planar laser induced fluorescence (PLIF) measurements of heating, evaporation, mixing, and flow visualization in hydrocarbon liquids and vapors, have been developed. These organic dopants interact with their surroundings, either through concentration-dependent effects such as quenching or through physical effects such as temperature and polarity, and reveal information about the surroundings through their fluorescence. The intent in this paper is to describe the photophysical principles on which the systems are based, to describe engineering applications (currently within the combustion/mechanical engineering community), and to explore applications of these and related diagnostics within the chemical process industry. While there exist many applications of fluorescence within the diagnostic community, this paper is restricted to a review of the photophysics and applications of these four novel systems, which have not yet widely known in the chemical process area.

The fluorescent diagnostic systems make use of PLIF measurements of intensity and/or fluorescent lifetimes; they fall into five broad categories:

(1) **exciplex-based vapor/liquid visualization (EBVLV)** systems, which are now available for automotive as well as for diesel and gas turbine fuels, make use of the photophysics of organic exciplexes in order to provide spectrally-separated emissions from the vapor and liquid phases.¹⁻⁴

(2) **fluorescence shift thermometry (FST)** systems also make use of the photophysics of organic molecules; these systems use either the ratio of the emissions from the exciplex to that from the excited monomer or the shift of the fluorescence band, both of which are temperature-dependent, as an optical liquid phase thermometer.⁵⁻⁶ Such thermometers have been used to track the temperature of falling, sub-millimeter diameter droplets in experiments directed toward understanding heat transfer from a hot gas to cold droplets.

(3) **streamlines by oxygen quenching (SOQ)**, a technique which exploits the efficient quenching of the fluorescence of organic molecules by oxygen has been used in connection with **droplet slicing imaging (DSI)** to provide dramatic qualitative evidence of the existence of internal circulation patterns within falling, sub-millimeter diameter droplets.⁷

(4) **fluorescence lifetime imaging (FLI)** requires the use of fast dual gated image intensifiers to obtain two PLIF images, one a few nanoseconds after the first. Quenching results in a reduction of the fluorescence intensity and a reduction of the fluorescence lifetime. The two images make it possible, in principle, to obtain a lifetime image and, after appropriate calculations, an intensity image, completely corrected for quenching.⁸ To date, the technique has been applied (a) to fuel/oxygen equivalence ratio imaging (ERI),⁹ and (b) to vapor phase temperature imaging (VTI).¹⁰

(5) **film thickness imaging (FTI)**

Fluorescent thickness imaging is under development. In this method the fluorescence of a molecule which has almost the same volatility as automotive gasoline will be used to track the evaporation of films of automotive gasolines. The system is used in an optically thin configuration, and the fluorescence intensity in a pixel is thus proportional to the film thickness.

PHOTOPHYSICS OF FLUORESCENT DIAGNOSTICS

A. processes

A recent review article discusses the photophysics of these combustion-related fluorescent diagnostics, and their fundamental limitations (volatility, quenching, etc.), in detail.¹¹

B. excited state complexes

An exciplex or excimer [excited state complex or excited state dimer, denoted E^* and called exciplex, unless the distinction is required] is formed in the reaction of an electronically excited molecule M^* with an appropriate ground state molecule G (for excimers $G = M$), as shown in eqn. 1.¹²



E^* may be bound by as much as 20-40 kJ/mole with respect to separated M^* and $G(M)$. Since there is no significant chemical binding of the ground state components of E^* , and there may even be significant repulsion at the distance at which E^* is most strongly bound, the fluorescence from E^* is necessarily red-shifted with respect to the fluorescence of the excited monomer M^* . The concentrations of M and G in the liquid can be adjusted to that the E^* emission dominates in the liquid. The exciplex is unstable in the vapor phase, and thus the M^* emission dominates in the vapor. Consequently, filters which isolate the E^* and M^* emission allow separate PLIF visualization of the liquid and vapor phases, respectively.

The reaction shown in equation (1) is temperature dependent, and the temperature dependence of the E^*/M^* intensity ratio can be exploited to make exciplex thermometers, which allow PLIF imaging of liquid phase temperatures within a few degrees over the temperature range 20 - 400 °C.

C. apparatus for PLIF

Most PLIF experiments make use of a pulsed laser (in order to provide time resolution of the flow phenomena under study) whose beam is formed, via cylindrical lenses, into a sheet which is a fraction of a millimeter thick and 5-10 cm wide. Typically the fluorescence from the flow is imaged onto a CCD array camera which is placed at 90° to the plane of the exciting laser sheet. The choice of laser is determined by the wavelengths required for excitation of the fluorescent dopants. Most studies have used nitrogen lasers (337 nm) or Nd:YAG lasers (third harmonic at 355 nm or fourth harmonic at 266 nm). This apparatus is generic and the specificity of the diagnostic is gained through choice of the fluorescent dopant system(s).

APPLICATIONS OF FLUORESCENT DIAGNOSTICS

A. exciplex-based vapor/liquid visualization

The best characterized, and most often applied, EBVLV system uses 0.5-1% (w/w) N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), $nbp = 265$ °C/10% (w/w) naphthalene, $nbp = 218$ °C/balance alkane (decane, tetradecane, or hexadecane). The liquid phase emission is dominated by the E^* emission (peak at 480 nm), and the vapor phase emission is dominated by the M^* emission (peak at 390 nm). Thus it is possible, by use of relatively broad-band filters to obtain separate images of the liquid or vapor phases in an evaporating fuel spray.

Most of the current applications of EBVLV have been in research automotive engines. Two examples are particularly noteworthy. Bardsley et al. acquired images for "diesel" and "automotive" sprays in a research engine, which was motored on nitrogen.¹³⁻¹⁴ Shimizu et al. achieved near-quantitative use of an EBVLV system by using the E^* emission to show that the liquid had completely evaporated. They were then able to calibrate the vapor phase emission as a function of the mixture fuel/oxygen ratio and crank angle in their automotive test engine. As a result, the spatial dependence of the equivalence ratio in the

precombustion portion of the engine cycle was displayed quantitatively.¹⁵

B. fluorescence shift thermometry

Fluorescence thermometry has been used with bulk liquids and droplets falling into heated nitrogen. Stufflebeam showed that, in sealed, bulk liquids, spatial resolution of less than 1 mm and temperature errors of less than 1 °C could be achieved over the range 20 - 100 °C.¹⁶ "Proof of concept" measurements of the temperature of decane or hexadecane droplets falling into heated nitrogen have been carried out with illumination of (1) the entire cross section of an optically thick droplet ("whole droplet, skin temperature"),¹⁷ (2) the entire cross section of an optically thin droplet ("whole droplet, volume averaged temperature"),¹⁸ and (3) a central slice of the droplet ("droplet slicing, temperature field").¹⁹ In more recent work, the evaporation of a fuel which had been sprayed onto a hot steel plate was followed through images of the temperature of the remaining liquid at intervals of a 0-100 msec after the injector was pulsed.²⁰

C. streamlines by oxygen quenching

The techniques of streamlines by oxygen quenching and droplet slicing imaging were developed for the purpose of testing whether aerodynamic drag on droplets of sizes typical of fuel sprays could induce internal circulation within the droplet, which circulation can dramatically alter the time required for the droplet to heat sufficiently for evaporation rates to become significant.⁷ For SOQ, the droplet is formed from a solution which contains a dopant whose fluorescence is easily quenched by oxygen (typically naphthalene in decane) and which solution has been purged of oxygen. The droplet falls into an oxygen containing atmosphere, and oxygen contacts and diffuses into the surface liquid. For DSI, the laser beam is formed into a sheet which is narrow compared to the droplet diameter and which illuminates an equatorial plane of the droplet. SOQ/DSI measurements on droplets which have internal circulation show dark (oxygen containing, fluorescence quenched) streaks curving into the light droplet disk.⁷

D. fluorescence lifetime imaging

In FLI, a rapid lifetime determination algorithm, which relies on two gated intensity images and the assumption that the fluorescence decay is a single exponential, allows the subsequent calculation of the fluorescence lifetime image.²¹ The fluorescence image was split, and each portion passed through a fast gated imaged intensifier (off/on/off time selectable from 1 to 12 nsec, intensifiers and high voltage pulser system supplied by Grant Applied Physics, Berkeley, CA) and an appropriate filter. The two gated fluorescence signals were finally focused onto two halves of a single CCD camera (Photometrics Star-1).

The equivalence ratio (ϕ) is the ratio of the fuel vapor concentration to the oxygen concentration, normalized so that the equivalence ratio is unity when there is just sufficient oxygen present to burn all the fuel to water and carbon dioxide. $\phi < 1$ is "fuel lean", and $\phi > 1$ is "fuel rich".

For equivalence ratio imaging (ERI), further processing is required. As shown in equations (2a) and (2b), the Stern-Volmer equations for intensity and for lifetimes have the same right hand side.

$$I_0/I = 1 + K' [O_2] \quad (2a)$$

$$\tau_{o0}/\tau_o = 1 + K' [O_2] \quad (2b)$$

where the "o" subscript denotes the quantity measured in the absence of the quencher, which here is O_2 . In a non-homogeneous mixture of fuel with air, variations in intensity may arise either from variations in the distribution of the fuel (and with it the fluorescent dopant which was mixed into the fuel), or from variations in the amount of oxygen (and consequent variations in the amount of quenching), or both. One needs to determine the unquenched intensity image (I_0) in order to determine the

distribution of fuel, however, only the intensity image with quenching (I) is experimentally accessible. With prior knowledge of the fluorescence lifetime in the absence of quenching, and measurement, pixel-by-pixel, of the mixture lifetime, the right hand side of equations (2a) and (2b) can be determined, and thus the unquenched intensity image, in which the intensity is directly proportional to the fluorescent dopant concentration, can be obtained. With further knowledge that quenching by oxygen is the only significant means of shortening the fluorescence lifetime in the system under study and with measurement of the rate of quenching of the fluorescence by oxygen, the oxygen concentration image can be obtained. If the system has been prepared in such a fashion that the concentration of the fluorescent dopant is in a fixed and known ratio to the fuel vapor concentration, then pixel-by-pixel ratioing and subsequent scaling of the ratio yields an image of the fuel/oxygen equivalence ratio. This technique has been demonstrated in fluoranthene doped jets of methane into air; typical results are shown in Figure 7.

For vapor temperature imaging, a fluorescent dopant whose lifetime is temperature sensitive is used. In this case a calibration curve of the fluorescence lifetime versus temperature is used to convert the fluorescence lifetime image to a vapor temperature image. The temperatures are obtained solely from lifetime data and do not depend upon the concentration of the fluorescent dopant so long as sufficient signal is obtained for accurate measurements. Since oxygen, particularly, also shortens the fluorescence lifetimes, it must be rigorously excluded in the VTI experiments. This technique has been demonstrated for a heated jet of naphthalene doped nitrogen at the center of a cold coflow of naphthalene doped nitrogen.¹⁰

POTENTIAL APPLICATIONS IN THE CHEMICAL PROCESS INDUSTRY

A significant drawback to the utilization of such fluorescent diagnostics in the chemical process industry is the sensitivity of the fluorescent dopants to quenching by molecules in the environment. It may be possible to show that the process stream does not contain significant quenchers, but this must be established on a case-by-case basis.

As described in the discussions of exciplex-based vapor/liquid visualization, exciplex fluorescence thermometry, streamlines by oxygen quenching, and fluorescence lifetime imaging, fluorescence measurements can also be generated under planar illumination conditions, and thus two-dimensional maps of a property field can be obtained. Thus fluorescence imaging is particularly useful for situations, such as studies of two phase flow or mixing, where such 2-D information is critical.

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