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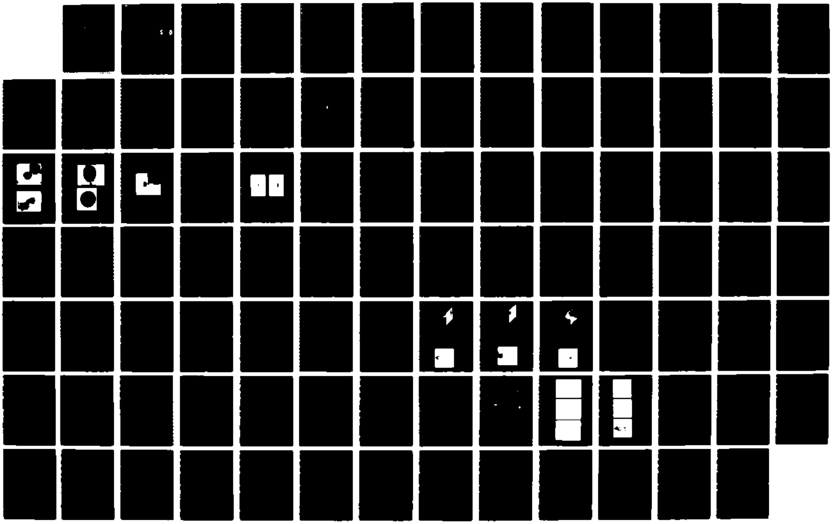

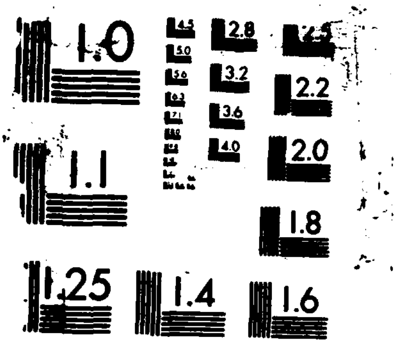

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INVESTIGATION OF REAL-TIME TWO-DIMENSIONAL VISUALIZATION OF FUEL SPRAY LIQUID/VAPOR DISTRIBUTION VIA EXCIPLEX FLUORESCENCE

FINAL REPORT

JAMES F. VERDIECK AND ARTHUR A. ROTUNNO
UNITED TECHNOLOGIES RESEARCH CENTER

AND

LYNN A. MELTON
UNIVERSITY OF TEXAS AT DALLAS

AUGUST 1987

UNITED STATES ARMY RESEARCH OFFICE
CONTRACT NUMBER DAAG29-84-C-0010

UNITED TECHNOLOGIES RESEARCH CENTER
EAST HARTFORD, CT 06108

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This final report describes the achievements of the research program carried out under the subject contract. The overall aim of the study was to develop a new and unique combustion diagnostic technique which would provide the real-time, two-dimensional visualization of both the liquid and vapor phase of a fuel spray by means of laser-induced exciplex fluorescence. Significant achievements toward this end were: (1) Demonstration and application of an exciplex thermometer, (2) Discovery of new exciplex systems, particularly intramolecular exciplex systems, (3) Formulation of a total scheme involving analysis of the exciplex spectral emissions for determining temperature, liquid and vapor concentrations, and the local oxygen pressure in the spray field, (4) Construction of an apparatus for studying single injected droplets into a controlled environment of temperature and pressure for observation of laser-induced exciplex fluorescence, (5) Modeling of single droplet vaporization in support of the experimental studies, (6) Observation of single (Cont.)

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droplet liquid and vapor phase fluorescence in two-dimensions, and (7) Experiments toward achieving quantitative exciplex fluorescence measurements.

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IV. Fluorescence Thermometers Using Intramolecular Exciplexes, H. E. Gossage and L. A. Melton.

FOREWORD

This report describes the results from a fundamental research program investigating the development and application of a laser-induced exciplex fluorescence diagnostic technique to the vaporization of sprays and single droplets. This program has been a joint effort between the United Technologies Research Center and the University of Texas at Dallas, jointly supported by the ARO and AFOSR.

It was demonstrated that, by means of exciplex fluorescence, the simultaneous two-dimensional distribution of both the liquid and vapor phases within an evaporating fuel spray, or from a single vaporizing droplet, can be detected. The fundamental concept of exciplex fluorescence visualization is to dope the fuel with non-corrosive, organic additives which can form an exciplex or excimer in the liquid phase, but not in the vapor phase [which retains the monomeric states of the additives]. An exciplex is an excited state complex between the dopant molecules added to the fuel. In the liquid phase the reversible equilibrium between the monomer and the exciplex lies toward the exciplex, hence the fluorescent emission from the liquid phase is predominantly that of the exciplex. The exciplex fluorescence is considerably [100 to 150 nm] red-shifted with respect to the monomer fluorescence; in the vapor phase the reverse is true, with monomer fluorescence dominating. By means of exciplex fluorescence, the addition of small amounts of carefully chosen organic additives to hydrocarbon fuels can lead to the real-time, non-intrusive, two-dimensional visualization of evolving fuel sprays. Clearly this diagnostic technique offers enormous potential for the study of vaporization in fuel sprays.

The method is generally applicable; exciplex additive systems have been formulated which function well with fuels of either low and high boiling points. A most significant development is that liquid phase temperatures can be calculated from the exciplex/monomer fluorescence ratio. This technique has the potential for measuring the surface temperature of a single droplet.

Early on in this program, it was recognized that a fundamental understanding of fuel vaporization is best approached at the single droplet level. To this end, a droplet-on-demand generator, along with a controlled-environment [temperature and flow] optical test chamber, was developed. This system permitted the study of vaporization of single droplets at a selected temperature by means of synchronized exciplex fluorescence. Frozen, digitized images of the fluorescence from single falling droplets were captured from both the liquid and vapor phases. These experimental investigations were aided by analytical modeling studies of vaporizing droplets, based upon a model developed by J.J. Sangiovanni of UTRC. While pursuing this course of action, various hardware [cameras and image-grabbers] and software [image analysis] systems were adapted for capturing and analyzing the digitized images of synchronized droplets and associated vapor cloud.

These achievements are described in more detail in the subsequent sections of this report, and in the publications reprinted in the appendices.

Acknowledgement

The authors would like to acknowledge the dedicated assistance in the fabrication, assembly and testing of the experiments described in this report by their technicians: Normand Gantick [deceased], Edward Dzwonkowski, Jeff Crandall and Jim MacLeod.

I. PROGRAM DEFINITION

The fundamental goal of this three-year, comprehensive research program, carried out under ARO Contract No. DAAG29-84-C-0010, was to develop a new and unique combustion diagnostic technique which would provide the real-time, two-dimensional visualization of both liquid and vapor phase of a fuel spray by means of laser-induced exciplex fluorescence. This program was a joint effort between the Laser Diagnostics Group of the United Technologies Research Center [UTRC] and Professor L.A. Melton of the University of Texas at Dallas [UTD] Chemistry Department. The Principal Investigator for the program was Dr. James F. Verdieck. Partial support of the Army Research Office Contract was provided by the Air Force Office of Research. The Contract Monitor for ARO was Dr. David M. Mann; the representative for AFOSR was Dr. Julian Tishkoff.

The research program consisted of two major portions:

I. Fundamental aspects of the photochemistry and photophysics of exciplex formation, that is, fluorescence characteristics [spectroscopy, quantum yields, concentration dependence, pressure and temperature dependence], selection of compounds for compatibility with fuel characteristics, and possible chemical synthesis of compounds were investigated at UTD under the direction of Prof. Melton. Additionally, new concepts for exciplex fluorescence applications were developed at UTD. These included liquid phase temperature measurement from exciplex fluorescence, the use of intramolecular [single-component] exciplex systems, and the investigation of exciplex systems which would determine oxygen content.

II. The more applied aspects of the program, such as testing of various candidate exciplex systems proposed by UTD in surrogate fuels [hexadecane, decane], improvement of visualization contrast, and the measurement of fluorescence intensity with respect to varying external parameters [pressure, temperature, oxygen concentration], were explored by the Laser Diagnostics Group at UTRC. Additionally, implementation of the appropriate optical and spectroscopic techniques and signal/data processing for realization of simultaneous, 2-D digitized images of fuel spray/single droplet exciplex fluorescence were developed at UTRC. This latter task of the investigation involved the use of array detectors [cameras] with various sensitivities and spectral ranges; image digitizers [frame-grabbers] with differing resolutions and dynamic ranges; and image analysis software.

As noted earlier, considerable effort was devoted to fundamental vaporization studies of single droplets; these investigations involved both modeling and experiments on exciplex-doped surrogate fuels [hexadecane and decane]. Care was taken to match the model to well-defined experimental conditions of temperature gradient and laminar flow in the laser-induced exciplex fluorescence experiments.

II. SUMMARY OF IMPORTANT RESEARCH FINDINGS

Fundamental Concepts of Exciplex-based Visualization Techniques

In 1982, Melton demonstrated that the photophysics/photochemistry of fluorescent organic exciplexes held promise for investigating the complex problems of vapor/liquid visualization in evolving fuel sprays [Ref. 1]. This demonstration experiment showed that the liquid and vapor phase fluorescent emissions, from a heated pendent drop, could easily be separated--visually--as a purple vapor cloud surrounding the green liquid. This experiment was superseded by a demonstration of laser-induced exciplex fluorescence from a hollow-cone fuel spray injected into a heated nitrogen flow. The fuel-spray cone was interrogated by a planar UV, pulsed laser beam. Exciplex fluorescence was observed at right angles. The vapor and liquid patterns were separately photographed with the aid of absorption filters. Color photographs were obtained by averaging over 3 to 5 seconds [30 to 50 laser pulses] and hence represented time-averaged flow patterns of the spray. Photographs of exciplex fluorescence excited by a single laser pulse were captured with high-speed black and white film. The equivalent shutter speed of these "frozen flow" snap-shots is governed by the exciplex fluorescent lifetime, approximately 100 nanoseconds for this case. The negatives for the color photographs were digitized with a scanning densitometer; the digitized images were computer analyzed to generate contour maps and 3-D perspective views of the fluorescent intensity over the 2-D field of that section of the cone sampled by the planar laser beam.

Complete details of these experiments and the photographs which were obtained, are given in the reprinted articles [Refs. 2,3] appearing in Appendices 1 and 2. These papers serve as a good introduction to laser-induced exciplex fluorescence and its application to fuel spray visualization.

Exciplex visualization systems are based on the following photochemical reaction:

$$M^* + G \rightleftharpoons E^* \qquad (1)$$

M^* is the first excited singlet state of a fluorescent organic molecule; the monomer M, is generally, but not always an aromatic molecule. G is an appropriately chosen ground state molecule, and E^* is the exciplex [excited state complex] formed in a reversible equilibrium with M^* and G. The exciplex has a significant binding energy in the excited state [5-20 Kcal/mole], but not in the ground state where it dissociates. Because E^* is bound with respect to separated M^* and G, and emits to the same ground state potential energy, its emission is necessarily red-shifted with respect to the M^* fluorescence emission. This shift may be as much as 100 to 200 nm. Again, the interested reader may consult the papers in the appendices [1,2] for more details.

As noted in the Program Definition [Section II], this research program was a joint effort between the United Technologies Research Center and the University of Texas at Dallas; with the latter laboratory investigating primarily the more fundamental issues of exciplex photochemistry, and the former group [UTRC] investigating the experimental problems of applying exciplex diagnostic methods to real sprays and single droplets. The significant research achievements of these two groups are listed separately.

Achievements at UTD

Exciplex Thermometry

Under this ARO contract, work at UTD resulted in the demonstration of exciplex fluorescence-based thermometers for two different temperature ranges: 20-140 C and 145-265 C. The key idea underlying this type of thermometry is that the exciplex formation reaction, equation 1, is temperature dependent.

At low temperatures, the solvent viscosity prevents M^* [excited monomer] from diffusing to G [ground state molecule] and achieving the proper alignment within its excited state lifetime to form the exciplex E^*; hence the ratio of exciplex fluorescence to monomer fluorescence increases as the temperature increases [kinetics-dominated mechanism]. At high temperature, M^* and E^* are in equilibrium, and the temperature dependence of the equilibrium constant for reaction (1) requires that the ratio of exciplex to monomer fluorescence decrease as the temperature increases [thermodynamics dominated mechanism]. It is estimated that, for either the kinetics- or thermodynamics-dominated thermometers, a measurement of the ratio of the fluorescence intensities of exciplex to monomer, if accurate to within 1%, will yield a determination of the liquid temperature accurate to within 1 degree Centigrade. A complete description of exciplex thermometry is provided in the reprinted paper [Ref. 4] in Appendix 3.

Exciplex Systems

During the major portion of this contract, the naphthalene/ N,N,N',N'-tetrametyl-phenylenediamine [TMPD] exciplex pair was investigated most thoroughly with regard to photochemical and photophysical properties. This system has several features which make it more attractive than other candidate systems considered; a wide temperature range, good solubility in hydrocarbon fuels, good spectral separation between the monomer and exciplex fluorescence, and reasonable quantum yield. Exciplex thermometry was first demonstrated with the naphthalene/TMPD system.

Prior to the initiation of this contract, Melton and coworkers at UTD examined nearly 100 potential exciplex systems, 31 of which were found to produce strong exciplex fluorescence, spectrally well-separated from the monomer fluorescence. Of these, five showed strong exciplex fluorescence which remained strong at 250 C. This work was supported by a one year AFOSR Grant, the results are detailed in the Final Report under AFOSR Grant 83-0307, Nov 1, 1984 [Ref. 5].

Intramolecular Exciplex Systems

In the fall of 1985, an improved set of exciplex-based thermometers was developed. This new type of exciplex probe is based on a single molecule containing two chromophores. Depending upon the internal conformation, the two chromophores may fluoresce independently, or, in concert as an internal exciplex. Two such examples are illustrated in Fig. 1, where in the first case two identical chromophores [pyrenyl groups] are linked by a three carbon alkyl chain, and in the second case, two dissimilar chromophores are linked [pyrenyl and dimethylanilino]. This type of intramolecular exciplex has been shown to be very sensitive and is useful in dopant concentrations as low as 1 x 10-4 % W/W [one part-per-million]. The compounds illustrated have been shown to be successful fluorescence thermometers up to 330 and 390 C, respectively. This type of exciplex thermometer has been described in more detail in a recently published paper [Ref. 6], reprinted here as Appendix 4.

Other Exciplex Systems

Outside of this program, several other exciplex systems have been developed; they are mentioned in this report for completeness and, more importantly, to indicate the broad range of applicability that exciplex visualization provides.

Exciplex System for Low Boiling Fuels

Under direct funding from UTRC, a series of exciplex-based visualization systems for low-boiling hydrocarbons [butane, pentane, hexane, etc.; boiling points, 10 to 100 C] were developed at UTD. These systems, listed in Table 1, utilizing various low-boiling trialkyl amines as the monomer, were designed for studies in which the evaporation rates of pentare droplets into hot nitrogen approximate the evaporation rates of gas turbine fuel droplets under actual combustor conditions. This study is described in detail in Ref. 7.

Exciplex Systems for Real Fuels

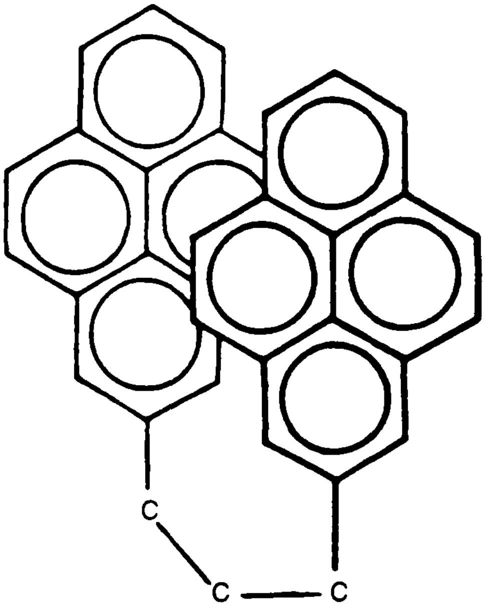
The applicability of current exciplex-based vapor/liquid visualization systems to real fuels--Jet A, JP-4, DF-2, and four experimental fuels--has been studied under a AFWAL subcontract from UTRC to UTD. The systems developed under this investigation utilized TMPD with naphthalene or substituted naphthalenes, and were useful over a wide range of temperature, for each of the fuels except diesel fuel No. 2 [because it is too strongly absorbing] and JP-4 [because it is too volatile]. A complete description is given in Ref. 8.

Innovative Applications

Finally, it has been conceptually argued [but not demonstrated], that a very complete analysis of the spectral emissions from a vapor/liquid visualization system in which all important species [M^*, G^*, and E^* fluoresce, would give the droplet temperature, liquid concentration, vapor

FIG. 1

INTRAMOLECULAR EXCIPLEX COMPOUNDS FOR HIGH TEMPERATURE THERMOMETRY



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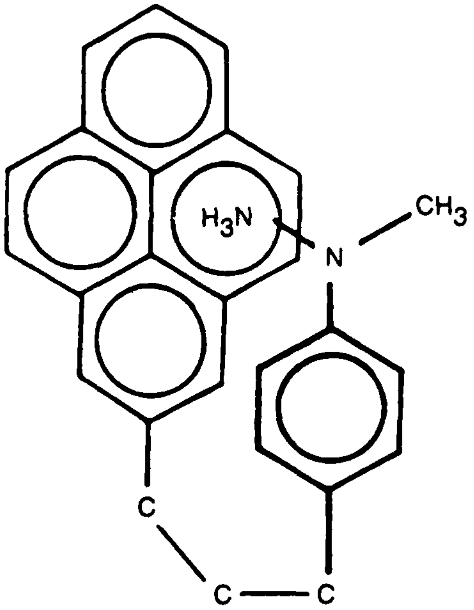


(2)

TABLE 1

EXCIPLEX SYSTEMS FOR LOW-BOILING FUELS

Fuel	T_b deg C	Monomer (M)	T_b deg C
Butane	0	Trimethylamine (TMA)	3-4
Pentane	36-38	Dimethylethylamine (DMEA)	36-38
Hexane	63-65	Diethylmethylamine (DEMA)	63-65
2-methylhexane	90	Triethylamine (TEA)	89

	Second additive (G)		
Compound (G)	T_b	Absorp.	Excplx fluoresc.
Benzonitrile (BzCN)	188	295 nm	424 nm
9-cyanophenanthrene (9 CNP)	> 340	374 nm	490 nm
N, N, N′, N′-tetramethyl-1, 3-propanediamine (PD) (Forms an INTRA-molecular exciplex)	145	295 nm	365 nm

concentration, and the local oxygen pressure at each spatial element in the field of view of the spray. This promising concept was presented at the Combined Central/Western States sections of the Combustion Society Meeting in San Antonio, April, 1985 [Ref. 9].

Achievements at UTRC

As stated previously, the major tasks to be performed at UTRC involved visualization technology, that is, obtaining two-dimensional images of sprays and single droplets, with the ultimate goal of achieving quantitative measurements of the liquid and vapor phases in a spray or in a single-droplet experiment. It was decided to devote the major effort to the study of droplets, rather than investigate sprays, for several reasons. The droplet is the fundamental unit of a spray; it is the most amenable to both modeling studies and experiment. Moreover, it is much easier to control the environment of a single droplet than that of a spray.

This task involved several different phases, which were:

1. The development and reliable operation of a droplet-on-demand generator which is synchronized with the pulsed laser,

2. The implementation of an associated environmental chamber, providing chosen conditions of temperature and near-laminar flow for the ambient gas, and provision for excitation and observation of UV laser-induced fluorescence at various positions along the trajectory of the injected droplet.

3. Droplet vaporization model computations in support of the design and construction of the test chamber; these calculations included computation of the velocity, surface temperature and radius as a function of time,

4. Two-dimensional imaging; this phase involved the adoption of specific two-dimensional detectors for these applications, an image digitizer with transfer and storage in the computer, and post-processing of the captured image for measurements and analysis.

5. Provision for excitation of the monomer/exciplex fluorescence which involved generating the appropriate laser wavelength, and achieving [and monitoring] a reasonably uniform spatial distribution of laser intensity [ideally, a TEM_{00} mode, or better yet, a "top-hat" distribution]. The latter point is most important; a reproducible excitation of the field of view is crucial for quantitative interpretation of the observed fluorescence.

Droplet Generator

The construction of a reliable droplet generator has been a challenging experience. The difficulties in achieving constant, reliable operation of these devices is well known to workers in the field. Several variants were built and tested. All were based on a piezoelectric cylinder driven by a square wave voltage pulse forcing liquid fuel through a small nozzle. It is the consensus opinion that, at the nozzle, a so-called Rayleigh instability

FIG. 2

SINGLE DROPLET EXCIPLEX FLUORESCENCE EXPERIMENT

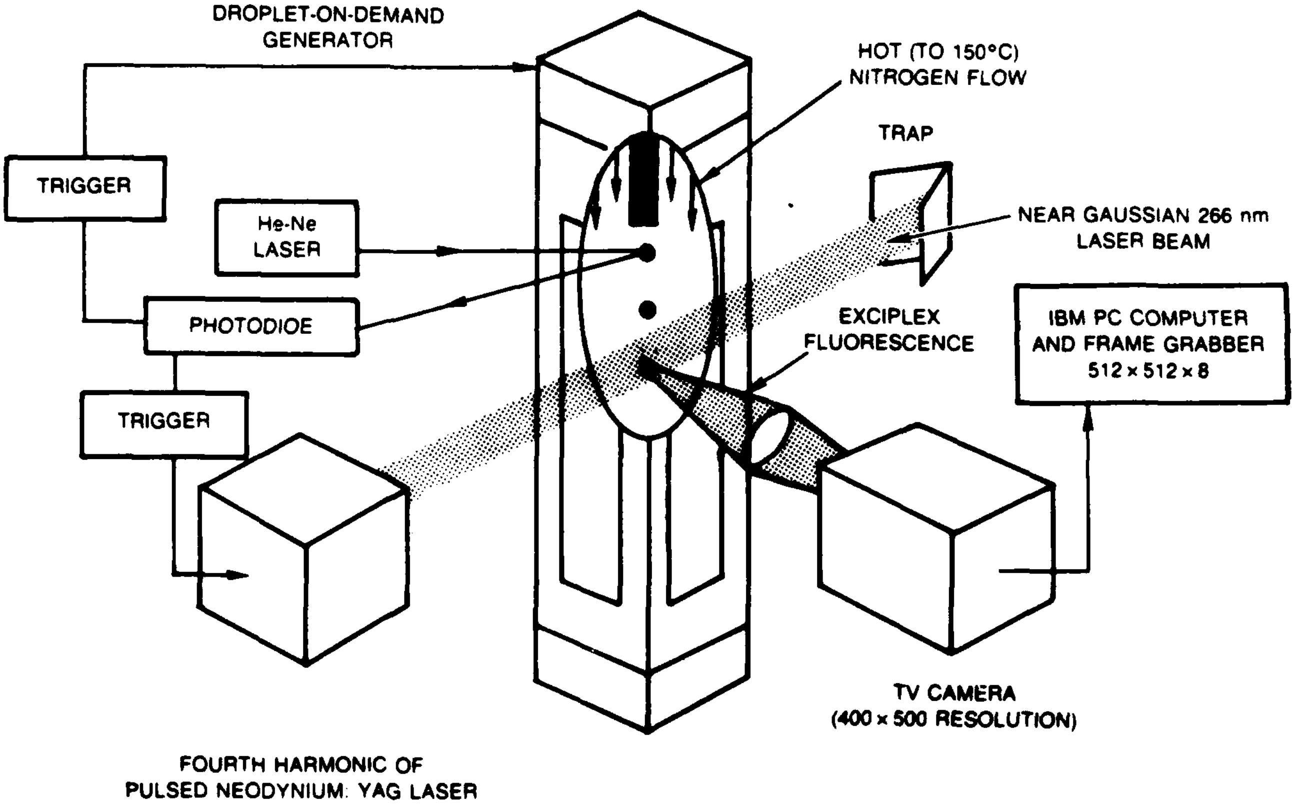
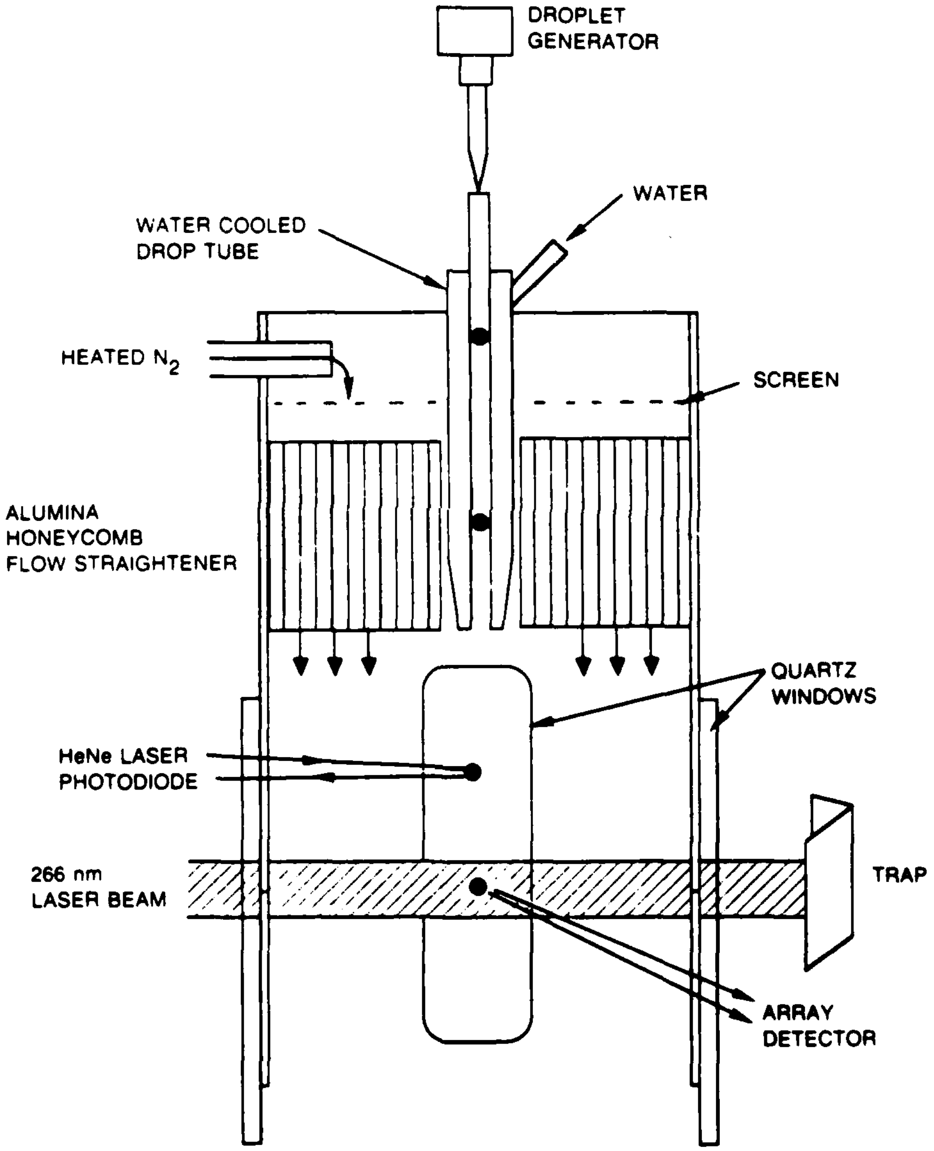


FIG. 3

DROPLET GENERATOR — DETAIL



forms, causing the liquid stream to break up into uniformly-sized, spherical droplets.

Early models developed at UTRC utilized a section of hypodermic needle nozzle which clogged easily and was difficult to clean. Relatively high voltages, usually greater than 1000 volts, were required to drive these units. Such high voltages often led to dielectric breakdown in or around the PZT; subsequent operation was usually erratic. Moreover, this type of unit was difficult to fabricate, as considerable delicate machining and careful, leakproof bonding of the nozzle holder to the inner conductive coating of the PZT cylinder was required. Typically only one in three units constructed was functional.

More recently a small diameter [.635 cm (.25 inch)], thin-walled [ca. .0508 cm (.020 inch)] PZT cylinder has been employed in place of the larger PZT [1.27 cm (0.5 inch)] cylinder used in the initial studies. The new style unit utilizes a detachable Pyrex glass nozzle. These nozzles were easily fabricated [by pulling, cutting, and lightly fire-polishing the end]; hence, are easily mass-produced. Most importantly, this type of nozzle can be easily cleaned, or simply discarded. These generators operate at much lower voltage, around 500 V [a result of the thinner wall], and have operated much more reliably.

The size of the droplets produced by these generators depends upon the nozzle bore; the droplet diameter is approximately twice the bore diameter. This was confirmed by microscopic measurement of the nozzle bore compared to droplet images calibrated against a microscope reticle. Droplets ranging from 200 microns to nearly 1 mm have been produced.

Test Chamber

The test chamber provides for the introduction of the injected droplet into coflowing heated nitrogen gas, and the subsequent laser-excitation and observation of exciplex fluorescence. A schematic view is shown in Fig. 2, presenting the overall arrangement. The upper portion of the test chamber is drawn in greater detail in Fig. 3. The generator injects droplets, with a velocity of approximately one meter/sec, at a 10 Hz rate, downward through a water-cooled tube of static gas. Upon exiting this constant temperature region, the droplet encounters an elevated temperature gas flow, made reasonably laminar by flowing though a 10 cm length of ceramic honeycomb, preceded by a screen to smooth the input flow.

The double-walled chamber has an observation region of nearly 30 cm in the vertical direction, with optical grade quartz windows which minimize fluorescence generation in the window itself by the 266 nm laser source. In order to obtain accurate synchronization it was found necessary to trigger the neodymium:YAG laser from a signal generated directly by the falling droplet encountering a He-Ne laser beam. Attempts to trigger both the droplet-on-demand generator and YAG laser [with appropriate delay] from a common pulse generator were unsuccessful because far too much jitter [presumably from the droplet generator] prevented accurate synchronization.

The He-Ne laser trigger system, when properly aligned, provides reliable synchronization of the 266 nm beam with the arrival of the drop. This was evidenced by the position of the frozen image, observed on a TV monitor, which appeared constant to better than one droplet diameter. This translates to a time synchronization of about 100 microseconds.

Droplet Vaporization Modeling

Modeling calculations of droplet vaporization for a selection of typical fuels were carried out to provide insight concerning the nature of droplet vaporization. These studies provided an estimate of the amount of vaporization a droplet would experience for a given set of conditions of ambient gas temperature, initial droplet size and temperature, and differential velocity between droplet and gas. These estimates were particularly useful in the experimental design of the test chamber. In addition to the amount of vaporization [droplet size] as a function of time, the model program also generates the temperature and velocity history. The model, developed by Dr. J.J. Sangiovanni of UTRC [Ref. 10], is outlined in Table 2. The pure compounds hexadecane and pentane were modeled under a wide range of initial conditions which are also shown in Table II. The results of model calculations for pentane drops of initial diameter of 250 microns are shown in Fig. 4. After falling through a constant temperature region of static air [of 15 cm distance], the droplets encounter coflowing air of velocity 1 m/s at 300 K. The surface temperature, velocity and fraction of droplet remaining are shown, in that order, as a function of time in the figure.

Two-Dimensional Imaging

Detection, capture of the digital image, and post processing of the digital image [image analysis] are of obvious importance in the successful performance of exciplex fluorescence spray visualization. Indeed, this rapidly evolving technology is of critical impact to this program. Those components which have been evaluated for 2-D imaging, both hardware and software, are described in this section.

Three different digital imaging systems, each complete and independent of the others, have been under development at UTRC in support of two-dimensional visualization investigations. These systems are outlined in Table 3; the third system is not discussed further as the software is still under development.

The first system consists of an intensified, rapid-imaging array camera by Microtex, a VAX 11/730 computer and a Metheus high-resolution color monitor. This system has an associated image memory of up to 7 megabytes, and therefore is capable of very high framing rates, of the order of several hundred per second with a spatial resolution determined by the 128 x 128 format with a 60 micron pixel spacing.

It was originally proposed that this system would serve as the workhorse of our imaging requirements, meeting the requirements of sensitivity, high data transfer rate, and connectivity to a fast computer. Unfortunately, the

TABLE 2

UTRC MODELING STUDIES

Model used: J.J. Sangiovanni, with slight modifications

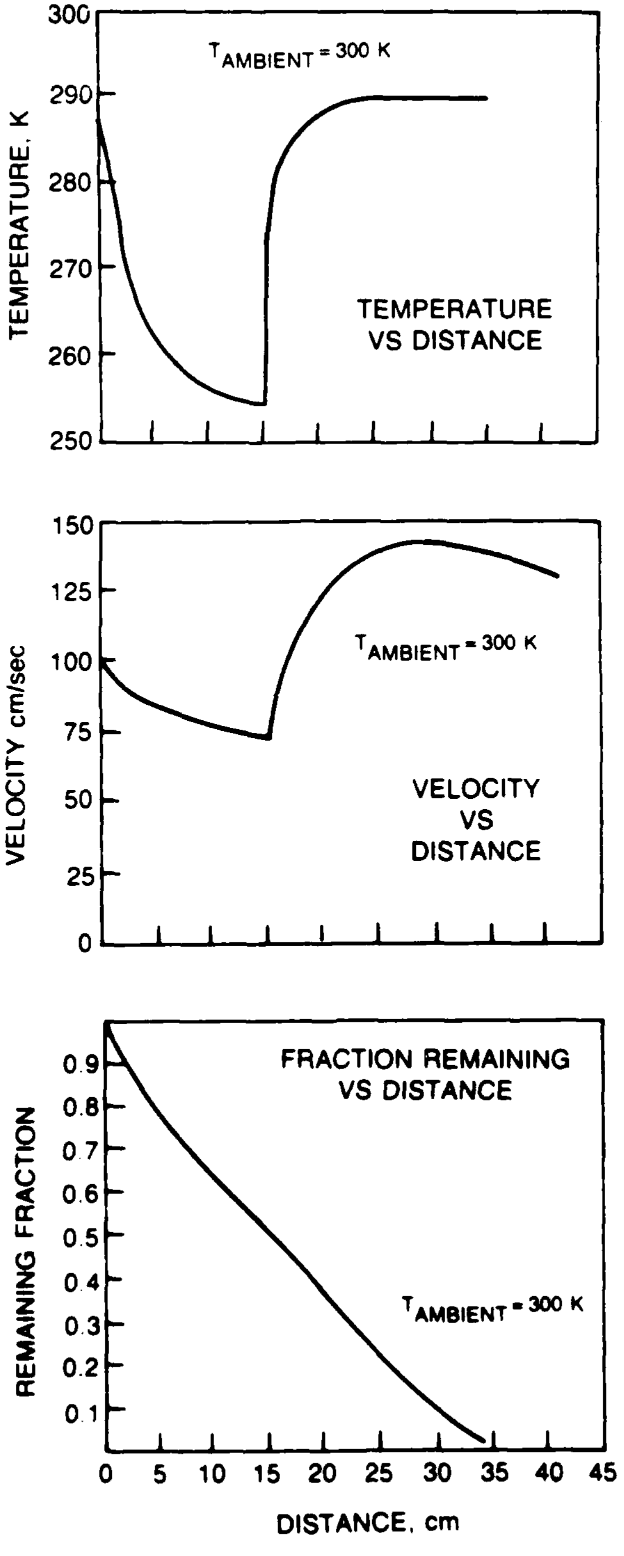
Brief description: Designed for vaporization and combustion of droplets of arbitrary size, composition, trajectory and environment....(including ambient gas parameters: temperature, flow velocity, and composition.)

Input parameters:	**Droplet thermodynamic and transport properties** **Size: 250 micron diam.** **Init. temp: 298 K** **Init. velocity: 100 cm/sec**
Environmental history:	**Droplet injected into constant 298 K path of 15 cm, abrupt transition into hot region of arbitrary temperature and flow, composition and distance.**
Output parameters: **(vs distance)**	**Fraction of droplet remaining** **Surface temperature** **Velocity**

FIG. 4

VAPORIZING DROPLET MODEL CALCULATION FOR PENTANE

AT 15 cm THE DROPLET ENCOUNTERS FLOWING AIR:
T = 300 K, V = 1 m/s



intensifier in the camera has not functioned properly and the unit has been returned to the vendor for repair; hence, this system has not been available for the development of imaging technology for application to this program. For these reasons, a reliable back-up imaging system was used to carry out the program goals.

The second system, which became the back-up system, replacing the unavailable Microtex system, is based upon a frame-grabber and an IBM/PC/XT microcomputer. The complete system employs a TV camera, image digitizer board residing in the computer, a B/W TV monitor and a commercial software package. This system is slower than the VAX-based system and does not offer the sensitivity of the intensified array camera. However, this system did permit the first observation of exciplex fluorescence from falling droplets, of simultaneous observation of liquid and vapor phase fluorescence of vaporizing pendent droplets, and for analyzing the laser beam.

Detection is achieved by means of several different vidicon [TV] cameras. All have relatively high spatial resolution, approximately 400 by 500 lines; but relatively low sensitivity. A Monozoom-7 [Bausch and Lomb] zoom microscope lens provides variable magnification up to a maximum of approximately 100. The frame grabber board [Imaging Technologies PCVision Board] has a resolution of 512 by 512 with 8-bit digitization [providing a gray scale of 256]. A commercial image analysis program [Image-Pro by Media Cybernetics] was installed and tested with the hardware system described above; this software package permits a wide variety of image operations and analysis. Digital filtering [high and low pass, median, and Laplacian, erosion and edge enhancement] is available to improve the image for measurement. Image analysis which can be performed include linear and area measurement [useful for measuring drop sizes]; these measurements can be performed in user-defined and calibrated units.

Several examples of captured fluorescent images with subsequent modification and/or analysis are given in this report; these include fluorescent imaging of an aromatic hydrocarbon solution to examine the laser beam intensity distribution, capture of the images of fluorescing droplets and the vapor cloud around the droplet.

Laser Excitation Source

The first image captured of fluorescing droplets exhibited considerable structure [striations and structural features]; this structure was thought to be an artifact--most probably caused by 'structure' in the laser beam. Under normal operating conditions the output of the neodymium:YAG laser is a complex annular beam in cross-section [a doughnut] the result of the diffractively-coupled unstable resonator cavity. After frequency doubling into the green [532 nm] and again doubling into the UV [266 nm], the intensity variations in the original 1060 nm laser beam are considerably magnified. It was decided to improve the laser beam distribution by changing the laser cavity optics by using different mirrors, and inserting an aperture, even though this change reduced the output power considerably. The resultant output beam appears to correspond to a nearly pure transverse TEM_{00} mode

TABLE 3

IMAGE CAPTURE AND ANALYSIS

- **Large system**
  - **Microtex intensified array camera**
  - **Vax 11/730 computer**
  - **Metheus color monitor**
  - ***Software under development***
- **Small system**
  - **IBM PC with hard disc**
  - **Imaging Technologies digitizer ("frame grabber")**
  - **Sony monitor, Panasonic camera**
  - **Imagepro software**
- **Alternative system**
  - **PAR OMA-II**
  - **PDP 11/34 computer**
  - **In-house software**

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[Gaussian mode]. The intensity distribution was observed and analyzed by capturing the frontal and profile views of the fluorescence induced in a solution of 9,10-diphenylanthracene.

The captured images were analyzed and a direct end-on view of the laser beam is shown in the left hand side of Fig. 5. The concentration of the fluorescing solution was adjusted so as not to be too optically thick, but have complete absorption over the pathlength of the cell. The TV camera with Monozoom 7 lens attached was placed directly against the cell to capture the image. The beam is obviously very circular and exhibits a near-Gaussian intensity distribution as the line contour shown in the inset graph demonstrates. The right side of Figure 5 exhibits a profile view of the fluorescence [upper picture] and the contour of the intensity along the line indicated [lower figure]. This view also confirms that the distribution was near-Gaussian, confirming that the beam approaches a TEM_{00} mode.

Liquid and Vapor Fluorescence Imaging from Droplets

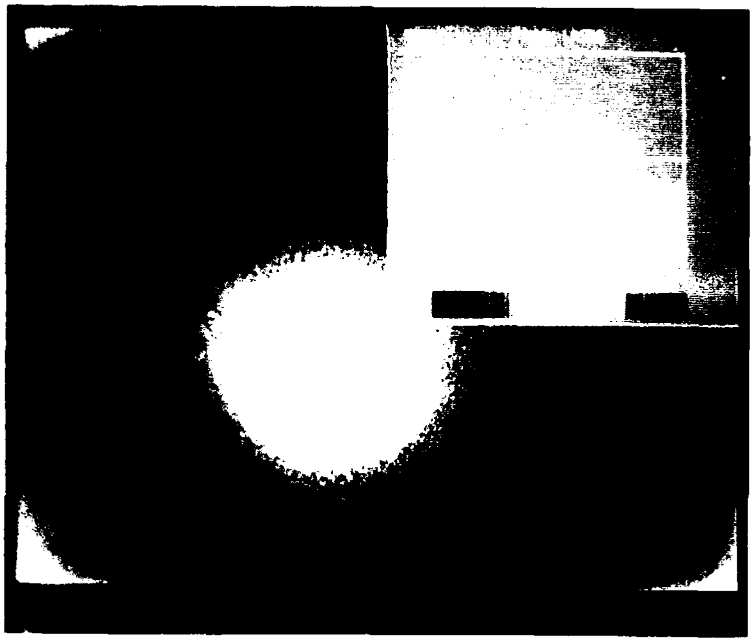
Images have been recorded of the liquid phase and surrounding vapor cloud from individual droplets. Figure 6, right, exhibits images taken of a fluorescing drop. These images demonstrated two important features: (1) that the exciplex dopant concentrations resulted in an optically thick solution of fuel, and (2) that considerable structure was present, most likely caused by variations in the laser beam intensity distribution discussed previously. The frozen droplet images were also recorded on video tape. It was noted that all drops were of uniform size and appeared perfectly round to the eye, as expected from the operating conditions and the mode in which this type of droplet generator functions.

After modifying the laser beam in the manner described above, dilute solutions [molar concentration of order 10-4] of 9,10-diphenylanthracene were employed to generate fluorescent droplets for observation. This solution was not optically thick, over the diameter of the droplet, as testified by the image shown in the left side of Fig. 6. Except for some slight focussing of the beam within the droplet, the fluorescent emission from the droplet appears very uniform. Refraction of the laser beam within the droplet was anticipated for a droplet diameter as large [compared to the laser wavelength] as those examined here. The effect of refraction of the laser beam within the droplet is being explored independently by Prof. Melton of UTD, and has recently been reported by Prof. R. Chang and coworkers [Ref. 11].

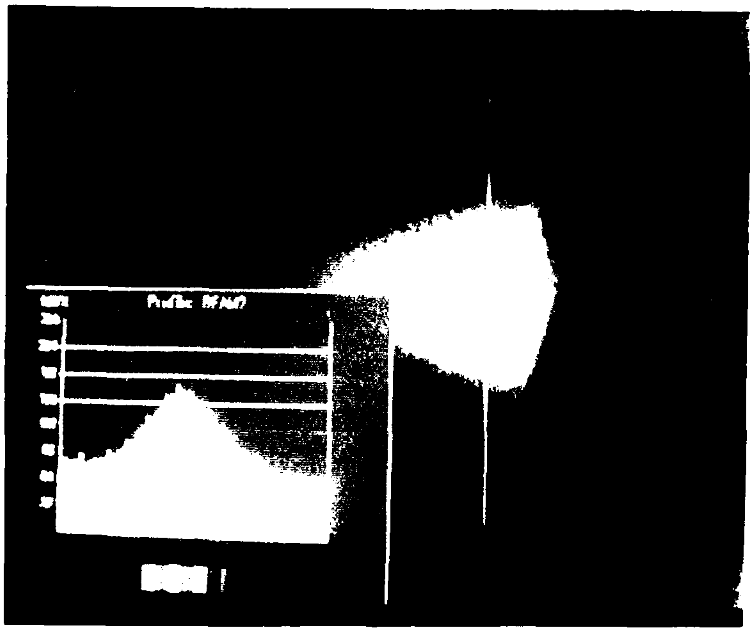
Examples of the type of image manipulation and analysis for a captured image of an optically thick drop are shown in Fig. 7, which demonstrates the histogram analysis of the area selected to lie within the box shown. The histogram is the distribution of intensity over all the pixels within the area of interest, according to the gray scale illustrated. The histogram can be determined for an individual pixel, a line, or an area of arbitrary size and shape. For the case shown the histogram indicated good contrast, but poor dynamic range.

FIG. 5

MODIFIED LASER BEAM



FLUORESCENCE IN 9, 10-DIPHENYL ANTHRACENE VIEWED END-ON, INTENSITY PROFILE ALONG A DIAMETER.



SIDE VIEW OF A MODIFIED LASER BEAM, FLUORESCENCE IN 9, 10-DIPHENYL ANTHRACENE, INTENSITY CONTOUR ACROSS PROFILE.

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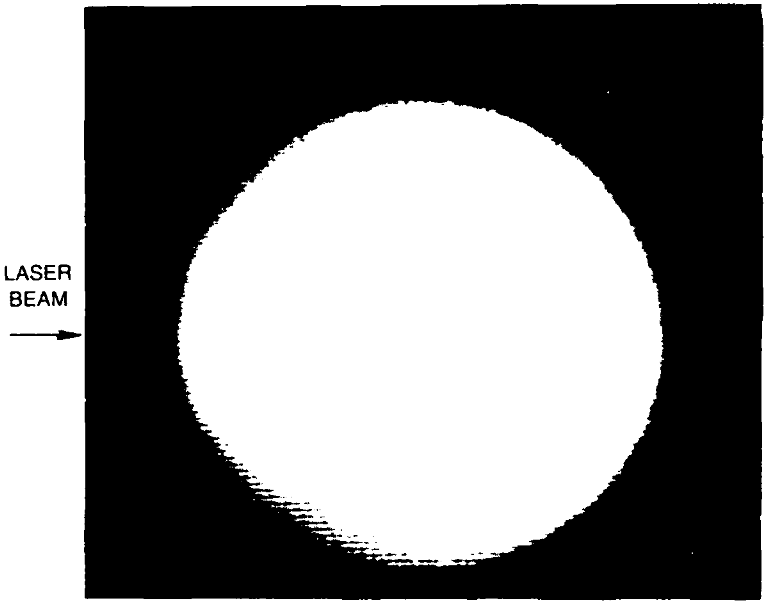
FIG. 6

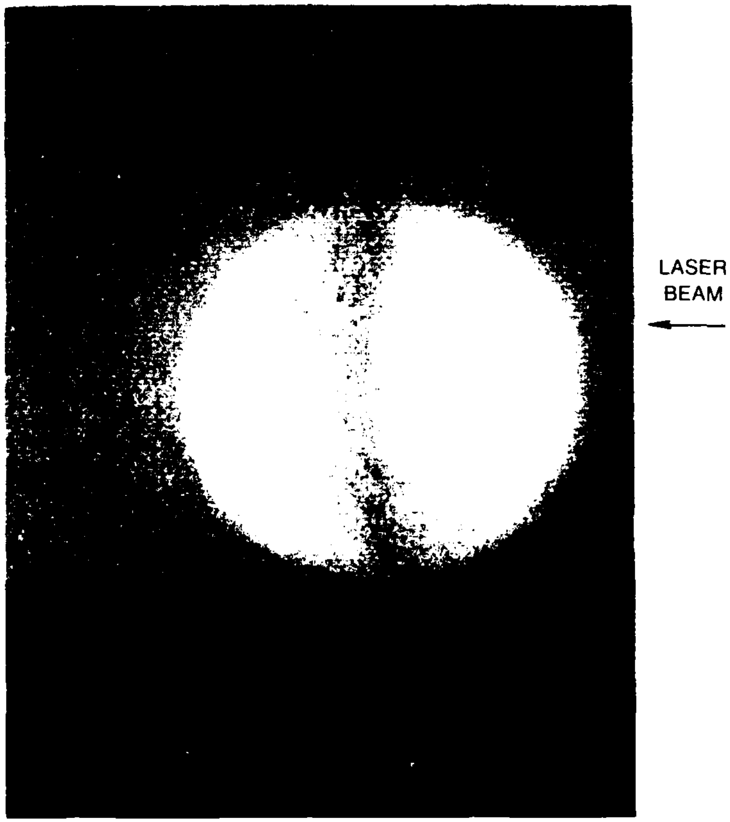
IMAGES OF FALLING DROPLETS

OPTICALLY THIN



9, 10-DIPHENYLANTHRACENE FLUORESCENCE. SLIGHT SELF-FOCUSSING IS APPARENT. UNIFORM LASER BEAM EXCITATION, MAGNIFICATION OF 90 AT FULL ZOOM.

OPTICALLY THICK

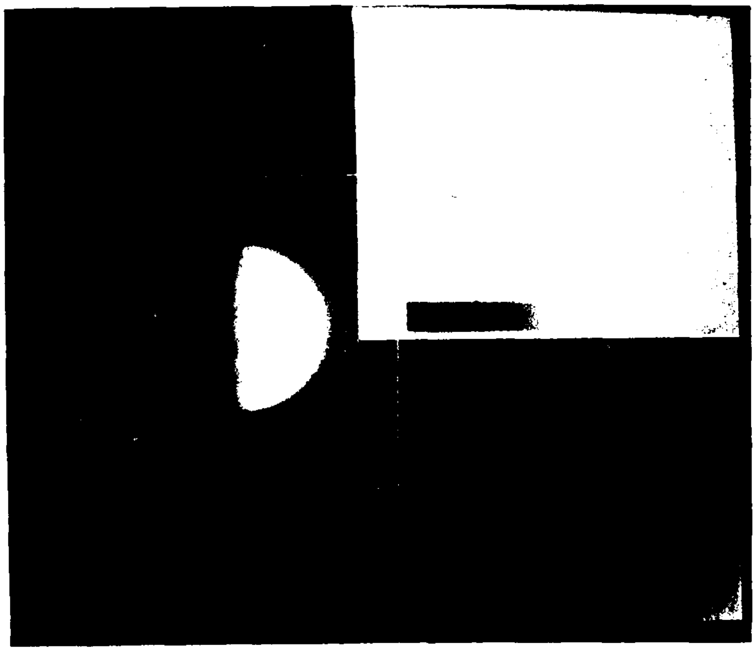


THE STRUCTURE IS BELIEVED TO BE DUE TO INTENSITY VARIATION IN LASER BEAM. NAPHTHALENE/TMPD EXCIPLEX.

87 - 7 - 19 - 4

FIG. 7

IMAGE ANALYSIS OF FLUORESCING DROPLET



HISTOGRAM OF MARKED SQUARE GRAY
SCALE = 256

87-7-19-6

Vapor Cloud Fluorescence Images

The capture of the fluorescent image of the vapor cloud surrounding the droplet is a formidable challenge for several reasons:

1. The vapor is much less dense than the liquid phase, by a factor of approximately 10 and

2. The larger fraction of the vapor fluorescence is in the ultraviolet below 300 nm, where normal lenses [optical glass] transmit very poorly, and, perhaps most importantly,

3. The liquid phase fluorescence, from both the exciplex and the monomer, which from the latter may be quite considerable for excitation at 266 nm, must be discriminated against. This is much less of a problem for excitation at wavelengths greater than 300 nm. Conversion of laser excitation to the third harmonic of Nd:YAG [355 nm] is available and its use as an excitation source will be investigated in future studies. It should be noted that for single droplet studies, the exciplex fluorescence can be discriminated against by the use of image analysis manipulation, i.e., because the location and geometry of drop are known, it can be subtracted out from the image.

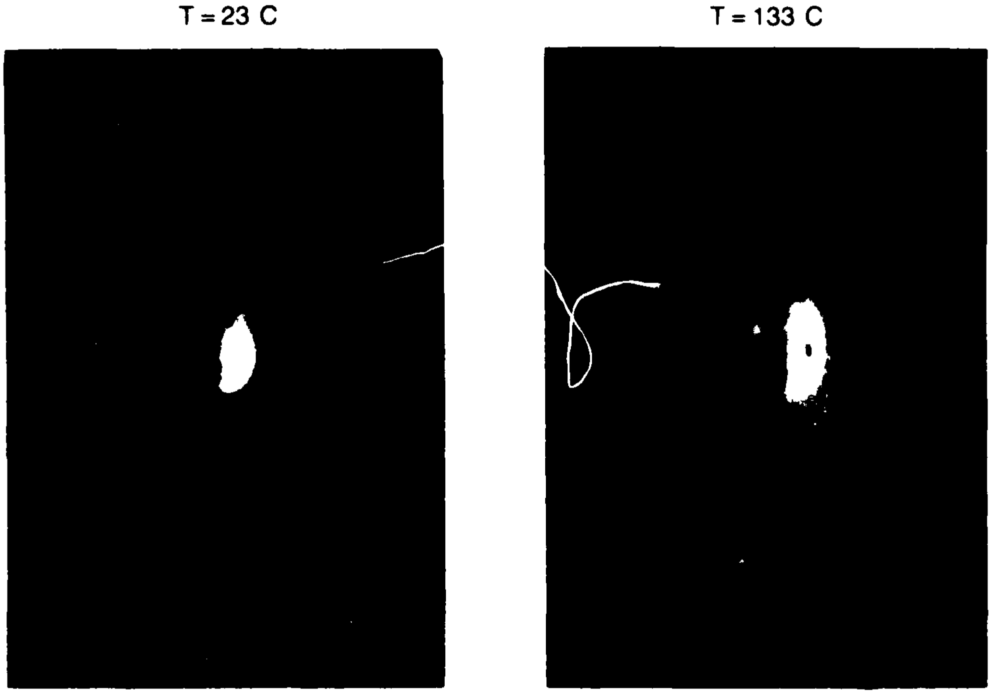
Figure 8 illustrates the laser-induced fluorescence obtained from the liquid and vapor phases from a pendent droplet at two different temperatures. The left side of the figure represents fluorescence from a cold [room temperature] pendent droplet from the exciplex system naphthalene/TMPD in decane. The solution is optically thick [of necessity, in order to insure formation of the exciplex] as may be noted from the half-shaded, half-lighted image. The right side of the figure displays the fluorescence from a heated [133 C] pendent droplet and the surrounding vapor cloud. Note that the vapor cloud fluorescence is asymmetric because the left side is in the shadow of the drop. The image shown was taken with the Newvicon camera, which barely has sufficient sensitivity to observe the vapor fluorescence. The problem of optically thick liquid solutions is one which will have to be addressed for investigation of sprays; possible solutions would include shifting the excitation wavelength and/or reduction of concentrations. Both of these solutions would likely require an attendant increase in sensitivity.

Increased snesitivity for detections vapor phase fluorescence will be possible in future research programs using a replacement camera. This camera, gated for precise synchronization with the laser excitation, will have three to four orders of magnitude greater sensitivity than those used in this study. Therefore, it appears that imaging problems caused by a lack of camera sensitivity do not present any insurmountable barrier to the practical use of exciplex-fluorescence diagnostic methods.

FIG. 8

PENDENT DROPS

NAPHTHALENE/TMPD IN HEXADECANE



LEFT, 266 nm EXCITED EXCIPLEX FLUORESCENCE FROM LIQUID; RIGHT, SIMULTANEOUS LIQUID AND VAPOR PHASE FLUORESCENCE. STRIATED REGION (RIGHT) INDICATES THAT CAMERA IS SATURATED.

Calibration Techniques for Quantitative Exciplex Fluorescence Visualization

Quantitative, non-perturbing, two-dimensional visualization is difficult to achieve, as is demonstrated by the absence of existing techniques which provide a quantitative measure of concentration of either liquid or vapor phases in an evaporating fuel. In order to achieve quantitative visualization, two distinct tasks must be completed:

(1) Calibration of the fluorescence signals against concentration of species in the vapor and liquid phases, most directly using an absorption method, and

(2) Calibration of the image itself; i.e., a determination of the gray-scale intensity distribution in the image.

Clearly, an implicit third task is to merge these two tasks together, and thereby achieve a correlation of image intensity with concentration. It should be emphasized that this calibration is a relative calibration, for a fixed, constant geometry; a recalibration must be made if the detector geometry is altered. Furthermore, it would appear that an absolute calibration would be very difficult to achieve, if not impossible.

With this outline of method in mind, the calibration experiments performed to date at UTRC and UTD are now described. It was decided to first calibrate the vapor phase fluorescence from the monomer TMPD.

The molar extinction coefficient, epsilon, for TMPD [N,N,N',N'-tetramethyl-1,4 phenylenediamine] was unknown for the vapor phase, thus requiring that it be measured before concentration could be determined by absorbance measurements. A sealed, evacuated cell, heated to a temperature to insure complete vaporization, was employed. This technique was suggested by Melton. A weighed sample of solid TMPD was quantitatively transferred to a quartz spectrophotometer cell equipped with a seal-off tubulation [commercially available]. The cell was cooled in liquid nitrogen, evacuated to approximately 100 microns, and the neck sealed off with a torch. The sealed, evacuated cell was transferred to a constant temperature fixture which could be placed in the sample chamber of a Varian SuperScan III spectrophotometer. The absorbance at 266 nm was measured as a function of increasing temperature. Sufficient time, about fifteen minutes, was allowed for the sample to reach thermal equilibrium at each successive temperature. A plateau was observed which indicated that all the sample had reached the vapor phase. This behavior is is shown in Figure 9. The temperature position for the onset of the plateau defined the minimum working temperature for the determination of the molar [decadic] extinction coefficient.

Figure 10 shows the results obtained for a series of four sample weights of TMPD; excepting the second point, which is clearly in error, a linear plot is evident. The value for epsilon is calculated to be 5500 L/mol-cm, at 266 nm, at 125 C. This is a reasonable value when compared to Melton's value at 304 nm [830 L/mol-cm], and scaling the approximate intensity ratio [7 to 10] from Berlman's spectrum [Ref. 12].

FIG. 9

TMPD ABSORBANCE VS TEMPERATURE
λ = 266 nm, SAMPLE #14

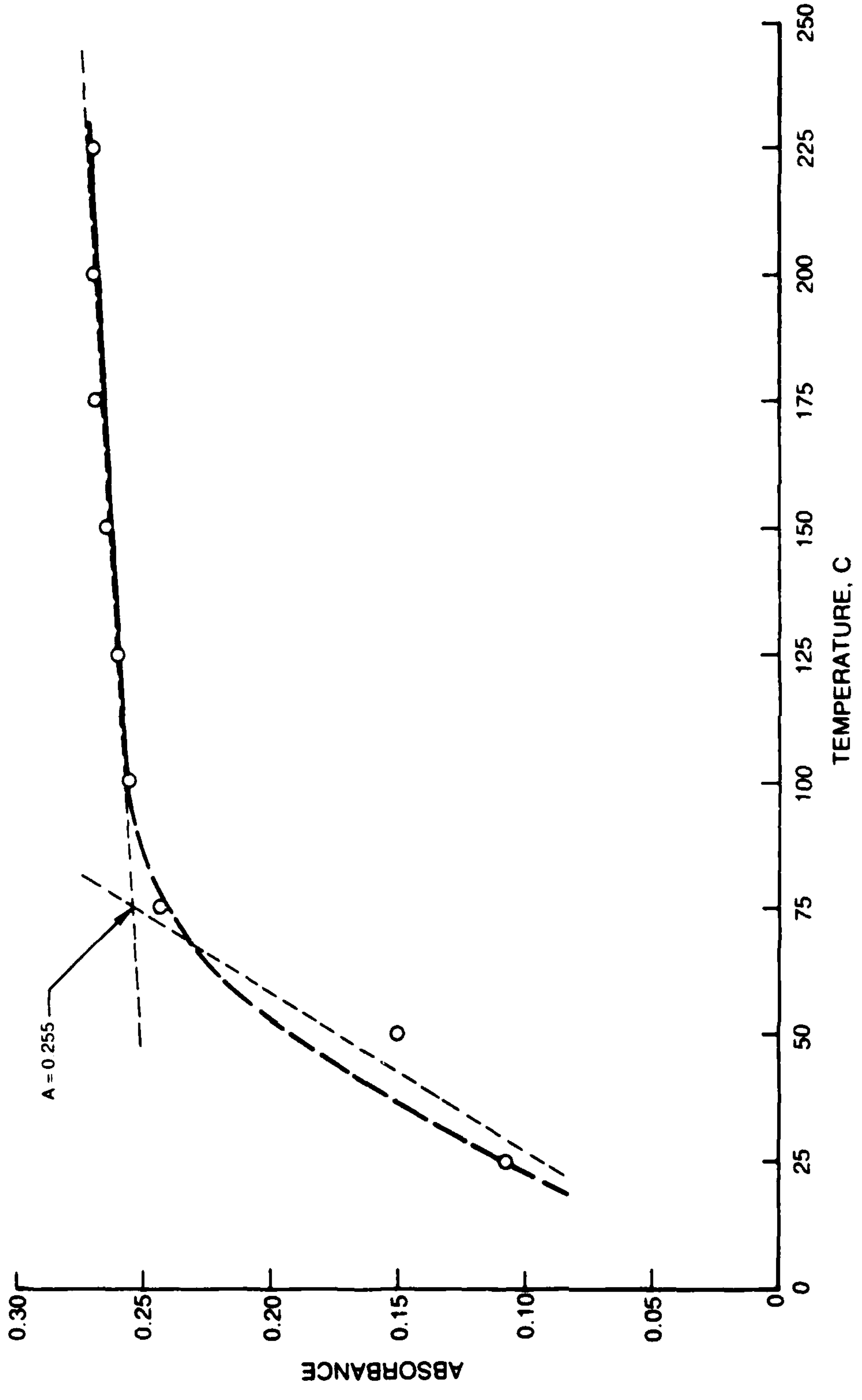


FIG 10

ABSORBANCE VS CONCENTRATION OF TMPD

λ = 266 nm, SEALED CUVETTES

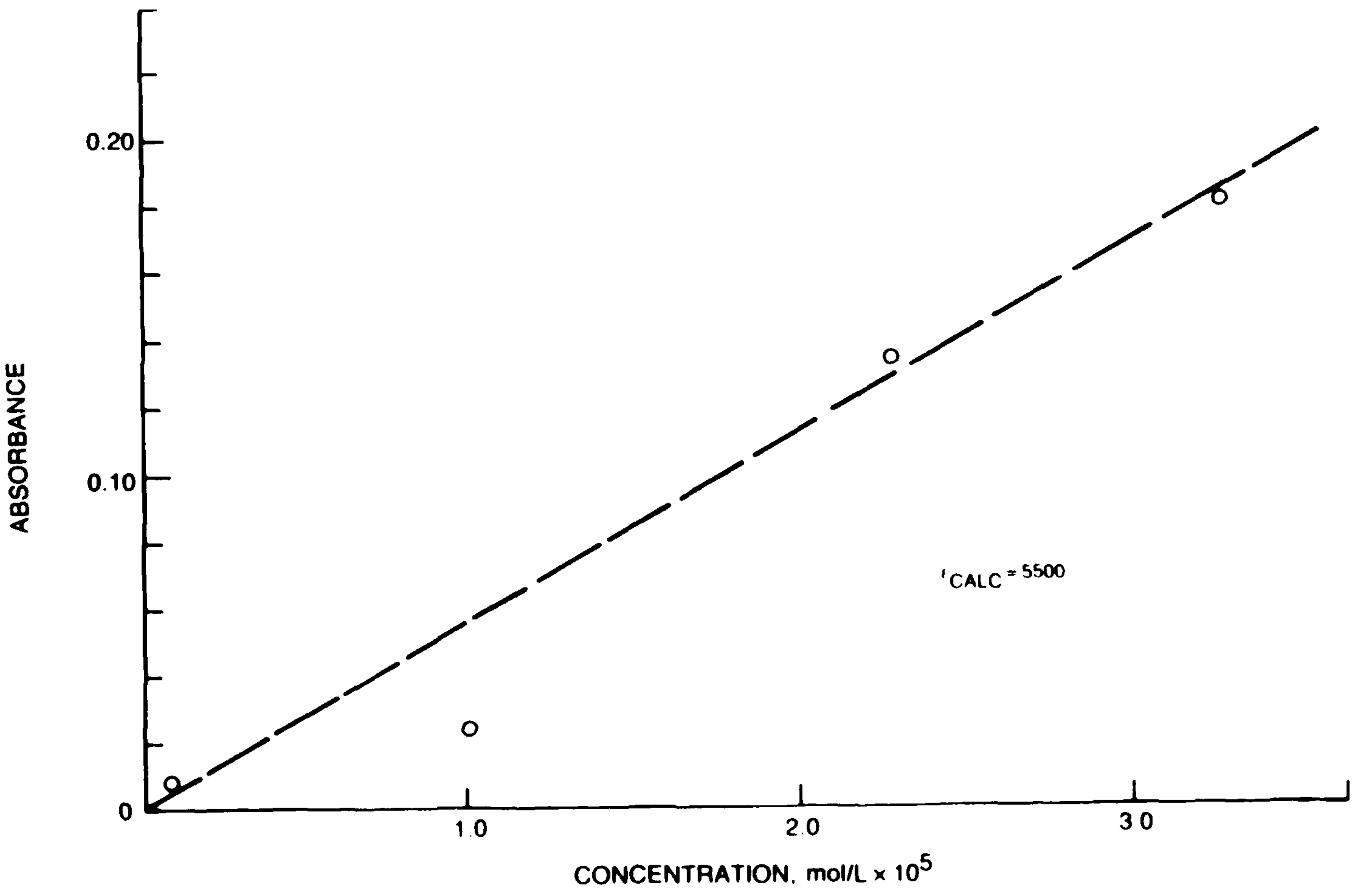


Figure 11 depicts the scheme for simultaneous measurement of absorption, fluorescence and the two-dimensional fluorescent image. Beginning at the upper left side of the diagram, the fourth harmonic [266 nm] of a neodymium:YAG pulsed laser is directed to a square, sealed quartz cuvette into which a weighed amount of TMPD has been placed. The cell is heated to a temperature sufficiently high to insure complete vaporization. The laser beam is sampled with a quartz plate beamsplitter for reference input [to compensate for instabilities in the laser output power] into a boxcar averager, and to provide a measure of I0 for absorbance measurements. The transmittance through the cell is measured to provide an absorbance measurement, and also serves to monitor the stability of the TMPD, which does exhibit some long time photochemical decomposition, possibly thermally assisted. This does not appear to be a severe problem over short time periods.

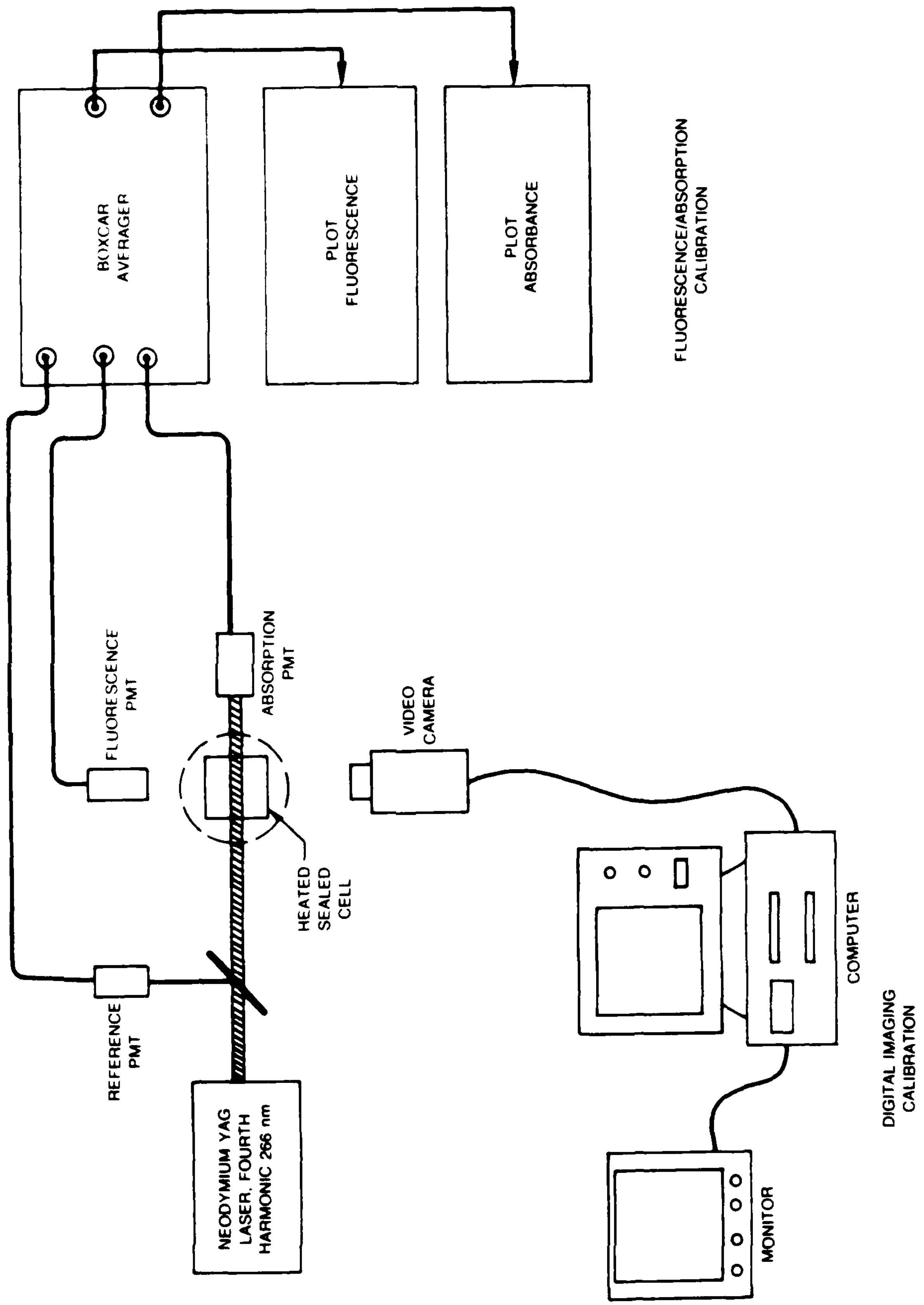
The fluorescence intensity, from a selected, constant excitation volume, fixed by a slit in the middle of the cell, is measured by a third detector. The fluorescence response will be examined for linearity over the anticipated range of concentrations and correlated with the absorbance. This fluorescence signal can then be used as a secondary standard for concentration measurements, in place of the absorbance measurements. Moreover, the fluorescence measurements can be extended beyond the lower range of the absorption techniques, provided a means of calibration [for instance, measured sample weights] is used. This would be necessary for low vapor concentrations.

At the same time these previous measurements are made, two-dimensional fluorescent images are recorded. The image is analyzed as described above [section on Two Dimensional Imaging] for maximum and minimum pixel brightness [dynamic range] and frequency distribution of the pixels over this range [histogram]. The dynamic range of the image digitizer is 256 gray levels [8-bits]. This distribution of fluorescence intensity over the image can then be calibrated against either the fluorescence or absorption signal to establish a concentration scale within the image. Subsequently, the vapor phase concentration distribution in any fuel spray image could be determined from the TMPD fluorescence, provided the detection geometry does not change.

Calibration of the liquid phase [exciplex] fluorescence presents a problem, because under typical operating conditions for spray visualization, concentrations are such that the liquid phase is optically thick. Calibration of the liquid phase exciplex fluorescence can be achieved by reducing the concentration or shifting the exciting wavelength. These conditions may have to be imposed for visualization, so that calibration of the liquid phase portion of the image field can be measured. Under conditions where the liquid droplet portion of the spray is optically thin, the fluorescence appears uniform [see for example, Figure 6], and a simple geometric area calibration, referenced to fluorescence from a single droplet whose diameter has been measured with a reticule. This calibration, based upon geometric scaling of the liquid phase fluorescence, was suggested by Prof. Melton.

FIG. 11

EXPERIMENTAL CONFIGURATION FOR CALIBRATION OF FLUORESCENCE/ABSORPTION VS CONCENTRATION



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III. CONCLUSIONS

The principal aim of this program was to develop and understand the application of laser-induced exciplex fluorescence to visualization of fuel vaporization from both sprays and single droplets. During the course of the contract, new exciplex systems [including the use of <u>intra</u>molecular exciplex systems] have been developed, the concept of exciplex thermometry was proposed and tested with good performance, and a method for determining liquid and vapor concentration was conceived, but not demonstrated. An apparatus for generating single droplets with injection into a flowing gas of selected temperature and pressure was constructed. Laser-induced exciplex fluorescence from single droplets was observed by means of two-dimensional digital imaging. Fluorescence from both vapor and liquid phases was observed simultaneously from pendent droplets. These experiments, coupled with modeling studies of droplet vaporization, have led to a better appreciation of the many problems of the vaporization process, and how exciplex fluorescence diagnostics can help further understanding in this complex field. Problems which remain in the application of exciplex fluorescence diagnostics are principally those of (1) achieving more nearly quantitative results and (2) the proper methodology for sprays. Initial efforts toward quantitative fluorescence measurements in the vapor phase have been made by calibrating the monomer absorbance and comparing it to the fluorescence. The problem of optically-thick sprays should be able to be addressed by shifting the laser excitation wavelength, reducing the exciplex concentration, using an intramolecular exciplex [thus requiring greatly reduced concentration of exciplex-former] or otherwise changing the exciplex formulation. There certainly appears to be no major obstruction to the quantitative application of exciplex diagnostics. Equally obvious, is that a great deal of experience needs to be gained--through experimentation with different exciplex systems in different fuels--before exciplex diagnostics can be deemed as mature a technique as CARS or the LIF of small molecules.

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2. Vapor/Liquid Visualization for Fuel Sprays, L. A. Melton and J. F. Verdieck, Combustion Science and Technology: Vol. 42, pp. 217- 222, 1985.

3. Fluorescence Methods for Determination of Temperature in Fuel Sprays, L. A. Melton and A. M. Murray, Applied Optics: Vol. 24, pp 2783-2787, 1985.

4. Exciplex-Based Diagnostics for Fuel Sprays, L. A. Melton, A. M. Murray, and J. F. Verdieck, Adv. in Laser Sciences-1; Proc. of First International Laser Science Conference, Dallas, TX, 1986 [AIP Conf. Proc. No. 146].

5. Laser Fluorescence Measurements for Fuel Sprays, L. A. Melton, A. M. Murray, and J. F. Verdieck, SPIE Vol 644--Remote Sensing, pp 40-47, 1986.

6. Fluorescence Thermometers Using Intramolecular Exciplexes, Henry E. Gossage and L. A. Melton, Applied Optics: Vol 26, pp 2256-2259, 1987.

Related Coupling Activities

Reports:

L. A. Melton: Exciplex Systems for Low Boiling Fuels, in support of NASA HoST Contract to UTRC.

Exciplex Systems for Real Fuels, in support of an AFWAL contract to UTRC on Fuel Vaporization.

PRESENTATIONS

Major Meetings:

XXth Combustion Symposium (International), The Combustion Institute, Ann Arbor, Michigan, August, 1984.

Combined Central and Western States Sections of the Combustion Society Meeting, San Antonio, Texas, April, 1985.

First International Laser Science Conference, Dallas, Texas, November, 1985.

SPIE 1986 Technical Meeting Southeast--Remote Sensing, Orlando, Florida, April, 1986.

Gordon Research Conference on Combustion Diagnostics, New Hampshire Summer, 1985.

Gordon Research Conference on Combustion Diagnostics, New Hampshire Summer, 1987

Regional Combustion Society meetings

Regional American Chemical Society meetings

University and Research Laboratory Seminars:

Princeton, Wesleyan, McGill, Yale, Rensselaer Polytechnic Institute, Brooklyn SUNY, Univ. of California [Berkeley], Stanford, Sandia CRL, Univ. of Texas [Austin], General Motors Research Center.

Contractor's meetings:

AFOSR, Yale, March, 1984; AFOSR/ONR, Pittsburgh, Jue, 1984; ARO, U/Calif Davis, March 1986; AFOSR, Stanford, April, 1986, AFOSR, Penn State, June, 1987.

V. PARTICIPATING SCIENTIFIC PERSONNEL

Degree awarded, if any.

UTD:

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Arthur A. Rotunno, Research Scientist
Normand Gantick [deceased], Technician
Edward Dzwonkowski, Technician
Jeffrey Crandall, Technician
James D. MacLeod, Technician

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3. L. A. Melton and J. F. Verdieck, Vapor/Liquid Visualization for Fuel Sprays, Combustion Science and Technology, Vol. 42, pp. 217-222, (1985).

4. L. A. Melton and A. M. Murray, Fluorescence Methods for Determination of Temperature in Fuel Sprays, Applied Optics, Vol. 24, pp. 2783-2787, (1985).

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8. L. A. Melton and A. M. Murray, Exciplex Systems for Real Fuels, Report on Subcontract from UTRC to UTD, in support of AFWAL Contract to UTRC.

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VII. APPENDICES

I. Vapor/Liquid Visualization in Fuel Sprays, L. A. Melton and J. F. Verdieck.

II. Vapor/Liquid Visualization for Fuel Sprays, L. A. Melton and J. F. Verdieck.

III. Fluorescence Methods for Determination of Temperature in Fuel Sprays, L. A. Melton and A. M. Murray.

IV. Fluorescence Thermometers Using Intramolecular Exciplexes, H. E. Gossage and L. A. Melton.

APPENDIX I

UTRC84-29

VAPOR/LIQUID VISUALIZATION IN FUEL SPRAYS

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Proceedings, Twentieth Symposium (International) on Combustion, 1985

August 1984

Vapor/Liquid Visualization in Fuel Sprays*

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Subject Areas:

05 02	Diagnostic Methods, Fluorescence
13 03	Heterogeneous Combustion, Sprays
20 02	Phase Changes, Evaporation

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Abstract

In a series of demonstration experiments, we have shown that exciplex visualization systems can be used to photograph either the liquid or the vapor pattern in a hollow cone fuel spray. Thus, vapor density information can be obtained without the analysis of droplets. Furthermore, through image analysis of digitized negatives, we have obtained a quantitative presentations as false color maps and contour density plots.

The exciplex visualization systems exploit the reversible equilibrium which may exist when an excited organic molecule (M^*) reacts with a suitable ground state organic molecule to form an emitting exciplex (E^*). The emission from M^* can be made characteristic of the vapor and the emission from E^* can be made characteristic of the liquid. Because the emission from E^* is shifted with respect to that from M^*, filters can suppress either the M^* or E^* emissions, and hence with laser sheet excitation, two dimensional vapor or liquid sections of the fuel spray can be photographed.

I. Introduction

The preignition and combustion behavior of fuel sprays has been the subject of hundreds of experimental and theoretical studies, as detailed in several recent reviews.[1-6] The dominant theme in these investigations is the necessity for understanding the evaporation, heat transport, and fluid dynamic interactions of droplets, either as isolated entities, carefully prepared arrays, or statistical aggregates. These studies are in close accord with the experimental technology, in which droplets themselves are readily measured, either through photography, holography, or laser light scattering. In contrast, direct measurements of vapor concentrations in a heterogenous, evolving fuel spray are very difficult and seldom made *in situ*. In this paper we present a spray visualization technique, based on spectrally distinct fluorescence emissions from the liquid and vapor phases, in which the *total mass* of liquid or vapor fuel within a specific element may be determined, without consideration of the extent of its dispersion into droplets.

In this exciplex visualization technique, the vaporization of the fuel spray is followed by adding to the fuel a fluorescent organic molecule (the monomer, M), and a second exciplex-forming organic molecule (the quencher, N). The exciplex (E^*) fluorescence is necessarily red-shifted with respect to the monomer fluorescence, and the concentrations of monomer and quencher in the fuel mixture can be adjusted so that the exciplex emission dominates the liquid fluorescence and the monomer emission dominates the vapor emission.[7] With careful control of the vaporization properties of the components, this fluorescent marker system can provide quantitative measurement of the mass of fuel vapor and the mass of liquid in a particular spatial element.

We have demonstrated this exciplex visualization technique in a hollow cone fuel spray.[8] The spray was irradiated with a sheet of UV laser light, and with appropriate filters, two-dimensional sections of the liquid and vapor fluorescence of the evaporating spray were separately photographed. The fluorescence lifetimes of the manomer and exciplex are typically less than 100 nsec, and hence with the short pulse laser, "frozen flow" photographs of the evolving fuel spray were readily obtained. Finally, we have taken selected photographs from these experiments and have subjected them to digital image analysis. The resulting density maps indicate the types of two-dimensional, "frozen-flow" information which these exciplex visualization techniques can make available. Indeed, it is anticipated that high repetition rate pulsed lasers and fast electronic imaging systems will make it possible to follow the evolution of an evaporating fuel spray in real time.

II. Visualization Photophysics

The optical measurement of the separate vapor and liquid portions of a fuel spray is made difficult because of the paucity of spectroscopic characteristics which differ significantly for organic (fuel) molecules in the two phases. Johnston investigated spontaneous Raman scattering but concluded that, in the C-H stretching region near 3000 cm^{-1}, there were insufficient differences between the spectra of the vapor and liquid to allow their separate measurement.[9,10] The remaining methods have exploited the index of refraction differences between the liquid droplets and the less dense ambient vapor/air surrounding the droplets and have used either direct photography, laser light scattering, or two-wavelength laser absorption/scattering.[11-16] The strategy used in the work described here is to recognize that modern diesel and gas turbine fuels already contain significant amounts of aromatic organic molecules which are themselves fluorescent, and to develop additives which cause the fluorescence of the liquid phase to be shifted significantly relative to that of the original aromatic molecules, which will mark the vapor phase.

An exciplex (<u>exci</u>ted state com<u>plex</u>) is a molecule which is formed in the reaction between an organic molecule (here called the monomer) in an excited electronic state and some other ground state molecule.[17,18] The binding energies in the excited state may be quite significant, say 20-30% of a normal chemical bond, but there is negligible binding in the ground state. Figure 1 illustrates schematically the processes involved. In particular, because the exciplex is bound with respect to the excited monomer, M^*, and ground state additive, N, its emission is necessarily at lower energy, i.e., longer wavelength, than that of the monomer. The spectral shift between the two emissions is then adjusted by varying the binding energy of the exciplex itself.[19] The naphthalene/tetramethyl p-phenylene diamine (TMPD) exciplex system used in this study has a binding energy of 15-20 kcal/mole and a spectral separation of 90 nm between the peak of the exciplex fluorescence and the peak of the monomer fluorescence.

The second important feature in the use of exciplexes for the visualization of evaporating fuel sprays is that the exciplex is a relatively polar species[19] and is formed in a reversible equilibrium with M^* and N.

$$M^* + N \rightleftharpoons E^* \qquad (1)$$

If the concentration of the additive N in the liquid is set sufficiently high, then the equilibrium lies far toward the exciplex; thus the liquid phase fluorescence is dominated by the exciplex emission. In the vapor phase, the densities are much lower, and one would expect, the potential for stabilization of the relatively polar exciplex is less; hence, the equilibrium shifts strongly toward the free monomer. Consequently the vapor phase fluorescence is dominated by the monomer emission.

The demonstration experiments reported here used an exciplex visualization system based on TMPD (M) and naphthalene (N). Other exciplex combinations are possible, and hence the visualization systems may potentially be selected for characteristics such as volatility of components, match of boiling points with that of the fuel, exciplex binding energy (which determines the equilibrium constant for the monomer-exciplex equilibrium),[19] and spectral separation of the monomer and exciplex emissions. A systematic search for new exciplex visualization systems useful in the range of 0-300°C is curently underway.[20]

III. Fuel Spray Visualization Experiments.

Previously reported work showed that the vapor and liquid phase fluorescent emissions could be distinguished for a suspended droplet heated by flowing nitrogen.[7] In a more recent series of demonstration experiments,[8] a fuel spray was generated with a simplex nozzle and irradiated with a sheet of UV laser light. The resulting fluorescent emissions were then photographed at right angles to the laser beam. Through use of the appropriate filters, the vapor and liquid emission patterns were separately photographed. With high speed film, adequate exposures could be obtained with a single laser shot, and since the laser pulse lasts only 10-20 nanoseconds and the fluorescence only 10-100 nanoseconds, these single-pulse photographs represent frozen-flow results.

The apparatus used in these experiments has been described previously[8] and only a brief description will be given here. The fourth harmonic of Nd:YAG at 266nm (approximately 80 mJ/pulse) is expanded in the vertical dimension to create a sheet of light approximately 40mm high. The simplex fuel nozzle (Delavan hollow cone, 0.5 gph, 45° cone angle) sprays preheated fuel/dopant mixture into heated nitrogen (200-250°C) which is flowing in the spray direction. The fluorescence from the spray is photographed at right angles to the plane of the laser light. The camera lens transmits the liquid fluorescence (λ_{max} = 470nm) and vapor fluorescence (λ_{max} = 380nm), but absorbs the scattered laser light. With appropriate spectral filters, one can isolate the vapor emission or the liquid emission, and thus photograph separately the vapor or liquid distributions.

The fuel mixture used in these experiments was 2.5% naphthalene (bp 218°C, MW = 128), 1.0% tetramethyl-p-phenylene diamine (TMPD) (bp 265°C, MW = 164), 96.5% hexadecane (cetane) (bp 287°C, MW = 226) by weight. The fluorescence emission spectra for the liquid and vapor taken in heated cuvets at 220°C are shown in Fig. 2.

The negatives were digitized using a scanning densitometer with a spot size resolution of 12.5 microns. A commercial program[21] assigned a 500 by 500 pixel block to the digitized images. Each pixel has a dynamic range of eight bits for each of the three basic colors, red, green, and blue of the color terminal. Thus, for a given image, a density range was found and a spectrum of colors assigned to illustrate the density pattern. Unfortunately, the black and white rendering of the color falls short of illustrating the vivid contrast provided by the color density maps, so these are not presented here. In order to provide a more quantitative measure of the fuel density, a contour mapping of the fluorescence intensity distribution was obtained. These density contours three-dimensional perspective views are presented in Figures 3b-5b for comparison with the original photographs. Note that the density scale is not absolute, but only relative for each individual image.

IV. Results

Figures 3, 4, and 5 summarize the results which can be obtained with the present exciplex/laser/camera/image analysis system. In each figure, section a) is a black and white print of an original color photograph in which the vapor pattern is purple and the liquid pattern is blue green.[8] Section b) shows contour maps of the emission intensities, and c) three-dimensional perspective views. In figures 3a, 4a, and 5a the color film pictures were taken with no filter, with Schott GG-475 glass (liquid fluorescence), and with Schott UG-11 glass (vapor fluorescence), respectively. The photographs shown in figure 3a-5a required approximately 50 laser shots (5 seconds at 10 Hz). They are, therefore, averaged results, such as one can see with the human eye.

The laser sheet is set to pass exactly through the apex of the hollow cone spray, and hence the "vee" of the conic section is readily seen. The emission from the vapor can be seen to be distributed fairly homogeneously within the nominal cone of the spray. Figures 4 and 5 show, respectively, the results which can be obtained when the liquid emission only or the vapor emission only is photographed by insertion of the appropriate filters. The liquid only pattern shows clearly the thin sheet of liquid coming out of the nozzle in a cone and breaking up into fine droplets. The vapor only pattern shows the nearly homogeneous distribution of the vapor within the spray cone.

Presumably the vapor pattern should not extend all the way back to the nozzle, but in this case, the fuel has been preheated, and there is rapid evaporation of the hot fuel as well as the evaporation through heat transfer from the surrounding nitrogen flow. Further, in taking these photographs, the fuel spray was turned off while the films were loaded into the camera; the laser was then peaked up, the fuel spray turned on for a few seconds to stabilize, and the camera shutter was then opened for the exposure. Hence, although the nominal conditions for the spray (fuel pressure, temperature, etc.) were identical, these photographs in fact represent sprays which may have slightly different transient conditions.

The color photographs originally obtained, and their black and white renderings here, show in broad measure the two-dimensional patterns of liquid and vapor within the fuel spray. However, the fluorescence lifetimes of the species in these exciplex visualization systems are typically less than 100 nanoseconds, and hence, with the short pulse (10 nanoseconds) of the Nd:YAG laser used, "frozen-flow" results can be obtained. With high speed film we have also obtained photographs with a single laser shot, which show individual droplets, instabilities in the expanding fuel sheet, and spatial inhomogeneities in the vapor pattern.[8]

V. Discussion

These exciplex systems currently have demonstrated great promise as optical probes for the determination of the relative spatial distributions of the liquid and vapor portions of a nondense fuel spray. The elements necessary to realize the full potential of the technique as a quantitative tool will now be discussed. The fluorescence technique possesses, by its nature, immediate assets and drawbacks. Most importantly, the fluorescence process is inherently linear in the number of fluorescent molecules, and as long as perturbations such as optical thickness, scattering in dense sprays, and quenching of the fluorescence by vapor phase molecules can be made negligible, the relative spatial profiles of both the liquid and vapor portions of the fuel spray should be readily measureable. As long as the spray is optically thin, the fluorescence from a droplet is proportional to its mass; thus the total droplet fluorescence in an individual spatial element is proportional to the total liquid mass present. The fluorescence from an optically thin vapor is, of course, directly proportional to the mass present. Thus the exciplex visualization technique provides a direct means of measuring the amounts of liquid and vapor present, without the necessity of determining droplet number densities and size distributions.

The spectral separation of the phases which we achieve with the naphthalene/TMPD system and the glass filters is not complete, i.e., some liquid emits in the spectral region we identify with vapor and vice versa. Using the results shown in fig. 2, we have estimated these effects by calculating the relative vapor and liquid spectra modified by the filters. Provided that the quantum yield for fluorescence of the monomer and exciplex are similar, when we filter the fluorescence through the UG-11 glass (vapor), the fluorescence efficiency of the liquid in the nominal vapor spectral region is about 8% of that for the vapor on a per mass basis. When the GG-475 filter is used, the fluorescence efficiency of the vapor in the nominal liquid spectral region is about 30% of that for the liquid. That is to say, vapor mass fraction measurements are virtually unaffected by the presence of similar mass fractions of liquid, but liquid concentration measurements may require correction for the presence of similar amounts of vapor. Further work is underway to extend this analysis; it is clear, however, that these effects are readily calibrated and may be accounted for.

Fluorescence trapping can be made negligible in these visualization systems. The exciplex emits at sufficiently long wavelengths that the molecules M and N do not absorb the fluorescence; the exciplex, having no bound ground state, cannot reabsorb its own fluorescence. The TMPD fluorescence starts at roughly 345nm and extends to 500nm,[26] with its peak at 380nm. The TMPD absorption bands start at 370nm, and the naphthalene absorption bands start at 320nm. Thus a filter which transmitted in the wavelength range 370nm to 400nm would insure that the TMPD visualization signal observed had been negligibly attenuated by the intervening fuel spray mixture. The UG-11 glass filter used in this work transmits roughly from 250nm to 400nm, and thus some fluorescence trapping may have occurred. No tests of the linearly of the TMPD fluorescence with TMPD vapor pressure were made in this work.

Optical thickness and intense scattering in dense sprays, such as found in diesel fuel injectors, will distort the spatial measurements by absorbing and scattering the laser beam excitation. Thus the portion of the spray which the laser beam enters will be excited more strongly than the far side of the spray. In many cases, the optical thickness effects, due to bulk absorption by the fuel/dopant mixture, can be avoided by choosing an excitation wavelength for which the absorptivity is lower; however, scattering from the numerous small droplets will remain a serious problem for any optical technique used with these dense sprays.

The quenching of the vapor phase fluorescence can be a serious problem. Nitrogen and aliphatic hydrocarbons appear to be nearly inert as far as the quenching of the fluorescence of organic molecules is concerned.[22,23] However, oxygen is highly efficient, and quenches the fluorescence of virtually every collision.[24,25] Hence, for a fuel spray into air, the portions of the spray which mix with the air will show much less vapor fluorescence than is to be expected on the basis of the vapor phase fuel concentration. In the case of TMPD in air at atmospheric pressure, a typical molecule would experience five quenching collisions during its fluorescence lifetime, and hence its fluorescence quantum yield would be reduced by approximately a factor of six. The quenching of the liquid (exciplex) fluorescence by oxygen is much less of a problem, since the dissolved oxygen may be purged out of the fuel with a nitrogen flow, and the atmospheric oxygen will not have time to diffuse into the fuel during the 50-100 milliseconds a fuel droplet persists in the flow. It should be noted, however, that many spray characterization experiments can be done in nitrogen, and thus one can avoid oxygen quenching problems.

In addition to the problems which may distort the measurement of accurate relative distributions of vapor and liquid portions of the fuel spray, there are particular problems which may affect the quantitative determination of the relative amounts of fuel and vapor in the spray, as for example, the relative absorption strengths and quantum yields of the monomer and exciplex. Such parameters should, however, be measurable in routine experiments. The more serious question regarding the relative amounts of liquid and vapor present is that neither the exciplex in the liquid nor the monomer in the vapor is the fuel itself; both species are <u>markers</u>, one for the liquid portion and the other for the vapor portion of the fuel. It is thus necessary to understand the ways in which the fuel concentrations derived from the markers may deviate from the marker concentrations themselves. In the limit of fast evaporation of a droplet, i.e., the rate of regression of the droplet surface is fast compared to the characteristic mass diffusion lengths in the droplet, the droplet evaporation, except for initial surface depletion, is limited by the evaporation of the least volatile component, and hence the droplet evaporates with each layer having approximately the bulk concentration.[2] Under these conditions the dopants serve as good linear markers since the ratio of marker to fuel in either phase remains virtually constant. In the limit of slow evaporation, particularly in the center of dense, cold sprays, the droplets may persist long enough for thermal equilibrium to be reached, i.e., the more volatile components will evaporate and leave behind the less volatile components as in a distillation. In terms of the design of future exciplex systems, we have chosen to match, as far as possible, the boiling points of the exciplex components and the fuel at one atmosphere, and thereby to reduce the tendency of the components to evaporate differentially. Recent work by Wang et al suggests that this adaptation will probably be adequate.[27] The cold dense spray case is the most stringent test in this respect, and more dilute sprays, with faster heat transfer and evaporation, will allow more nearly ideal (linear) operation of the exciplex/monomer marker systems.

VI. Conclusions

The exciplex visualization technique has been applied to a realistic, hollow-cone fuel spray. Color photographs showing both the blue-green liquid pattern and the purple vapor pattern have been obtained by use of appropriate visible and ultraviolet filters. The feasibility of single shot, "frozen-flow" photographs has also been demonstrated. Photographs can yield additional quantitative information when subjected to digital methods of image analysis.

In considering the use of exciplex visualization systems for the study of evaporating fuel sprays, it should be noted that these fluorescent sensors provide little information about the droplets themselves. Rather, the intensity from the exciplex emission in a particular spatial element measures, in an optically thin system, the total liquid mass in that element, regardless of its degree of atomization. The information provided by this real-time, two-dimensional visualization technique should be useful in stimulating our understanding of the dynamics of fuel sprays.

VII. Acknowledgements

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Figure Captions

1. Schematic Potential Energy Diagram for an exciplex system

2. Relative Emission Spectra for 15% naphthalene/1% TMPD/84% cetane obtained in cuvet at 220°C; excitation at 313 nm. — — —, emission obtained with GG-275 filter; — · — ·, emission obtained with UG-11 filter. The unfiltered curves are each normalized to unity.

3. Emission from hollow cone fuel spray, 50 laser shots for exposure, no filter (both liquid and vapor patterns shown)

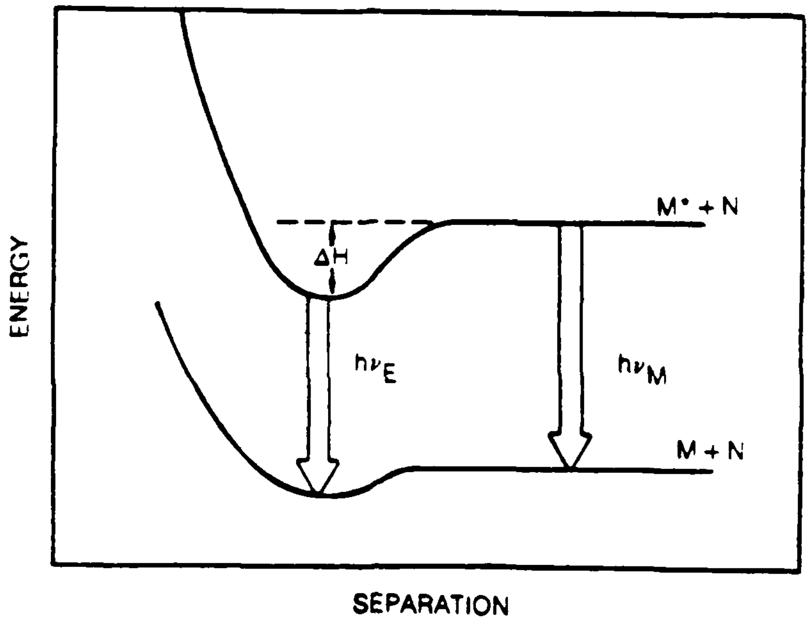
   a) black and white rendering of original color photograph

   b) contour density map of a)

   c) three-dimensional perspective view of density function

4. Same as 3) except GG-475 filter was used (only liquid pattern shown)

5. Same as 3) except UG-11 filter was used (only vapor pattern shown)



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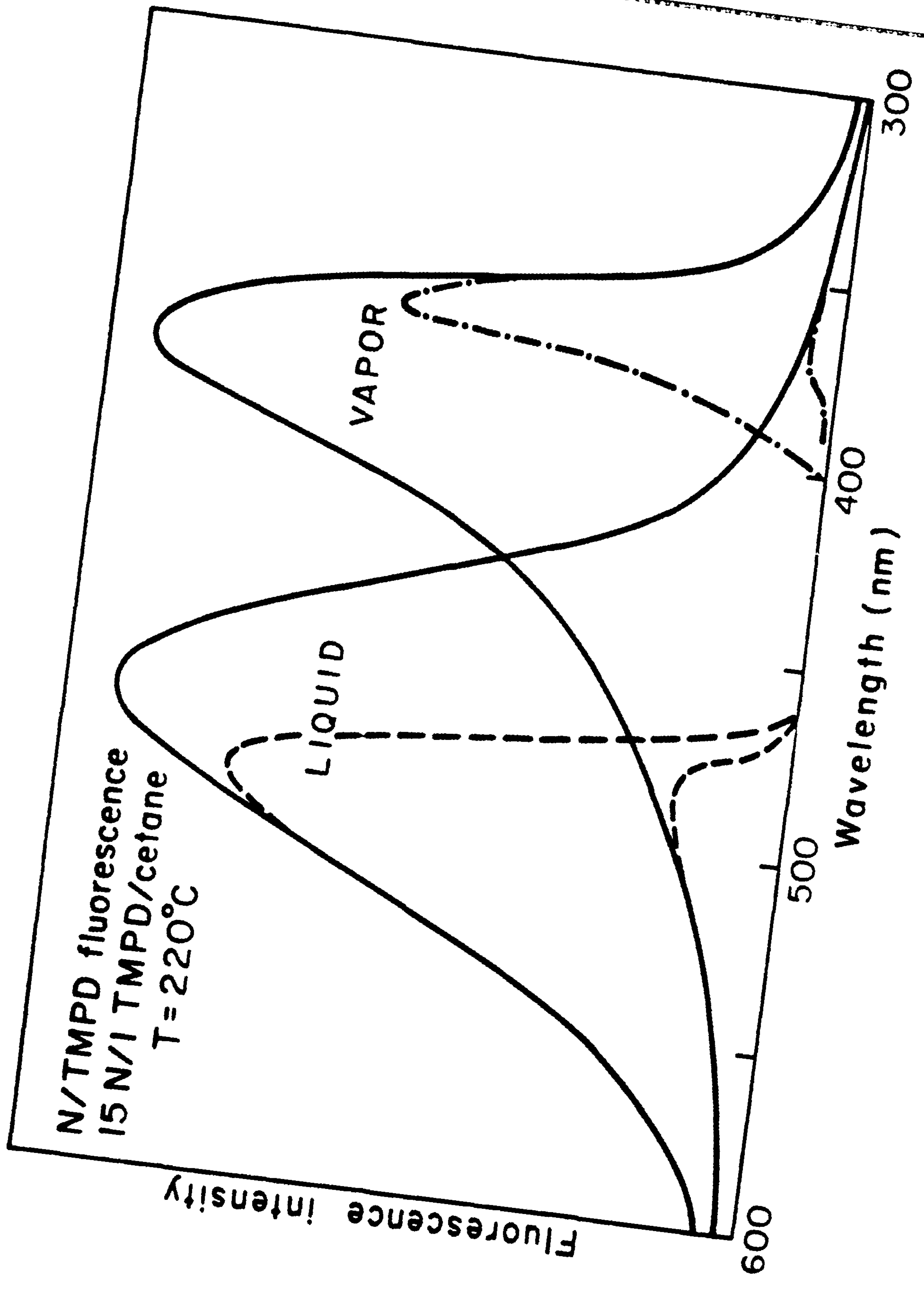
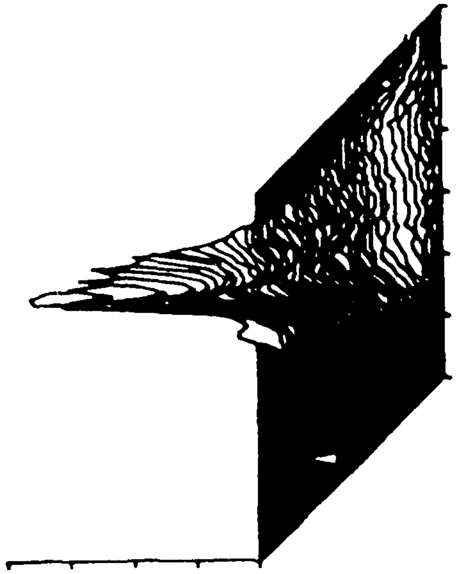
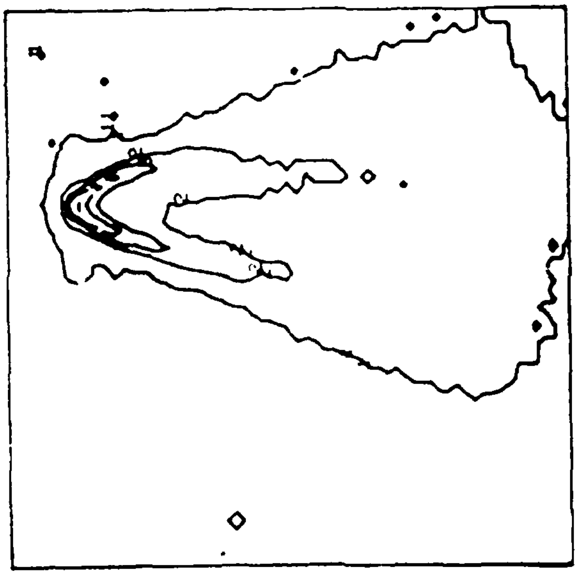
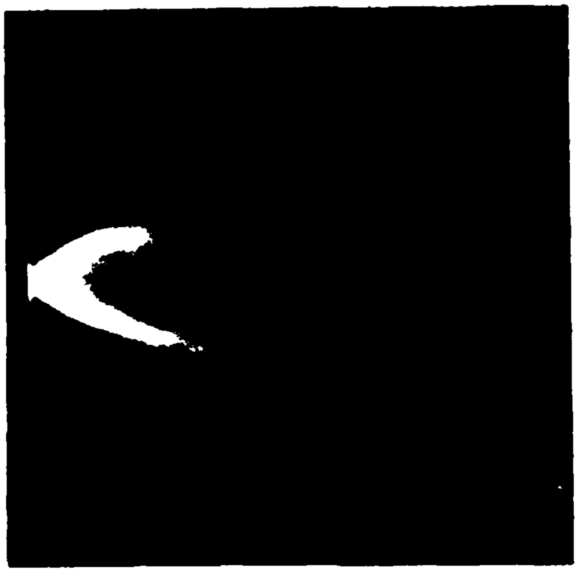

N/TMPD fluorescence
15 N/1 TMPD/cetane
T=220°C
LIQUID
VAPOR
Fluorescence intensity
Wavelength (nm)
300
400
500
600







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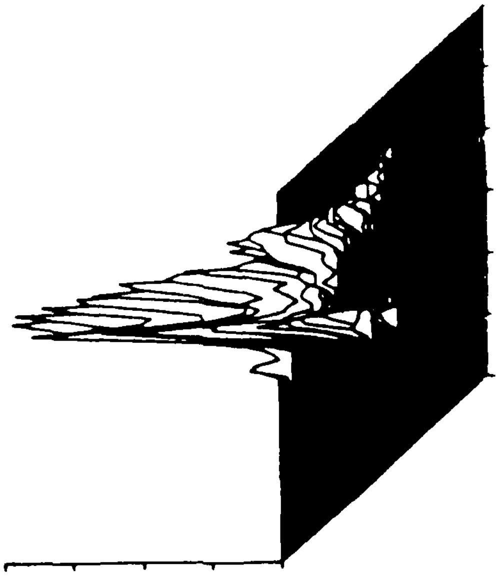

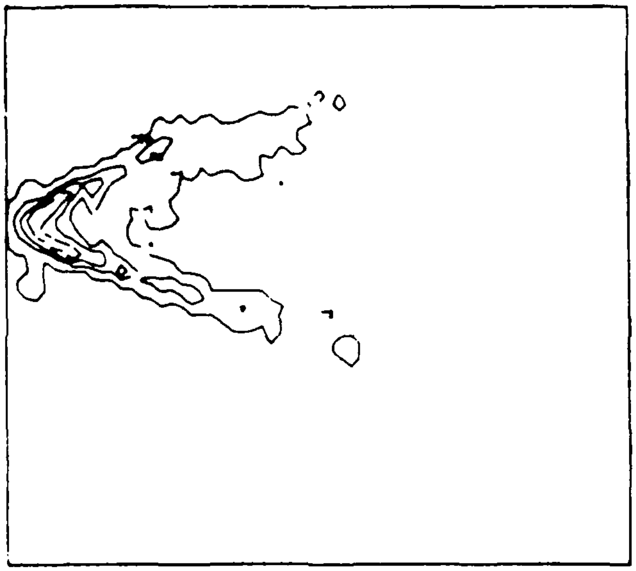

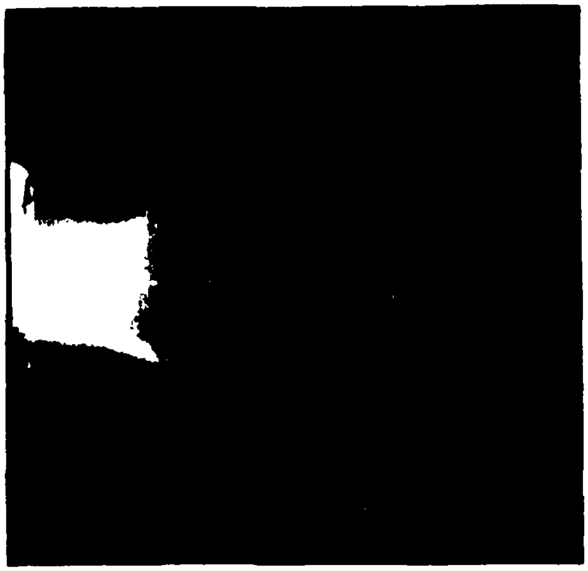

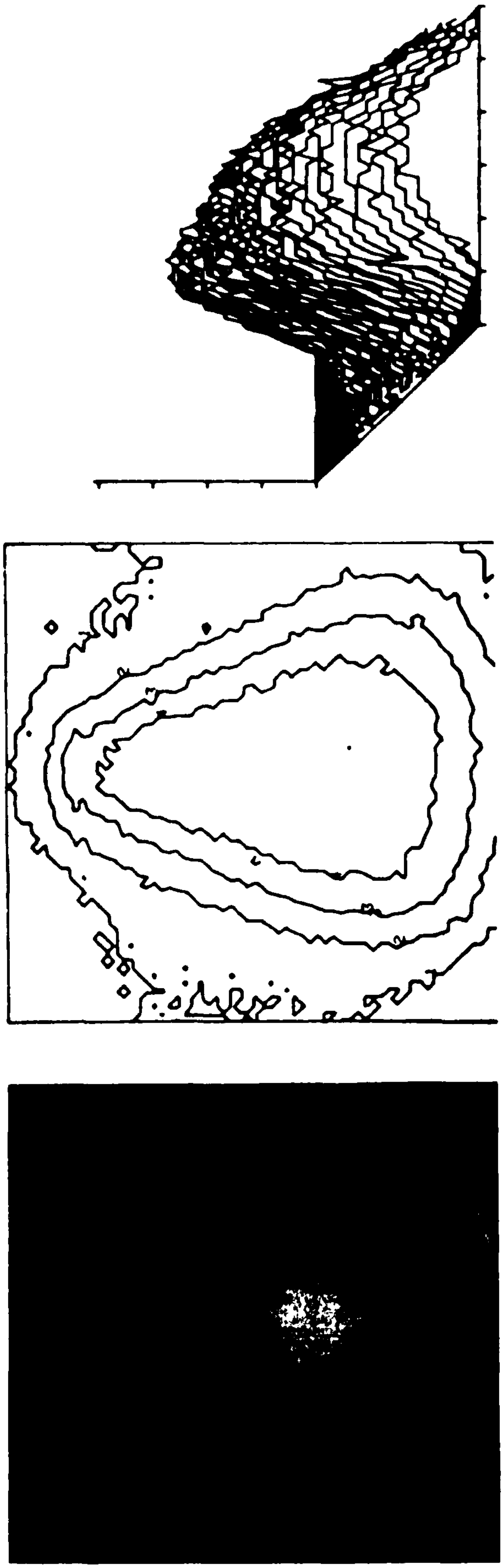

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VAPOR/LIQUID VISUALIZATION FOR FUEL SPRAYS

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Abstract

In a demonstration experiment, the vapor and liquid distributions in a hollow-cone spray have been separately photographed using laser-excited fluorescent dopants which form organic exciplexes. In color photographs, the fluorescence from the liquid appears blue-green and the fluorescence from the vapor appears purple. With high speed black and white film, "stopped action" pictures of the liquid and/or vapor portions of the spray were obtained. This technique may lead to the development of real-time visualization diagnostics for evaporating fuel sprays.

I. Introduction

In previous work (Melton, 1983), we have shown that organic exciplexes can be used as probes of the vaporization process in droplets of a diesel-like fuel. In this paper we report extensions of that work to the visualization of realistic fuel sprays. In this technique, the exciplex is formed in the liquid phase only, and causes a shift of up to 150 nm of the liquid phase fluorescence relative to that of the vapor phase. We have exploited that spectral shift and, by use of appropriate filters, have photographed in color the separated liquid and vapor patterns in a fuel spray. With high speed black and white film, satisfactory exposures were obtained with a single 10 nsec laser shot, and hence these photographs represent "stopped action" in the fuel spray. These results, interesting and useful in themselves, suggest also that electronic imaging systems can be developed for the real-time, two dimensional imaging of the liquid and vapor patterns in evolving fuel sprays.

II. Visualization Photophysics

The optical measurement of the separate vapor and liquid portions of a fuel spray is made difficult because of the paucity of spectroscopic characteristics which differ significantly for organic (fuel) molecules in the two phases. Johnston (1981) investigated spontaneous Raman scattering but concluded that, in the C-H stretching region near 3000 cm^{-1}, there were insufficient differences between the spectra of the vapor and liquid to allow their separate measurement. Other optical methods have exploited the index of refraction differences between the liquid droplets and less dense ambient vapor/air surrounding the droplets and have used either direct photography (Hussein, et al. (1982); Sangiovanni, (1982); Peterson and Alkidas (1983)), laser light scattering (Yule et al. (1981)), or two-wavelength laser absorption/scattering (Chraplyvy (1981); Tishkoff et al. (1982)). The strategy used in this work is to develop additives which cause the fluorescence of the liquid phase to be shifted significantly relative to that of the vapor phase.

The absoprtion and fluorescence spectra of organic molecules are virtually identical in nonpolar solvents, such as typical fuels, and in the vapor phase. However, photochemists have shown that in many cases it is possible to react the fluorescence excited state M^* with an appropriate molecule N to form a second emitting species $(M-N)^*$, an exciplex (excited state complex), whose emission is red-shifted with respect to that of M^*. The reaction between M^* and N to form $(M-N)^*$ is reversible, and in favorable cases one can adjust the concentration of species N so that 1) the exciplex $(M-N)^*$ is the dominant emitter in the liquid phase, and 2) the dissociated species M^* is the dominant emitter in the less concentrated vapor phase. In the napthalene/tetramethyl-p-phenylene diamine (TMPD) exciplex system used here, the peaks of the monomer (380 nm) and exciplex (470 nm) emission are separated by approximately 90 nm. A more complete discussion of exciplex photophysics is available elsewhere (Melton (1983); Rehm and Weller (1970); Birks (1969); Förster (1969)).

The key point in these visualization studies is that the emitting species M^* and $(M-N)^*$ serve as markers for the vapor and liquid portions of the evaporating fuel spray. If the spray is optically thin and if the fluorescer M coevaporates with the fuel, then the emission from these markers, viewed through appropriate filters, will measure the amounts of fuel in the vapor and liquid phases. A more complete discussion of the elements necessary to achieve quantitative visualization of the vapor and liquid pahses will be given in a subsequent paper (Melton and Verdieck (1984)).

III. Fuel Spray Demonstration Experiments

Previously reported work showed that the vapor and liquid phase fluorescent emissions could be distinguished for a suspended droplet heated by flowing nitrogen. In the experiments described here, a fuel spray was generated with a simplex nozzle and irradiated with a sheet of UV laser light. The resulting fluorescent emissions were then photographed at right angles to the laser beam. Through use of the appropriate filters, the vapor and liquid emission patterns were separately photographed. With high speed film, quite satisfactory exposures could be obtained with a single laser shot, and since the laser pulse lasts less than 10 nanoseconds and the fluorescence only 10-100 nanoseconds, these photographs represent frozen-flow results.

Figure 1 shows the fuel spray apparatus schematically. The simplex fuel spray nozzle (Delavan hollow cone, 0.5 gph, 45° cone angle) is contained within a six arm glass cross to confine the fuel vapor from the spray and to prevent atmospheric oxygen from supporting combustion of the spray or quenching the vapor phase fluorescence. The major (vertical) axis of the cross is 6" in diameter. The fuel tube for the nozzle enters through an upper flange on this 6" diameter primary arm of the cross and supports the nozzle within the field of view seen through 4" diameter side arms of the cross. The nitrogen flow also enters through the top flange, passes over a coiled heating tape, through a 2" thickness of aluminum honeycomb (used as a flow straightener), and past the nozzle. The temperature was monitored with a thermocouple attached to the nozzle near its exit. A modest deflection cone immediately below the honeycomb lessens the amount of spray and vapor reaching the windows. Below the spray visualization region, a 6" glass tee provides a duct for the nitrogen/fuel vapor exhaust to be carried to the fume hood. At the bottom of the tee, the liquid fuel is collected and reused in subsequent visualization experiments.

The laser sheet enters through 2" quartz windows mounted on the 2" diameter side arms of the cross. The fourth harmonic of Nd:YAG at 226 nm (approximately 80 mJ/pulse) is expanded in the vertical dimension through use of a cylindrical lens telescope to approximately 40 mm. A final cylindrical lens focuses the laser sheet to a thickness of 1-2 mm. Strong exciplex fluorescence can be seen from the liquid which accumulates on these windows, but since they are not within the photographic field of view, there is no interference. The photographs are taken through quartz windows mounted on the 4" diameter arms of the cross. The liquid accumulation on these windows softens the focus of the camera, and requires that they be cleaned often during a series of photographs.

The camera was a Graphlex 4 x 5 Model FP Speed Graphic with a 135 mm focal length lens and was used with 4" x 5" sheet film. The transmission of the lens was measured and found not to fall off significantly above 350 nm; thus, the lens allowed the liquid (λ_{max} = 470 nm) and vapor (λ_{max} = 380 nm) fluorescence to reach the film but not the scattered laser light (λ = 266 nm). The overall magnification of the camera was approximately 1.5.

The nominal operating pressure of the fuel spray nozzle is 100 psi, but because the fuel is preheated by flowing through the heaters, its viscosity drops and the atomization of the fuel increases (Lefebvre, 1983), and lower pressures may be used. In order to obtain a fuel pattern which illustrates the capabilities of the exciplex visualization method, the nozzle was typically operated at 28 psi. Thus, the liquid sheet, droplets, and vapor are present in the photographs.

The fuel mixture used in these experiments was 2.5% naphthalene, 1.0% tetramethyl-p-phenylene diamine (TMPD), 96.5% hexadecane (cetane) by weight. With these concentrations, it is estimated that the overall optical density at 266 nm (neglecting scattering) at 3 cm distance from the nozzle is approximately 0.2. The emission spectra for the liquid and vapor at 220°C have been published previously (Melton (1983)).

A. Time Averaged Photographs

Figures 2 and 3 illustrate the results which can be obtained with the present exciplex/laser/camera system. In figures 2a, b, c, the color film results were taken with no filter, with Schott GG-475 glass (liquid fluorescence), and with Schott UG-11 glass (vapor fluorescence), respectively. The color film is rated at ASA 75, and adequate exposures could be obtained with approximately 20 laser shots (2 seconds at 10 Hz); the photographs shown in Fig. 2 required approximately 50 laser shots (5 seconds at 10 Hz). They are therefore averaged results such as one can see with the human eye. In Fig. 2a, with no filter, the full fluorescence is shown. The blue-green of the exciplex marks the liquid, which emerges from the nozzle as a conical sheet and atomizes as the sheet stretches away from the nozzle.

The laser sheet is set to pass exactly through the apex of the hollow cone spray, and hence the "vee" of the conic section is readily seen. The purple emission from the vapor can be seen to be distributed fairly homogenously within the nominal cone of the spray. Figures 2b and 2c show, respectively, the results which can be obtained when the liquid emission only, or the vapor emission only, is photographed by insertion of the appropriate filters. The liquid only pattern exhibits shows clearly the thin sheet of liquid coming out of the nozzle in a cone and breaking up into fine droplets. The vapor only pattern shows the nearly homogenous distribution of the vapor within the spray cone.

B. Frozen Flow Photographs

In Fig. 3, a series of black and white photographs corresponding to the color photographs shown in Fig. 2 is presented. Figure 3a is photographed without filters; Fig. 3b is photographed with the visible transmitting filter, and exhibits the liquid only; Fig. 3c is photographed with the ultraviolet transmitting filter and exhibits the vapor only. The Nd:YAG 1.06μ laser pulse has a width of approximately 10 nsec FWHM; when quadrupled the pulse width may be 5-6 nsec FWHM. The fluorescence lifetime of the exciplex is presently unknown, but typical exciplex lifetimes are on the order of 10-100 nsec. Hence, these photographs, taken with Royal X Pan (ASA 1000) with a single laser shot, are frozen flow photographs, i.e., the motion of the particles in the spray is stopped because the effective shutter speed is 10-100 nsec. In Fig. 3a, the liquid sheet and the flow instabilities which lead to breakup of the sheet can be seen as well as the individual droplets. No particular significance should be assigned to the sizes of the small droplets since the precision of focus of the camera system can radically alter the perceived photographic size. The gray interior of the hollow cone spray is predominately vapor. In Fig. 3c, the vapor pattern is shown; as before the vapor pattern lies within the spray cone, but now there are apparent lighter and darker areas within the vapor region. There are apparently temporal and spatial inhomogeneities in the evaporation of the spray.

The photographs shown in Figs. 2 and 3 illustrate the type of information which these exciplex visualization techniques can make available. At present, two dimensional photographs from which the relative distribution of vapor or liquid can be readily determined, even in single shot exposures, are feasible. With further apparatus development, including photoelectric detection, real time visualization should be possible. It should be noted that the excited states created by the laser excitation process have died away in times significantly less than one microsecond, and hence, these fluorescent dopants potentially allow independent measurements to be made at rates of at least one megahertz.

IV. Conclusions

Photographs showing separately the vapor and liquid portions of a fuel spray have been taken using a single short laser pulse. These frozen-flow photographs demonstrate that the qualitative two dimensional vapor and liquid patterns in a fuel spray can be observed. Further experiments are underway to extend the technique to the quantitative, real-time visualization of the vapor and liquid components of fuel sprays. Further discussion of this technique and its potential application will be given in a subsequent paper (Melton and Verdieck (1984)).

VI. Acknowledgements

This work was supported by the United Technologies Research Center. The support and encouragement of Alan C. Eckbreth is gratefully acknowledged. Able technical assistance was provided by Mr. Normand Gantick and Mr. Edward Dzwonkowski.

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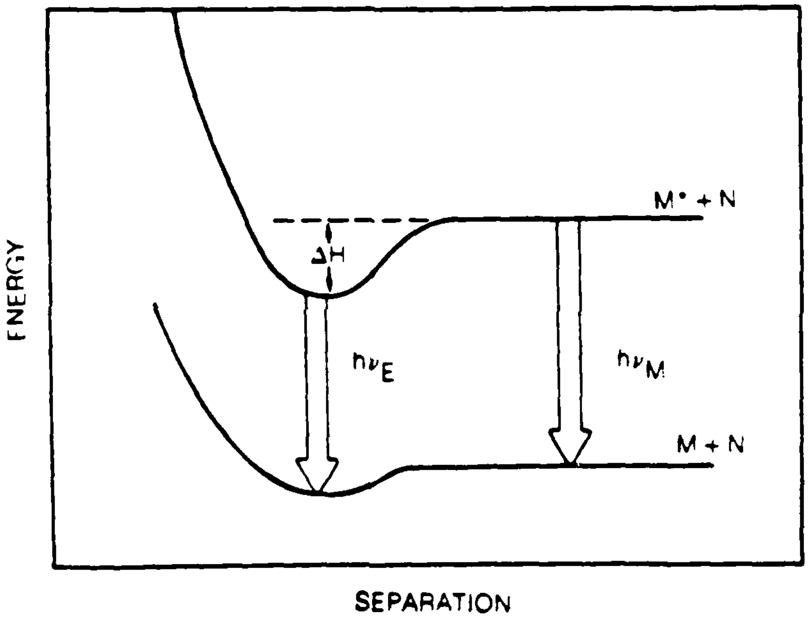
Figure Captions

Fig. 1. Schematic potential energy diagram for an exciplex formed from moelcules M and N.

Fig. 2. Schematic diagram of fuel spray visualization apparatus which generates laser-induced fluorescence from a planar sheet.

Fig. 3. Laser-induced fluorescence from a planar section of a hollow cone spray. Approximately 50 laser shots used for each photograph. a) no filters, liquid and vapor fluorescence combined; b) green filter (GG-475), liquid fluorescence only; c) UV filter (UG-11), vapor fluorescence only.

Fig. 4. Single laser shot fluorescence ("frozen flow") obtained with black and white film. Effective exposure time is approximately 100 nanoseconds. Same sequence as Fig. 3.



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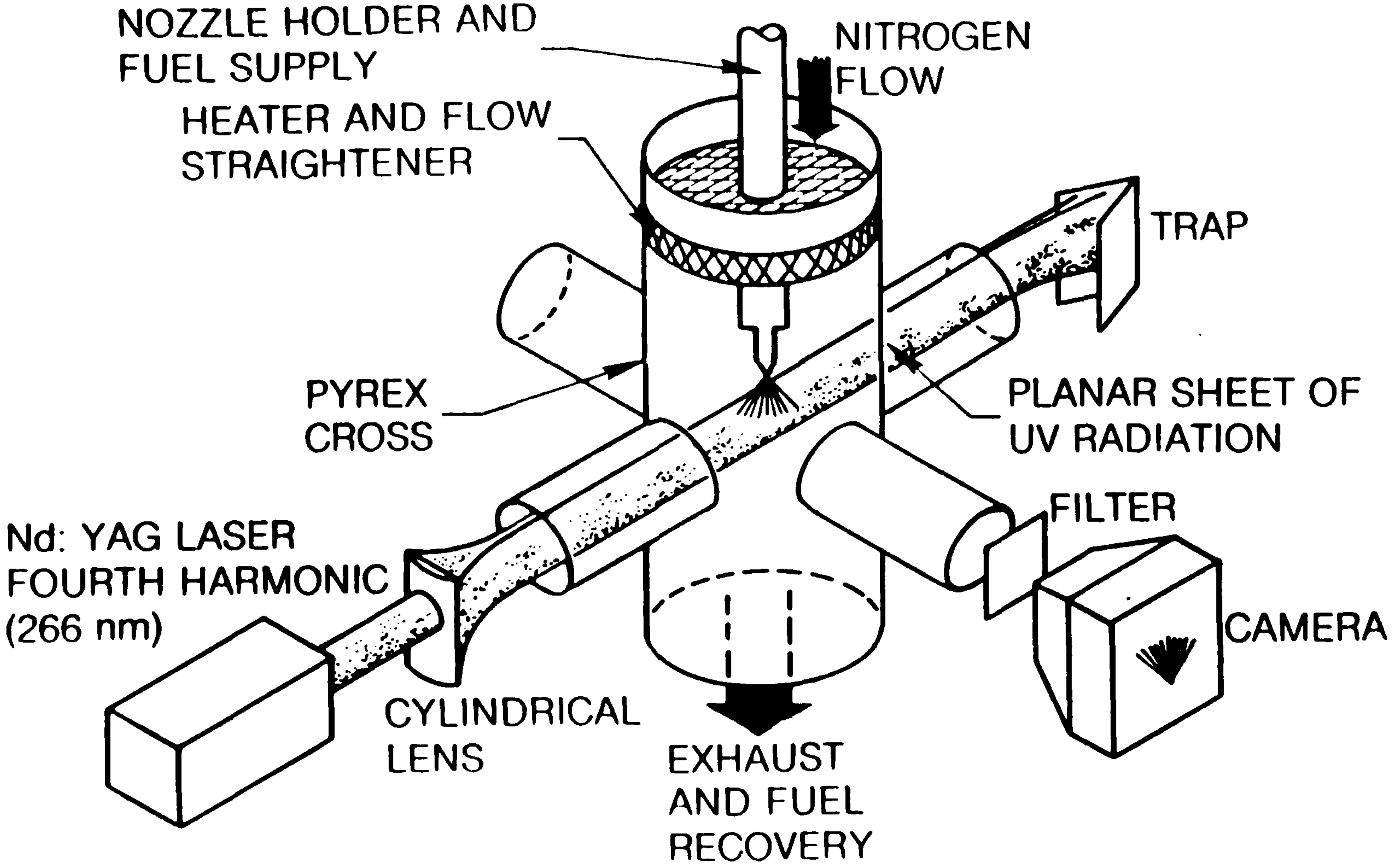
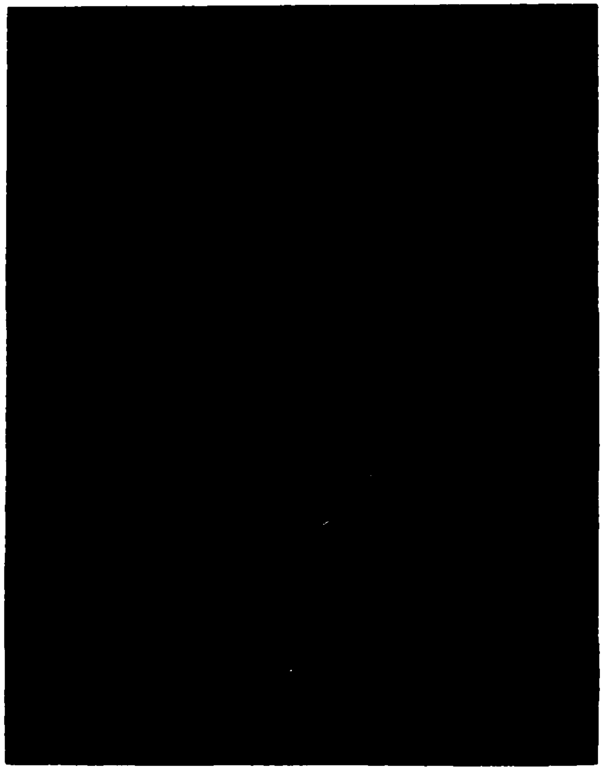
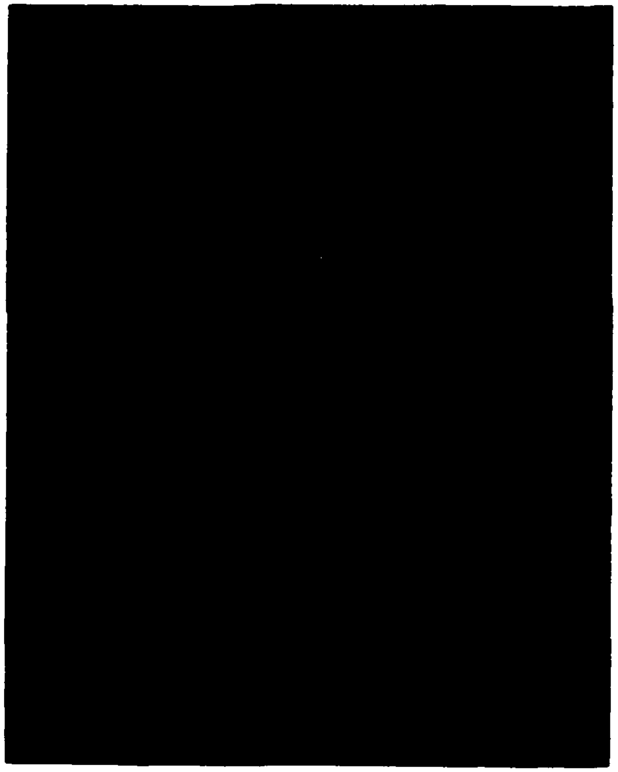

NOZZLE HOLDER AND
FUEL SUPPLY
NITROGEN
FLOW
HEATER AND FLOW
STRAIGHTENER
TRAP
PYREX
CROSS
PLANAR SHEET OF
UV RADIATION
FILTER
Nd: YAG LASER
FOURTH HARMONIC
(266 nm)
CAMERA
CYLINDRICAL
LENS
EXHAUST
AND FUEL
RECOVERY

83-12-42-1

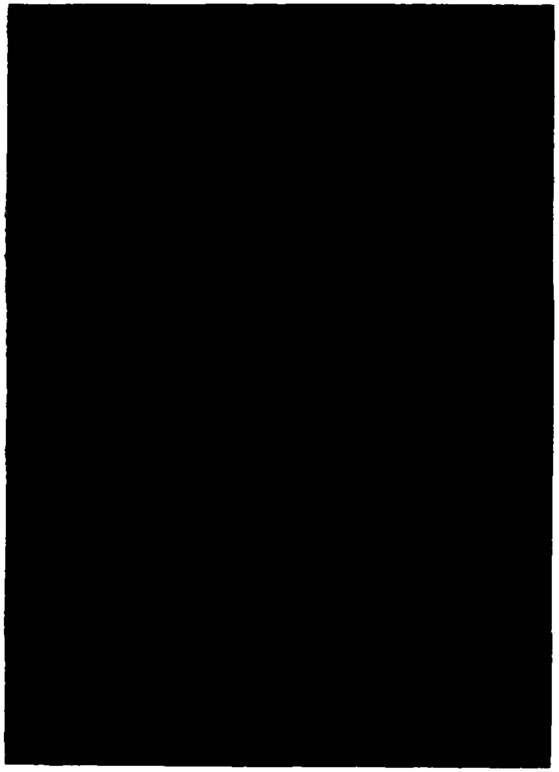
EXCIPLEX VISUALIZATION OF LIQUID/VAPOR FUEL DISTRIBUTION



Liquid and vapor



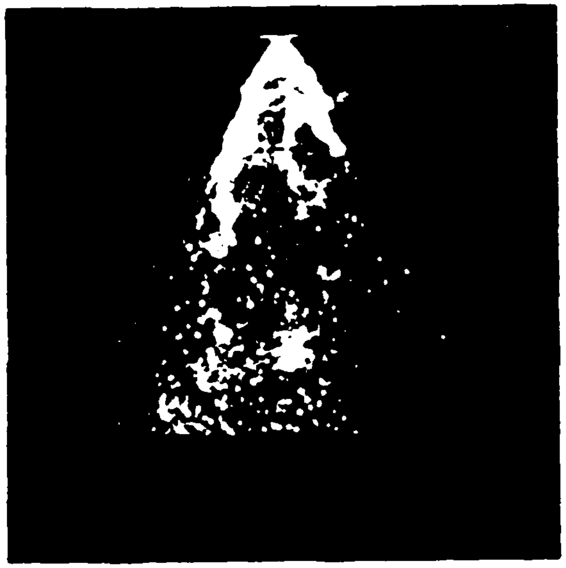
Liquid only



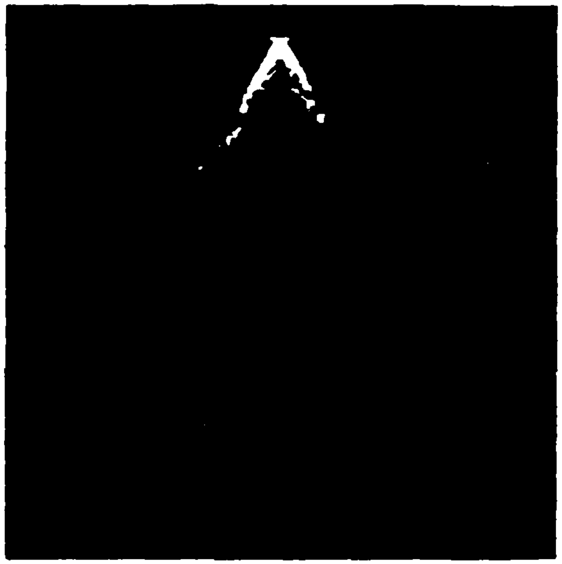
Vapor only

LASER-INDUCED EXCIPLEX FLUORESCENCE FROM CONICAL FUEL SPRAY

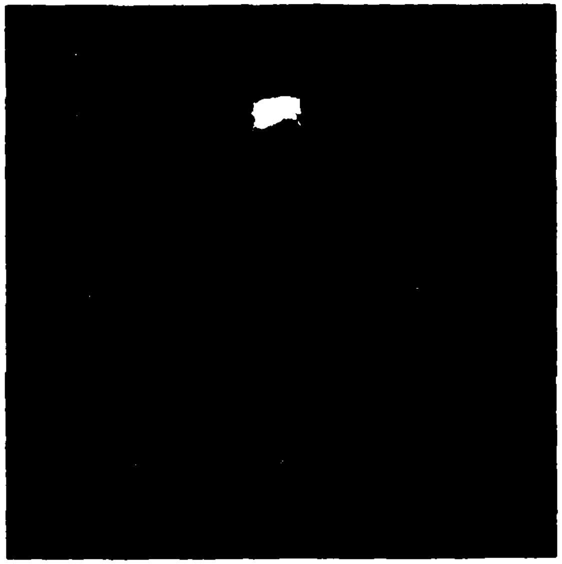
Experimental results



Liquid and vapor



Liquid only



Vapor only

- Commercial nozzle operating with cetane doped with naphthalene/tetramethyl phenylene diamine (TMPD)
- Single, 10 nanosecond, fourth harmonic (266 nm) Nd:YAG laser excitation
- Two-color fluorescence separated with absorbing glass filters

APPENDIX III

Fluorescence Methods for Determination of Temperature in Fuel Sprays

Reprinted from Applied Optics, Vol. 24, page 2783, September 1, 1985

Fluorescence methods for determination of temperature in fuel sprays

A. M. Murray and L. A. Melton

Fluorescent additives which allow the determination of droplet temperatures in hydrocarbon fuel sprays have been developed. These systems, which exploit the chemistry of organic exciplexes, should make possible the determination of droplet temperatures within 1°C. Two specific systems are described: 3,10-dicyanophenanthrene/diethylaniline over the 20–135°C range, and naphthalene/tetramethyl-*p*-phenylene diamine over the 140–265°C range. These additives should allow 2-D real-time nonintrusive visualization of the droplet temperatures in an evolving fuel spray.

I. Introduction

When liquid fuel is injected into a hot gas atmosphere, as in a gas turbine or diesel engine, the atomized droplets evaporate as heat from the surrounding atmosphere is transferred into the interior regions of the spray. The temperature within the individual spray droplets is thus a key parameter in estimating the heat transfer, the extent of mixing of the droplets with the surrounding air, and the vaporization rates. However, directly measured droplet temperatures have not been available, and it has been necessary to estimate liquid temperatures. Most often, it is assumed that the droplet temperature rises rapidly and homogeneously to the boiling point of the fuel[1] although more recent work regarding internal circulation[2] and multicomponent evaporation[3] has called this assumption into question. Conventional experimental methods for spray analysis—photography, laser light scattering, multiphase probes, etc.—do not measure droplet temperatures, and thus there has been no direct measurement of this key parameter for evaporating droplets within evolving fuel sprays.

We report here a method involving fluorescent additives in which the droplet temperatures should be obtainable within 1°C over the evaporation range of the fuel. As with other diagnostic methods based on fluorescence, this scheme should be readily adaptable to 2-D imaging with nonintrusive real-time measurements of the temperature distribution in an evolving fuel spray.

II. Basic Photophysics

The temperature measurement schemes described here are modifications of the previously described vapor/liquid visualization schemes based on the formation of suitable organic exciplexes.[4–6] In the vapor/liquid visualization work, the potential dependence of the exciplex emission on the droplet temperature was a problem to be suppressed; here it is enhanced and exploited. In particular, in the vapor/liquid visualization work, the concentrations of the dopants were chosen to favor the exciplex fluorescence and to suppress the monomer fluorescence in the temperature range of interest. In these temperature probe studies, the concentrations of the dopants were chosen to enhance the changes in the relative intensities of exciplex and monomer fluorescence, within the liquid phase, as a function of temperature. For example, in a 15% naphthalene/0.5% TMPD solution, the monomer fluorescence is almost entirely suppressed in the studied temperature range of 25–250°C, and thus it is an excellent solution for the vapor/liquid visualization experiments. On the other hand, a 1% naphthalene/2.5% TMPD solution yields dramatic variations in the relative intensities of the monomer and exciplex liquid phase fluorescence between 150 and 260°C and thus makes a good thermometer.

An exciplex E^* is an excited state complex formed by the reaction of an excited state organic molecule M^* with a ground state organic molecule N. The binding in the excited state may be substantial, the exciplex being bound by 20–100 kJ/mole with respect to separated M^* and N, but the binding of M and N in their electronic ground states is negligible. Although the exciplex itself may participate as an intermediate in a variety of interesting photochemical reactions, we are interested primarily in strongly fluorescent exciplexes in which the photochemical pathways are minimal.[7] Thus, on irradiation of a sample containing M,N, and

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the balance hydrocarbon fuel, M is excited to form M^*, and the reaction

$$M^* + N \rightarrow E^* \tag{1}$$

begins. Fluorescence can be observed from both electronically excited M^* and E^*. Since E^* is bound with respect to M^*, it is necessarily at lower energy, and its emission to yield ground state $M + N$ is red-shifted with respect to the emission from M^*. The populations of M^* and E^*, which are coupled by reaction (1), can be strongly temperature dependent, and thus the ratio of the fluorescence intensity from M^* to that emitted from E^*, once calibrated, can be used to obtain the temperature of the droplets.

Depending on the composition and temperature of the specific sensor system, it is possible for the ratio of monomer emission to exciplex emission to increase or to decrease with increasing temperature. In the former case, equilibrium in reaction (1) is obtained, and the temperature dependence of the equilibrium constant is the dominant element. The equilibrium constant for reaction (1) has the approximate temperature dependence $\exp(-\Delta H/RT)$, where ΔH is the binding energy of the exciplex with respect to separated M^* and N. With increasing temperature, this factor decreases, and the equilibrium shifts away from E^* and toward the separate M^* and N. It is this phenomenon which has affected the previously described fluorescent vapor/liquid visualization methods.[6] In the latter case, equilibrium in reaction (1) is not obtained, primarily because M^* and N must diffuse toward each other during the several nanoseconds that M^* is excited. If the viscosity of the medium is sufficiently high, diffusion is slow, and only a fraction of the M^* initially formed actually reacts to form E^*. As the temperature rises, the viscosity decreases dramatically, and the thermodynamic equilibrium of reaction (1) becomes established. This balance between kinetic and equilibrium control has been noted and discussed extensively in the exciplex literature.[8] In the systems presented here, one (3,10-dicyanphenanthrene/diethylaniline/*m*-xylene) shows the kinetics dominated (diffusion) behavior, and the other (naphthalene/tetramethyl-*p*-phenylene diamine/hexadecane) shows the thermodynamics dominated (equilibrium) behavior.

III. Experimental Methods

A. Solutions

Naphthalene (N), tetramethyl-*p*-phenylene diamine (TMPD), diethylaniline (DEA), hexadecane, and *m*-xylene were purchased from Aldrich Chemical Co. (Milwaukee, Wis.); all were used without further purification except TMPD which was sublimed at 4 Torr and 30–40°C. 3,10-dicyanophenanthrene (DCNP) was prepared according to Ref. 9.

The solutions were prepared on a weight-percentage basis, the solids being weighed and the liquids being measured by volume. TMPD reacts readily with oxygen at elevated temperatures, and consequently the solutions containing TMPD were purged with nitrogen for ~20 min before heating; the other solutions were used without purging.

B. Fluorescence Apparatus

The excitation source for all fluorescence spectra was a Lumonics 861S excimer laser operated on the XeCl transition at 308 nm. The beam was masked so that only 1–2 mJ/pulse at 8 Hz was incident on the fluorescence cuvette. The cuvette was positioned at an angle of ~50–55° to the incident beam so that front surface spectra could be obtained from these optically thick solutions without the reflected laser beam entering the monochromator. The fluorescence emitted at 90° to the incident laser beam was focused through a single quartz lens (5-cm diameter, 15-cm focal length) onto the entrance slit of a quarter-meter Jarrell-Ash monochromator. The fluorescence was detected with a 1P28 phototube, whose output went to a PAR 134 electrometer. The amplified output of the electrometer was read by a 8-bit ADC and the results stored in computer readable files.

The cuvette was suspended within an insulated chamber. The cuvette holder, which was developed for use in previous vapor/liquid visualization studies, allows rotation of the cuvette about a line contained in its front surface, vertical movement of the cuvette, and movement of the cuvette transverse to the entering laser beam. In this work, the cuvette was held fixed in the front surface fluorescence position. The cuvette chamber was heated with flowing house air, which had first flowed over cupric oxide (400°C) to remove any traces of oil and then through a final heating section of heating tape wrapped on a glass tube. The temperature once set was stable within 1–2°C. All temperatures were measured with a copper–constantan thermocouple located in a groove within the aluminum body of the cuvette holder, ~2 mm behind the back wall of the cuvette.

Because the fluorescence is pulsed, with lifetimes of 10–100 nsec, it was necessary to ascertain that the phototube was not being saturated. These checks were performed by comparing the spectra of TMPD with reference spectra[10] and with spectra obtained on an arc lamp excited laboratory fluorimeter (Farrand Mark IV). Additional checks were made by comparing the measured spectral shapes of monomer fluorescence as a function of phototube voltage.

The relative spectral response of the Jarrell-Ash/phototube system was determined by two methods: (1) the measured fluorescence spectra of 2-naphthol[11] and quinine[12] were compared with reference spectra, and (2) the emission of a calibrated lamp was compared with its stated emission spectrum.[13] The two methods agreed in the 400–570-nm range; the lamp results were used to calculate corrected spectra over the 320–600-nm range.

IV. Results

A. 0.04% DCNP/0.12% DEA/*m*-xylene

The solubility of DCNP in *m*-xylene at room temperature is ~0.04%, and this result then established the concentrations to be used. *m*-Xylene was chosen as a medium boiling point solvent, which was sufficiently polar to dissolve some of the very polar DCNP.

The fluorescence from DEA peaks at 340 nm, and that from DCNP peaks at 380 nm; at room temperature the exciplex fluorescence peaks at ~560 nm. These solutions fluoresce with a light purple color at room temperature, and as the temperature is raised near the boiling point of *m*-xylene (139°C) the fluorescence becomes distinctly yellow. The spectra in Fig. 1 confirm this effect: as the temperature is raised the emission from the exciplex relative to that from the two monomers becomes stronger. In Fig. 2, the logarithm of the ratio of the corrected emission intensity at 530 nm (E^*) to that at 390 nm (DCNP*) is plotted as a function of temperature. The ratio increases rapidly with temperature, starting with a value of ~0.4 at 25°C and rising to 1.3 at 130°C. If a higher boiling solvent had been used, the dramatic rise in the intensity ratio could have been followed even further. Since this is a case in which the kinetic effects (viscosity) determine the temperature effect, the ratio must eventually level off and begin to decrease. Nonetheless, it is apparent that this thermometry system can be useful at temperatures well above 130°C.

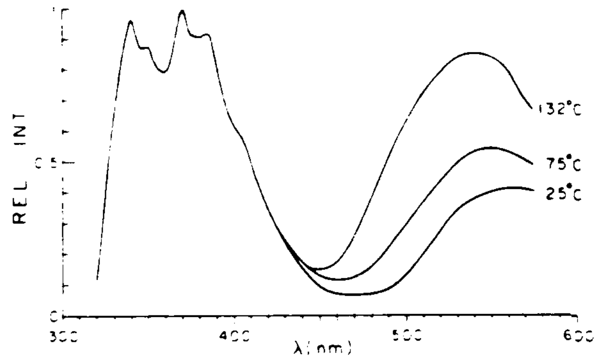

Fig. 1. Fluorescence spectra of DCNP/DEA solutions as a function of temperature.

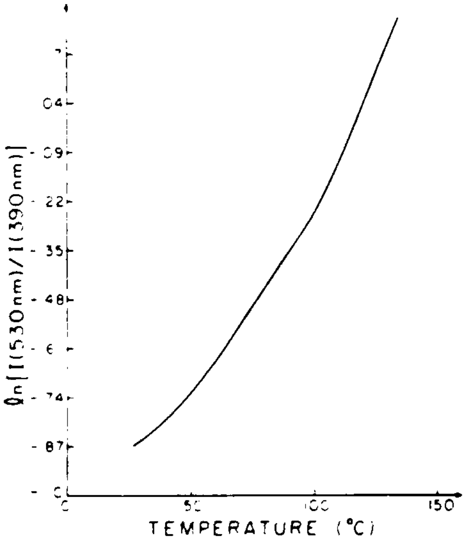

Fig. 2. Logarithm of the ratio of the DCNP/DEA exciplex fluorescence intensity at 530 nm to the DCNP monomer fluorescence intensity at 390 nm as a function of temperature.

In the region between 20 and 130°C, the intensity ratio changes by ~1.1%/°C. This means that a measurement of the intensity ratio which is accurate within 1% should yield a temperature determination which is accurate within 1°C.

B. 1.0%N/2.5%TMPD/Hexadecane

This naphthalene/TMPD system contains the same components which have been successfully used in the vapor/liquid visualization systems and for similar reasons: an exciplex thermometer useful at high temperatures must have a large enthalpy of binding for the exciplex to persist at these temperatures. Figure 3 shows the spectra obtained with this system as a function of temperature. Between 25 and 140°C, the changes in the spectra are quite modest, but between 140 and 265°C, the changes are dramatic. Figure 4 summarizes these changes more quantitatively; the logarithm of the ratio of the fluorescence intensity at 500 nm (E^*) to that at 400 nm (TMPD*) is plotted as a function of temperature. Once again the effect is quite large, although in this case the intensity ratio decreases as the temperature increases. In the 140–265°C range, the intensity ratio increases by ~1.5%/°C, and once again, if the intensity ratio can be measured within 1%, the temperature can be determined within 1°C.

V. Discussion

The results in Figs. 1–4 demonstrate that these exciplex systems can potentially be used to determine the temperature of a liquid droplet which is irradiated by a UV laser source. Some points of the spectra and potential applications, however, deserve a more thorough discussion.

Closer examination of the spectra in Figs. 1 and 3 shows that the exciplex emission shifts slightly to shorter wavelengths as the temperature increases. This effect has been previously observed by organic photochemists but is as yet unexplained.[14] The primary argument about the variation of the ratio of exciplex emission intensity to that of the monomer has been made in terms of the populations of M^* and E^* as coupled by reaction (1) and is still valid since the spectral shift has only a modest effect. In both the DCNP/TEA system and the N/TMPD system, the wavelengths at which the exciplex emission is measured have been chosen so that the shift in exciplex emission accentuates the effect of the shift in the populations of E^* and M^*.

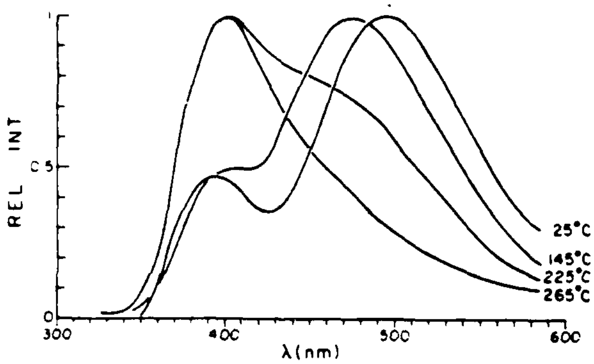

Fig. 3. Fluorescence spectra of N/TMPD solutions as a function of temperature.

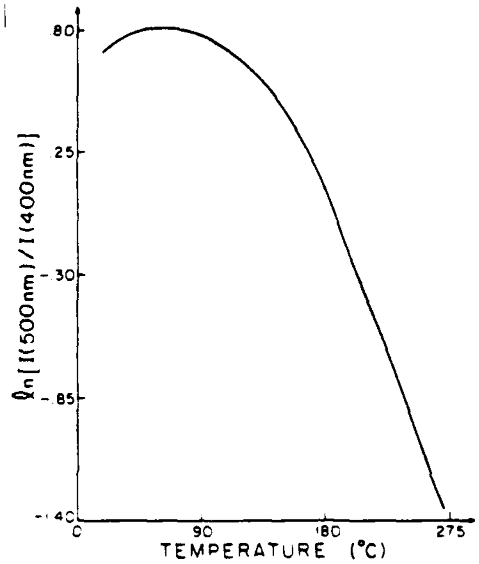

Fig. 4. Logarithm of the ratio of the N/TMPD exciplex fluorescence intensity at 500 nm to the TMPD monomer fluorescence intensity at 400 nm as a function of temperature.

It is not sufficient to measure an intensity ratio and derive a temperature from it. The variation of the temperature within spray droplets is potentially important, and one must know what temperature is being measured. In the optically thin limit, where either the dopants are present in very low concentrations or the excitation takes place at wavelengths where they are weakly absorbing, the fluorescent molecules within spray droplets will be uniformly excited. In this case, the emission from a single droplet will be a volume averaged temperature, and the emission from a spatial element in the spray will be weighted toward the volume averaged temperatures of the largest drops in that element, since they will contribute the greatest fluorescence intensity. *In the optically thick limit, one cannot* dope the entire spray, but it is possible to study isolated single droplets or to inject a doped probe droplet into an undoped spray. In either case, with accessible molecular extinction coefficients of 10,000 liter/mole-cm and dopant concentrations in the few weight percent range, it should be possible to achieve complete absorption of the incident light within the first 10 μm of liquid, i.e., within the 10-μm skin of a 100-μm diam droplet. The emission from this optically thick droplet would measure then a skin temperature.

As a fuel spray heats and evaporates, it is inevitable that the fluorescent dopants will evaporate also. The interference from exciplex emission in the vapor phase is likely to be negligible, since the relatively polar exciplex will be less stable in vacuum. However, emission from monomer vapor may well be a problem. In this case it would be well to study sprays into air rather than into nitrogen, since oxygen is an efficient quencher of the fluorescence of organic molecules and the atmospheric oxygen would readily quench the vapor phase emissions. In a worst case analysis (outer layer of droplet continuously saturated with oxygen, no boundary layer formed by evaporating fuel, and no recession of the droplet surface) assuming an oxygen diffusion constant of 3×10^{-5} cm^2/sec,[15] the oxygen could penetrate ~8 μm into the droplet in 10 msec. Such penetration would affect the intensity ratios, and thus this strategy should be checked prior to its use in sprays.

Finally, it should be noted that the intensity ratio measurements described here imply a particular type of data collection apparatus. It will be possible to photograph doped fuel sprays through filters and to obtain thereby qualitative information regarding the temperature distribution in the spray. However, the more powerful method is to image the irradiated section *of the spray through two separate filters onto two halves* of an electronic array detector.[16] The intensities can then be read point by point, ratioed at the same spatial element, and converted to a temperature at that spatial element.

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APPENDIX IV

Fluorescence Thermometers Using Intramolecular Exciplexes

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Fluorescence thermometers using intramolecular exciplexes

Henry E. Gossage and L. A. Melton

Exciplex-based fluorescence thermometers have been developed which should allow the nonintrusive real-time determination of temperatures in hydrocarbon liquids within 1°C at temperatures as high as 400°C. The two-candidate dopant molecules—1,3-bis-(1′-pyrenyl)-propane and 3-(4′-dimethylaminophenyl)-1-(1′-pyrenyl)-propane—are commercially available and may be used at concentrations as low as 1 ppm.

I. Introduction

Murray and Melton have previously demonstrated that the fluorescence from exciplex-based visualization systems can be used to determine the temperature of hydrocarbon liquids nonintrusively at temperatures as high as 275°C.[1,2] Because these visualization systems provide nonintrusive submicrosecond measurements of the liquid temperature in planar laser-induced fluorescence (PLIF) conditions, they have potential application in the visualization of the droplet temperature field in evaporating fuel sprays as well as other remote sensing applications.

The systems reported by Murray and Melton consisted of two components, a fluorescent organic compound (monomer) M and a ground-state exciplex-forming compound G. The key chemistry is summarized in Eq. (1):

$$M^* + G \;(==)\; E^*, \tag{1}$$

where M^* is the first excited singlet state of M and E^* is the exciplex (excited state complex), which is bound in the excited state and unbound in the ground state. Because M^* and G are separate compounds, the resulting exciplex is an intermolecular exciplex. The fluorescence emission from E^* is red-shifted with respect to the emission from M^* by 50–150 nm, and thus there may be two distinct emission bands in the spectrum of such a mixture, one from M^* and one from E^*. The reaction in Eq. (1) is temperature dependent, and thus the relative amounts of emission from M^* and E^* change as a function of temperature. A key feature of these measurements is that one need only measure the ratio of the intensities of these two emissions and compare that ratio with a previously established calibration curve rather than having to measure absolute intensities.

The intermolecular visualization systems previously reported can be used in the exciplex thermometry of hydrocarbon systems with an accuracy of 1°C over a temperature range of 100–150°C, but they are not optimal. For example, it is implicitly assumed in the exciplex thermometry method that the M^*/E^* intensity ratio is a function of temperature only; however, in an evaporating fuel droplet, the concentrations of the components M and G may change as the more volatile component preferentially distills. In addition, the concentrations of M and/or G may have to be as much as 1–10% (w/w), and thus there is the possibility that the dopants themselves may affect the evaporation behavior of the droplet. In the new systems reported here, the two exciplex-forming components, M and G, are chemically linked by a three-carbon alkyl chain, and hence they cannot separately distill. Furthermore, the probability of forming this intramolecular exciplex no longer depends on the separate concentration of G and M—they are tethered together—and thus the M-$(CH_2)_3$-G dopant molecule can be used as extremely low concentrations, even 1 ppm.

II. Experimental Apparatus and Procedures

A. Apparatus

Fluorescence spectra were obtained on a Farrand Mark I spectrofluorimeter. The excitation wavelength was 345 nm for both dopants. To obtain fluorescence spectra at temperatures up to 420°C, solutions were transferred to 15-cm lengths of 2- × 6-mm quartz tubing, which had been sealed at one end, degassed using several freeze–pump–thaw cycles, and sealed under vacuum. The standard sample compartment was removed and replaced with a 5-cm (2-in.) diam by 8.8-cm (3.5-in.) long brass cylinder, whose axis

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was at the intersection of the optic axes of the excitation and emission monochromators. The axis of the cylinder was vertical, and 2.5- × 0.6- × 2.5-cm (1- × 0.25- × 1-in.) deep vertical entrance and exit slots were milled in the cylinder, 90° apart, to match the standard right-angle fluorescence geometry of the Mark I. A 0.6-cm axial hole was drilled through the cylinder to accept the 6-mm sample tube. Four 0.6- × 7.6-cm (3-in.) deep holes, equally spaced on a 3.8-cm (1.5 in.) bolt circle, were drilled to accept four cartridge heaters (each 150 W at 240 V), which were connected in parallel to a 120/140-V variable autotransformer. A 1.58-mm ($\frac{1}{16}$-in.) × 2.5-cm radial hole was drilled at the midpoint of the cylinder for a stainless-steel sheathed-type J Omega thermocouple which was read by an Omega HH-70JC meter (±1°C). The entire assembly was covered with a layer of 19-mm ($\frac{3}{4}$-in.) thick ceramic wool (Kaowool) insulation, and the thermocouple junction was within (3.17 mm ($\frac{1}{8}$ in.) of the quartz sample tube. Because the cylinder was well-insulated and the brass has a high thermal conductivity, the temperature measurements are likely to be accurate estimates of the sample liquid temperature, once thermal equilibrium is reached.

Spectra were simultaneously recorded on an x-y recorder and logged via a 12-bit ADC to a Commodore 64 computer and saved on disk for further analysis.

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The two fluorescent dopant molecules, 1,3-bis-(1′-pyrenyl)-propane (PYPYP) and 3-(4′-dimethylaminophenyl-1-(1′-pyrenyl)-propane (PYDMAP), were obtained from Molecular Probes, Inc.,[3] and were used without further purification. Hexadecane (97%) was purchased from Aldrich.

The PYPYP and PYDMAP solutions were 3.8×10^{-5} and 4.4×10^{-5}M in hexadecane, respectively.

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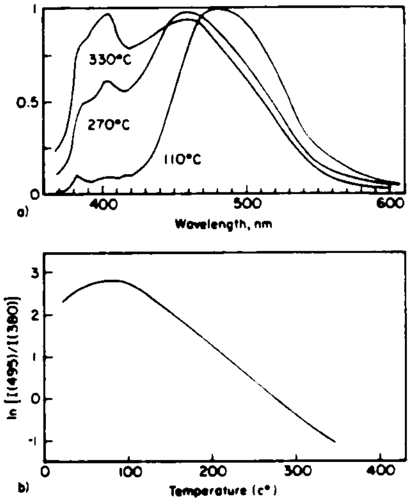
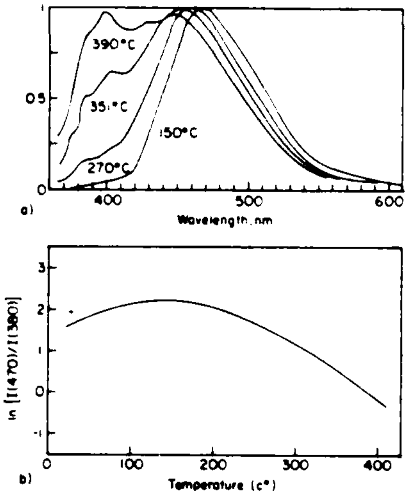


Fig. 1. (a) Normalized fluorescence spectra of PYPYP as a function of temperature; (b) analytical working curve, $\ln[I(495)/I(380)]$ vs temperature (°C).

Figure 2(a) shows selected spectra for PYDMAP as a function of temperature. PYDMAP consists of a pyrene and a dimethylaniline moiety linked by a chain of three aliphatic carbons. The monomer properties of pyrene, and to a lesser extent, dimethylaniline, will carry over into the intramolecular system, as will the properties of the pyrene/dimethylaniline exciplex. Figure 2(b) shows an analytical working curve in which $\ln[I(470)/I(380)]$ is plotted against the temperature. The intensities $I(470)$ and $I(380)$ are proportional to the E^* and M^* concentrations, respectively. For PYDMAP, over the 180–410°C temperature range, the intensity ratio $I(470)/I(380)$ changes by 1.0%/°C, and thus measurement of this intensity ratio with 1% accu-



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The linkage of the two chromophores into an intramolecular system not only eliminates the possibility of differential distillation but also allows the dopants to be used at much lower concentrations than those required for the intermolecular systems. High concentrations are not required since M and G are tethered only a few bond lengths apart. In these conditions, the primary consideration in choosing the appropriate concentration of dopant is the intensity of fluorescence required, and we have obtained adequate signals from samples containing as little as 1-ppm PYPYP. The effective upper limit for the concentration of the intramolecular dopant is ~1 mM, since above this concentration the G end of one molecule may interact with the M^* end of another and thus yield more E^* fluorescence than expected on the basis of temperature calibrations made with more dilute solutions. These low dopant concentrations allow a user the confidence that the dopant has a negligible effect on the evaporation properties of the droplet. Furthermore, the low concentrations can eliminate optical thickness effects due to bulk absorption in a fuel spray and thus lead to more easily interpretable experiments.

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B. Comparison of Intramolecular and Intermolecular Exciplex Thermometers

Table I. Comparison of $[E^*]/[M^*]$ for Intramolecular and Intermolecular Systems

Temp. (K)	K_A $[E^*]/[M^*]$ intramolecular	$[G] \times K_B$ $[E^*]/[M^*]$ intermolecular
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450	6.4	0.02
500	3.2	0.005
600	1.2	0.001
700	0.6	0.0003

The temperature regimes in which intramolecular and intermolecular exciplex thermometers are useful can be dramatically different. A brief discussion of the thermodynamics underlying the M^*/E^* equilibrium can provide insight into these different regions of application.

For an intermolecular exciplex thermometer at a temperature at which the formation and dissociation kinetics are fast enough for equilibrium to be obtained within the radiative lifetime of M^*, the equilibrium constant is given by

$$K_A = [E^*]/([M^*][G]), \tag{2a}$$

where $[X]$ is the concentration of X. For an intramolecular exciplex thermometer, again at a temperature at which equilibrium is attained, the equilibrium constant is given by

$$K_B = [E^*]/[M^*], \tag{2b}$$

where $[E^*]$ and $[M^*]$ are now interpreted as the concentrations of the bound and unbound conformations of the M-$(CH_2)_3$-G molecule. In either case the equilibrium constant is related to the thermodynamic parameters of the system as follows:

$$K = \exp[\Delta S/R] \cdot \exp[-\Delta H/RT], \tag{3}$$

where ΔS and ΔH are the entropy change and enthalpy change for the formation of E^* from M^* and G, R is the gas constant, and T is the temperature in degrees kelvin.

We now consider the pyrene–PYPYP systems in particular. For the intramolecular exciplex, $\Delta S = -10$ cal/mole-deg (approximately),[5] a value characteristic of the kinetics of cyclic intermediate,[6] and $\Delta H = -6.2$ Kcal/mole.[7] For the intermolecular exciplex, $\Delta S = -20$ cal/mole-deg (approximately)[8] and $\Delta H = -10.0$ Kcal/mole[9]; $[G]$ is taken here as 5×10^{-3} M, a concentration which makes the E^* emission dominant over the M^* emission in the pyrene system at room temperature.[10] With these parameters, the results in Table I can be calculated.

As can be seen in Table I, the $[E^*]/[M^*]$ ratio for the intermolecular exciplex, which at 300 K is only a factor of 7 less than that for the intramolecular exciplex, falls so rapidly that by 700 K it is more than a factor of a thousand smaller than the ratio for the intramolecular exciplex. In terms of the thermodynamic parameters, the intermolecular system with its large negative value of ΔH, has about the same room temperature value of the $[E^*]/[M^*]$ ratio but a much more rapid decrease with increasing temperature. The intramolecular system makes a better wide-range high-temperature thermometer; the intermolecular system makes a better higher-sensitivity limited-range thermometer. Since the values of ΔS are expected to be similar for other intramolecular/intermolecular exciplex comparisons, and since ΔH for the intermolecular exciplex is expected to be more negative than ΔH for the corresponding intramolecular system (easier movement to obtain the strongest binding energy), similar behavior is expected in other intramolecular/intermolecular exciplex thermometer comparisons.

IV. Conclusion

Two intramolecular exciplex-based thermometers have been tested for use in hydrocarbon liquids. By measuring the ratio of the exciplex emission intensity to that of the monomer within 1%, it should be possible to determine the liquid temperature within 1°C at temperatures as high as 400°C. Intermolecular exciplex-based thermometers are expected to be more sensitive but to be useful over a lesser temperature range.

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Fluorescence thermometers using intramolecular exciplexes

Henry E. Gossage and L. A. Melton

Exciplex-based fluorescence thermometers have been developed which should allow the nonintrusive real-time determination of temperatures in hydrocarbon liquids within 1°C at temperatures as high as 400°C. The two-candidate dopant molecules—1,3-bis-(1′-pyrenyl)-propane and 3-(4′-dimethylaminophenyl)-1-(1′-pyrenyl)-propane—are commercially available and may be used at concentrations as low as 1 ppm.

I. Introduction

Murray and Melton have previously demonstrated that the fluorescence from exciplex-based visualization systems can be used to determine the temperature of hydrocarbon liquids nonintrusively at temperatures as high as 275°C.[1,2] Because these visualization systems provide nonintrusive submicrosecond measurements of the liquid temperature in planar laser-induced fluorescence (PLIF) conditions, they have potential application in the visualization of the droplet temperature field in evaporating fuel sprays as well as other remote sensing applications.

The systems reported by Murray and Melton consisted of two components, a fluorescent organic compound (monomer) M and a ground-state exciplex-forming compound G. The key chemistry is summarized in Eq. (1):

$$M^* + G \rightleftharpoons E^*, \qquad (1)$$

where M^* is the first excited singlet state of M and E^* is the exciplex (excited state complex), which is bound in the excited state and unbound in the ground state. Because M^* and G are separate compounds, the resulting exciplex is an intermolecular exciplex. The fluorescence emission from E^* is red-shifted with respect to the emission from M^* by 50–150 nm, and thus there may be two distinct emission bands in the spectrum of such a mixture, one from M^* and one from E^*. The reaction in Eq. (1) is temperature dependent, and thus the relative amounts of emission from M^* and E^* change as a function of temperature. A key feature of these measurements is that one need only measure the ratio of the intensities of these two emissions and compare that ratio with a previously established calibration curve rather than having to measure absolute intensities.

The intermolecular visualization systems previously reported can be used in the exciplex thermometry of hydrocarbon systems with an accuracy of 1°C over a temperature range of 100–150°C, but they are not optimal. For example, it is implicitly assumed in the exciplex thermometry method that the M^*/E^* intensity ratio is a function of temperature only; however, in an evaporating fuel droplet, the concentrations of the components M and G may change as the more volatile component preferentially distills. In addition, the concentrations of M and/or G may have to be as much as 1–10% (w/w), and thus there is the possibility that the dopants themselves may affect the evaporation behavior of the droplet. In the new systems reported here, the two exciplex-forming components, M and G, are chemically linked by a three-carbon alkyl chain, and hence they cannot separately distill. Furthermore, the probability of forming this intramolecular exciplex no longer depends on the separate concentration of G and M—they are tethered together—and thus the M-$(CH_2)_3$-G dopant molecule can be used as extremely low concentrations, even 1 ppm.

II. Experimental Apparatus and Procedures

A. Apparatus

Fluorescence spectra were obtained on a Farrand Mark I spectrofluorimeter. The excitation wavelength was 345 nm for both dopants. To obtain fluorescence spectra at temperatures up to 420°C, solutions were transferred to 15-cm lengths of 2- × 6-mm quartz tubing, which had been sealed at one end, degassed using several freeze–pump–thaw cycles, and sealed under vacuum. The standard sample compartment was removed and replaced with a 5-cm (2-in.) diam by 8.8-cm (3.5-in.) long brass cylinder, whose axis

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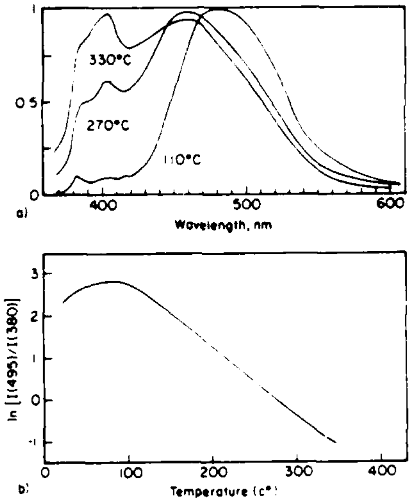

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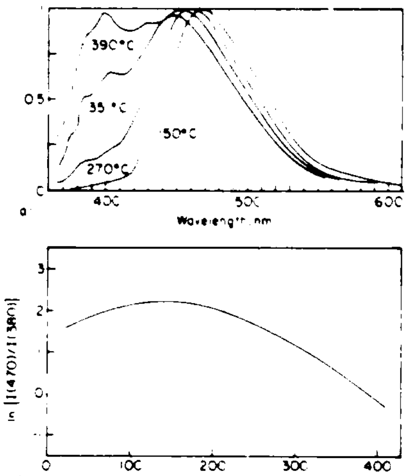

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