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Lanthanide-based laser-induced phosphorescence for spray diagnostics

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Laser-induced phosphorescence (LIP) is a relatively recent and versatile development for studying flow dynamics. This work investigates certain lanthanide-based molecular complexes for their use in LIP for high-speed sprays. Lanthanide complexes in solutions have been shown to possess long phosphorescence lifetimes (~ 1 – 2 ms) and to emit light in the visible wavelength range. In particular, europium and terbium complexes are investigated using fluorescence/phosphorescence spectrometry, showing that europium-thenoyltrifluoroacetone-trioctylphosphineoxide (Eu-TTA-TOPO) can be easily and efficiently excited using a standard frequency-tripled Nd:YAG laser. The emitted spectrum, with maximum intensity at a wavelength of 614 nm, is shown not to vary strongly with temperature (293–383 K). The decay constant of the phosphorescence, while independent of ambient pressure, decreases by approximately $12 \mu\text{s/K}$ between 323 and 373 K, with the base level of the decay constant dependent on the used solvent. The complex does not luminesce in the gas or solid state, meaning only the liquid phase is visualized, even in an evaporating spray. By using an internally excited spray containing the phosphorescent complex, the effect of vaporization is shown through the decrease in measured intensity over the length of the spray, together with droplet size measurements using interferometric particle imaging. This study shows that LIP, using the Eu-TTA-TOPO complex, can be used with different solvents, including diesel surrogates. Furthermore, it can be easily handled and used in sprays to investigate spray breakup and evaporation. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4943224>]

I. INTRODUCTION

The breakup of sprays is an important issue in the field of spray combustion. It determines the size of droplet distribution and therefore has an effect on the generation of pollution and on the efficiency of the combustion process.¹ Investigating the fundamental properties of the breakup in the near-nozzle regime, such as velocity, dispersion, and evaporation, has been a focus of optical diagnostics for decades.² The small scales, high optical densities, and large velocities that occur in sprays have proven to complicate the analysis of sprays and associated breakup phenomena. Laser-induced phosphorescence (LIP) has been used as a diagnostic tool for investigating flows for over a decade.^{3,4} The characteristic long lifetime of phosphorescence, in the order of milliseconds, caused by efficient intramolecular transfer of energy to a metastable state after electron excitation, allows for flow tracking in sprays.^{5,6} However, the usefulness of phosphorescence in sprays depends on the tracer/molecule used. Solvent phosphorescence, such as used in acetone and biacetyl sprays,^{7,8} has a relatively short lifetime ($\sim 1 \mu\text{s}$) which limits its use for flow tracking. Lanthanide-based phosphorescence, where rare earth metal ions are added to a solvent, is known to have a relatively long lifetime of

milliseconds instead of microseconds. Of the lanthanide ions, europium and terbium exhibit the most intense emission in the visible spectrum, as well as particularly long lifetimes.⁹

Excitation of the “bare” ions remains difficult, due to high attenuation, environmental quenching, and a large temperature dependence, although this latter dependence permits utilization for thermometry.¹⁰ As a result these lanthanides are often contained within a molecular complex,¹¹ such as europium-thenoyltrifluoroacetone-trioctylphosphine oxide (Eu-TTA-TOPO) or terbium-pyridinedicarboxylic acid (Tb-DPA). The ions and ligands together constitute a supramolecule. While a metal ion can only be excited by very specific wavelengths, a large organic molecule has every electronic energy level split up into multiple rovibrational levels essentially resulting in a band structure. The organic ligand can therefore be excited by a wide range of wavelengths. After absorption, in the singlet system, energy is transferred through the triplet state of the organic ligand to the lanthanide, which will subsequently phosphoresce. The organic ligands thus have the dual function of light harvesting and shielding the excitation against quenching, through protective shell formation around the susceptible metal ion.¹²

Lanthanide complexes have been used in the past to experimentally investigate sprays. Krüger and Grünefeld³ used a Tb-DPA complex to study spray formation by adding the molecules in low concentration to a liquid spray and tracking excited lines to obtain a spray velocity field. More recently,

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Wissel⁴ and Brands *et al.*⁵ used terbium molecular complexes to determine spray velocities by tagging a part of the spray close to the nozzle and tracking the movement of the glowing fluid, showing that measurements are possible even in high-speed sprays. In previous work,⁶ we have used an europium complex to investigate spray breakup and dispersion through phosphorescent fluid tracking, showing that even the small droplets ($<10\ \mu\text{m}$) in a spray can be tracked over time using phosphorescence at velocities of 150 m/s. However, the properties of lanthanide-complex phosphorescence as a function of experimental conditions occurring in such high-speed, high-temperature, and dense sprays are still mostly unknown, and some will be addressed in this investigation. In Section II the spectral properties of phosphorescent molecular complexes are investigated. The influence of pressure and temperature on the emission lifetime is discussed in Section III, while light absorption and saturation of the tracer molecules is discussed in Section IV. Together, these give a general overview of the influence on the phosphorescent properties. In a more applied setting, the influence of evaporation on the measurement of spray phosphorescence is investigated through high-speed intensified imaging and droplet size measurements in Section V. Finally, applicability for LIP on spray breakup research is discussed and quantified.

II. SPECTRAL PROPERTIES

One of the most important properties in using phosphorescent or fluorescent tracers is the wavelength of excitation and emission. The lanthanide complexes investigated here are known to have excitation wavelengths in the ultraviolet, while emitting at visible wavelengths.¹² To investigate the spectral properties of the Eu-TTA-TOPO and Tb-DPA supramolecules, the compounds were dissolved in an ethanol-water mixture (1:9 V/V) with a 0.1% concentration by volume of Triton X-100 (see Table I). These solutions can be created from stock solutions of the individual components, which can be diluted to obtain the low concentrations in this work. In polar solvents, the TOPO ligand causes a turbidity in the fluid, which is removed by the Triton surfactant. The surfactant increases the efficiency and transparency with water-based (polar) solvents due to the formation of hydrophobic micelles around the phosphorescent tracer. When using non-polar

TABLE I. Concentrations of the components used in the europium- and terbium-based phosphorescent solutions. The concentration ratios follow measurements by Arnaud and Georges¹² to obtain optimal phosphorescence lifetimes, while the concentration was a factor 10 lower than recommended to obtain a large laser penetration into the cuvette of the spectrometer.

Component Eu-based	Concentration (M)
EuCl ₃	10^{-5}
TTA	10^{-4}
TOPO	10^{-3}
Component Tb-based	Concentration (M)
TbCl ₃	10^{-5}
DPA	10^{-5}

FIG. 1. Excitation-emission spectrum of Eu-TTA-TOPO.

solvents, such as *n*-heptane or *n*-dodecane, the surfactant can be omitted. The two solutions were analyzed using an LS55 Perkin Elmer fluorescence spectrometer, recording an emission spectrum between 400 and 700 nm as a function of excitation wavelengths between 200 and 450 nm. The excitation bandwidth was scanned in steps of 10 nm, with the resulting spectral properties shown in Figures 1 and 2. The europium-based solution shows a sharp emission at 614 nm (of the $^5D_0 \rightarrow ^7F_2$ transition in the europium ion) from a broad excitation band around 350 nm. Obviously, the europium complex can be efficiently and conveniently excited by the third harmonic of a standard Nd:YAG laser ($\lambda = 355\ \text{nm}$). The excitation of the Triton surfactant, only present in the alcohol-water mixtures, can be seen in the deep UV around 250 nm and at 290 nm, decreasing the energy available for phosphorescence emission at around 614 nm and emitting a broad fluorescence spectrum.

Tb-DPA shows two sharp green emission peaks, the $^5D_4 \rightarrow ^7F_5$ transition of the terbium ion around 544 nm and an unassigned transition around 495 nm. Most notable is that the excitation of the terbium mixture is most efficient between 240

FIG. 2. Excitation-emission spectrum of Tb-DPA.

and 250 nm. This excitation wavelength is not easily generated from standard commercially available lasers, and requires a wavelength-tunable (dye) laser or a KrF excimer laser. Excitation by frequency-quadrupled Nd:YAG laser radiation at 266 nm is possible, as shown in previous work,^{4,5} but the efficiency is poor compared to the europium solution, which might lead to problems at the low imaging exposure times required for the investigations of high-velocity sprays. The europium solution can be excited efficiently using a standard frequency-tripled Nd:YAG laser, and it has a large emission intensity compared to the terbium-DPA solution. For this reason, the Eu-TTA-TOPO molecular complex was chosen for further investigation.

III. PHOSPHORESCENCE LIFETIME

The phosphorescence lifetime is another crucial parameter of a molecular complex. It determines the expected reduction of signal over time, and therefore the maximum duration of a LIP experiment. The decrease in phosphorescence intensity I_P is given by

$$I_P(t) = I_0 e^{-\frac{t}{\tau}}, \quad (1)$$

with I_0 the measured intensity at time $t = 0$ and τ the phosphorescence decay constant. The phosphorescent decay constant is partly dependent on several environmental factors, collectively called quenching (non-radiative decay processes). In the gas phase, molecular oxygen and the metastable tracers themselves are often limiting the achievable phosphorescence lifetime.^{13,14} The structure of Eu-TTA-TOPO in the liquid phase of interest here protects against this quenching by long organic ligands forming a shell around the sensitive ion¹² (see Figure 3). The temperature of the fluid is expected to have

FIG. 3. A simplified Lewis structure of the Eu-TTA-TOPO complex. The sensitive interactions between the europium ion and the TTA ligand, indicated with perpendicular bars between the oxygen atoms and the ion, is protected by the long TOPO carbon ligands, shortened here for size considerations. In polar solvents, a surfactant (Triton X-100) can be added to form a protective micelle around the molecule, indicated by the dotted line. A more detailed explanation can be found in Arnaud and Georges.¹²

a large effect on the lifetime, with the solution at increasing temperatures suffering from increased vibrational quenching.

To investigate the influence of temperature, pressure, and solution composition on the phosphorescence decay constant, the experimental setup shown in Figure 4 is used. It consists of a temperature- and pressure-controlled environment with predetermined ambient gas composition and quartz windows for optical access. Three solutions are tested inside the setup: the phosphorescent complex dissolved in either a water-based solvent or in one of the two diesel surrogate fuels (*n*-heptane and *n*-dodecane), with properties shown in Table II.

FIG. 4. Experimental setup used for the phosphorescence characterization. A thin laser sheet excites fluid in a quartz cuvette in an optically accessible high-pressure high-temperature cell. A high-speed camera measures the phosphorescent penetration and decay.

TABLE II. Viscosity μ , density ρ , and surface tension γ for each solution at a temperature of 293 K. All values were taken from the literature,¹⁵ except for the surface tension of water (due to the addition of surfactants), which was measured using contact angle goniometry.

Solvent	$\mu \cdot 10^{-3}$ (Pa · s)	ρ (kg/m ³)	γ (N/m)
water-ethanol	1.32	969	0.03
<i>n</i> -heptane	0.409	682	0.02
<i>n</i> -dodecane	1.35	749	0.024

It should be noted that these properties will change with increasing temperature, however, they are applicable to the room temperature experiments reported in Sections IV and V. The solutions are excited in a cuvette using a frequency-tripled Nd:YAG laser, emitting 10 mJ 355 nm (UV) laser pulses. A Photron SA-Z high-speed camera (Photron Lim., UK) is synchronized to record approximately 100 sequences of 50 images at 20 kHz, starting 3 μ s after excitation to ensure the TTA ligand fluorescence has died out. During the experiments the temperature was slowly increased from 298 K to 393 K, measuring at regular intervals. A type T thermocouple was placed inside the cuvette containing the solution, to monitor the fluid temperature. The maximum change in temperature during individual recordings was 0.2 K. The temporal dependence of the intensity (see Figure 5) for each measurement is used to determine the decay constant by fitting $I = A \cdot e^{-Bt} + C$. The coefficient C was added to represent the background level. The measured decay constants for each sequence are then averaged, with the standard deviation indicating the variation between measurements.

Figure 6 shows the temperature dependence of the phosphorescence decay constant for each of the solvents listed in Table II. While the decay constant at room temperature depends on the solvent used, the temperature-dependent behavior is similar for each solution. Starting at ≈ 325 K the

FIG. 5. Normalized intensity over time for a heptane-based Eu-TTA-TOPO solution at 303 K, with the background already subtracted. The red line is a fit of exponential decay with a decay time of $748 \pm 8 \mu$ s, the intensity plotted in a log scale.

FIG. 6. Phosphorescent decay time as a function of temperature for three different solvents. The error bars indicate the standard deviation of the variation in measured decay times over 110 sequences.

measured decay constant decreases with 12 μ s/K, independent of the solvent. This large temperature dependence indicates that the decay constant could be used as a proxy for the local temperature of the fluid in an experiment, as long as the time scale of the temperature change or the evaporation process is much larger than the time scale of the phosphorescence. For high temperature spray research, such as in investigations of combustion processes where fluid temperatures can easily approach the boiling point of the solvent, the decreased decay constant should be taken into account in interpreting the signal levels. The phosphorescence wavelength (measured using an Ocean Optics spectrometer) did not show a significant change in wavelength over temperature, as shown in Figure 7, indicating that the spectral temperature dependence of the complex as a whole is small. The influence of ambient pressure on the phosphorescence decay constant at 312 K was measured between 0.1 and 1.5 MPa (see Figure 8) and is negligible, as expected.

FIG. 7. The normalized emission spectrum of Eu-TTA-TOPO dissolved in water-ethanol for temperatures of 298 K and 363 K over 3.8 ms.

FIG. 8. Measured phosphorescent decay time of the water-based Eu-TTA-TOPO solution at 312 K. The increased pressure has no observable effect on the measured lifetime.

IV. ABSORPTION AND SATURATION

The penetration of the excitation laser light into the spray becomes an issue when investigating dense sprays. To determine the absorption of light by the solutions, a thin 355 nm light sheet (0.5×160 mm) enters a quartz cuvette containing a water-ethanol phosphorescent solution (see Figure 4). The emitted light is measured perpendicular to the light sheet, using a 1024×1024 camera recording frames at 20 kHz. The energy of the laser is adjusted between 0.2 and 1.4 mJ/cm of the light sheet, resulting in a fluence of approximately 4–28 mJ/cm². Pixel values from five columns of 39- μ m pixels in the center of the cuvette (see Figure 4), to avoid complications due to light scattering/refracting on the wall of the cuvette, are averaged and plotted as a function of depth (i.e., penetration distance) in Figure 9. It shows saturated absorption close to the interface, and a more classic Beer-

FIG. 9. The measured (solid line) and saturated attenuation modeled (dashed line) decrease of normalized intensity over distance. The laser fluence of the laser sheet is indicated for the measurements. The numerical data are shown as a function of a dimensionless surface intensity I_s , which is a function of the laser power.

Lambert absorption further down, where the remaining laser energy is low.

The penetration is determined by the absorption of the laser energy by the phosphorescent molecules, i.e., the decay of energy is dependent on the concentration c of Eu-TTA-TOPO in the solution. This relation is typically given in the form of the Beer-Lambert law,

$$\frac{dI}{dx} = -\alpha c I, \quad (2)$$

with x the distance traveled into the medium, I the laser beam intensity, and α the absorption coefficient. Since the liquid is homogeneous, we take the recorded emission strength to be proportional to the laser excitation intensity. The nonlinear absorption coefficient is required when saturation of the excited molecules is to be accounted for. It can be described by¹⁶

$$\alpha(\omega) = \frac{\alpha_0 G(\omega)}{1 + |G(\omega)|^2 I}, \quad \text{with} \quad G(\omega) = \frac{\gamma}{\gamma + i(\omega - \nu)}, \quad (3)$$

with α_0 the (constant) linear absorption coefficient, γ the damping constant, ω the (angular) laser frequency, and ν the central frequency of the absorbing transition. The real part of Equation (3) determines the actual absorption and is given by

$$Re(\alpha) = \frac{\alpha_0 \gamma^2}{\gamma^2(1 + I) + (\omega - \nu)^2}. \quad (4)$$

Following Meystre and Sargent III¹⁶ in assuming a resonant excitation ($\omega = \nu$), and neglecting the laser beam intensity variation of the sheet thickness, Equation (4) can be simplified to

$$\alpha = \frac{\alpha_0}{1 + I}. \quad (5)$$

The imaged intensity can be obtained by inserting Equation (5) into the differential form of Equation (2),

$$\frac{dI}{dx} = -\alpha c I = -\alpha_0 c \frac{I}{1 + I}, \quad (6)$$

and then integrating from I_s , the intensity at the interface, to the intensity $I(x)$ at depth x to obtain

$$\ln I(x) + I(x) = -\alpha_0 c x + \ln I_s + I_s, \quad (7)$$

which satisfies $I(x = 0) = I_s$. Figure 9 shows this implicit equation for a concentration of $c = 10^{-5}$ M, an attenuation coefficient α_0 of $34.6 \cdot 10^6$ m²/M, and an incident intensity I_s that varies with laser power. It is qualitatively similar to the experimental results, indicating that the saturated absorption model is sufficient to describe the phosphorescent process, i.e., the intramolecular energy transfer to the europium has an essentially constant efficiency.

V. PHOSPHORESCENT SPRAY

To investigate the experimental characteristics of a high-speed, dense spray, an optically accessible mount with a 200 μ m single hole nozzle is pressurized up to 130 bar to generate a continuous spray (see Figure 10) into air with ambient conditions of atmospheric pressure and a temperature of 293 K. By guiding the UV laser light through the internal

FIG. 10. Internal nozzle excitation setup. A UV laser is guided to the nozzle using a quartz rod inside the nozzle mount. Luminescent fluid exits the nozzle and is imaged using an intensified high-speed camera.

quartz rod inside the mount, a volume of fluid close to the nozzle exit can be excited. If the excitation survives the passage of the fluid through the nozzle capillary, this should result in a luminescent spray. Using an intensified (GaAsP HICATT, Lambert) high speed camera (Photron SA-Z) the emerging glowing fluid is imaged at 120 kHz, with an exposure time of 270–300 ns to minimize motion blurring, at a resolution of 1024×144 and a magnification of $20 \mu\text{m}/\text{pixel}$. Note that this method provides direct imaging of the liquid phase in the spray, which luminesces by itself. It is a zero-background technique, and not sensitive to the surrounding gas phase: if there is no liquid, there will be no signal.

Figure 11 shows the measured sprays for both the water-ethanol and heptane-based solutions (see Table II). The water-based solution (bottom panel) breaks up through Kelvin-Helmholtz instabilities, generating ligaments that break up into droplets. The heptane-based solution (top panel) breaks up in a far more atomized manner, but shows a stronger decrease in intensity over the distance from the nozzle (see

FIG. 12. Ensemble averaged normalized intensity of internally excited sprays, $183 \mu\text{s}$ after excitation, over distance x normalized by the nozzle diameter d_{nozzle} . The ensemble average is performed over 88 and 260 experiments for the heptane and water-ethanol sprays, respectively. The running average is performed over 60 samples.

also Figure 12). The characteristic shape of the decrease in intensity is caused by the longitudinal dispersion in the core of the spray, causing a slight accumulation of glowing fluid close to the nozzle exit. The stabilized level further downstream, however, has a lower intensity for the heptane spray. As all of the fluid is excited at the same time, this is not expected from regular decay mechanisms. Considering that the phosphorescent process of the Eu-TTA-TOPO complex only functions in the liquid phase,¹⁷ and that the vapor pressure of heptane is higher compared to that of the water-ethanol blend, evaporation seems a likely mechanism for this enhanced decay. Because the more energetic molecules will be the ones to escape during evaporation, the temperature of the fluid will decrease, an effect called evaporative cooling. In the experiments shown in Figure 11, fluid temperature was measured before and after the experiment using a T-type thermocouple sensor (Omega HH200A), calibrated with

FIG. 11. Snapshots of a heptane (a) and water-ethanol (b) spray created by a $200 \mu\text{m}$ nozzle, taken $183 \mu\text{s}$ after excitation inside the nozzle, with a gamma-compressed intensity scaling ($I = I_{\text{im}}^{1/2.2}$). The Reynolds ($\text{Re} = v d_{\text{nozzle}} / \nu$) and Weber number ($\text{We} = \rho v^2 d_{\text{nozzle}} / \gamma$) of the sprays are $\text{Re}_{\text{heptane}} = 50.000$, $\text{Re}_{\text{water-ethanol}} = 18.300$, $\text{We}_{\text{heptane}} = 1.5 \cdot 10^5$, and $\text{We}_{\text{water-ethanol}} = 1.01 \cdot 10^5$. The difference in formed structures, or the absence thereof, shows the difference in atomization between the two fluids.

FIG. 13. The interference between laser light traveling through a droplet and refracting off its surface can be imaged by defocusing the camera lens. The fringe spacing can be used to determine the droplet size.

a mercury thermometer to within 0.1 K. During the spray breakup the heptane temperature decreased from 292.6 K to 281.5 K, compared to a temperature decrease from 291.9 K to 290.5 K for the water-ethanol blend. The large (11.1 K) decrease in temperature of the heptane spray indicates that evaporation is significant.

To evaluate the possible evaporation of the sprays, droplet size distributions will play a large role, as the surface area between the interfaces is a dominant factor in evaporation. When a spray breaks up into smaller droplets, the interface area will be larger, and therefore have more surface molecules that can potentially escape. Furthermore, if large droplets created through primary breakup are evaporating, they will also shift the distribution towards smaller droplet sizes. To investigate the droplet size distributions, a droplet sizing technique called interferometric particle imaging^{18–20} (IPI) is used. This technique uses the interference between refractions and reflections of coherent light on the droplet to create a fringe pattern on defocused droplet images (see Figure 13). The spacing of the fringes $\Delta\phi$ is directly related to the size of the droplet through

$$\Delta\phi = \frac{2\lambda v d_s}{A(\theta) d_p d_a}, \quad (8)$$

with λ the wavelength of the light, d_p the diameter of the droplet, d_s the size of the defocused droplet image, d_a the aperture size of the camera lens, v the object distance, and $A(\theta)$ a geometric factor which depends on the angle θ between the light sheet and the lens (see Glover *et al.*¹⁸ or Bocanegra Evans *et al.*²⁰ for more details).

Using a frequency-doubled Nd:YAG laser, with a 10-Hz repetition rate and a pulse energy of 15 mJ, a sheet of 532-nm (green) light, is used to illuminate a plane in the area immediately below the nozzle exit. Only one side of the spray is imaged, keeping the liquid jet out of the imaging plane to obtain a proper contrast. The IPI measurements are performed with a 1600×1200 CCD camera (IDT Redlake), measuring an area of approximately 19×25.3 mm, defocused to show discs of 130 pixels in diameter. The disc size determines the longest measurable wavelength, and thus the minimum drop size.

FIG. 14. The droplet distribution of a water- and heptane-based spray close to the nozzle exit. Droplets too small to accurately determine the fringe spacings ($\Delta\phi > d_s$) have been removed from the graph. The heptane jet generates smaller droplets, indicating a larger evaporation rate.

Figure 14 shows the droplet size distribution in water-ethanol- and heptane-based sprays under similar conditions as the phosphorescent sprays, accumulated over 500 images. It shows that the heptane spray generates smaller droplets compared to the water spray. These smaller droplets, generated through primary and secondary breakup as well as evaporation, will increase the surface area of the fluid in contact with the ambient gas, indicating a stronger evaporation can take place in the heptane-based spray. Since the molecular complex only luminesces in the liquid state, this can explain the intensity drop over distance in phosphorescent sprays, as observed in Figure 11.

VI. CONCLUSION AND OUTLOOK

This investigation shows that laser-induced phosphorescence can be a useful tool for spray research. While the decay constant of the fluid decreases with increasing temperature, external pressure has no effect on phosphorescent

emission. The europium-based molecular complex can be excited with readily available wavelengths, and the spectrum of the emitted light remains steady over a large range of temperatures. The property that only the liquid phase emits light allows for a wide range of investigations, without the ambiguity that usually accompanies dense spray research, and may indicate evaporation of the fluid as well. This can lead, for instance, to more accurate measurements of liquid lengths in fuel sprays. We have shown that excited molecular complexes survive the passage through a narrow metal nozzle channel, which suggests that the phosphorescent spray may be a useful tool to investigate spray-wall interactions. For high temperature investigations, such as in a combustion environment, other phosphorescent complexes, such as a terbium- or praseodymium-based complex could be more sensitive and will be investigated in future work.

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