Molecular Tagging Techniques
Part - 2

Hui Hu
Department of Aerospace Engineering, Iowa State University
Ames, Iowa 50011, U.S.A
Molecular Photoluminescence Phenomena

- **Fluorescence emission:**
  - Radiative process from a *singlet excited state to its singlet ground state*.
  - Singlet-singlet transitions are quantum mechanically allowed, making fluorescence *short-lived* with emission lifetimes on the order of 1-100 ns.

- **Phosphorescence emission:**
  - Radiative process from a *triplet excited state to its singlet ground state*.
  - Such transitions are quantum mechanically forbidden, phosphorescence is *long-lived* with emission lifetimes that may approach milliseconds.

- Both fluorescence and phosphorescence may be used for fluid *temperature measurement* by qualification of photoluminescence intensity.
LIF Technique with Temperature Dependent Fluorescent Dyes: Rhodamine B and Fluorescein

<table>
<thead>
<tr>
<th></th>
<th>308nm UV laser</th>
<th>488nm Argon-ion laser</th>
<th>514nm Argon-ion laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine B</td>
<td>-1.55% K⁻¹ (5°C ~ 65°C)</td>
<td>-1.17% K⁻¹ (6°C ~ 66°C)</td>
<td>-1.48% per K⁻¹ (6°C ~ 66°C)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*Sakakibara and Adrian</td>
<td>*Coppeta and Roger</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-2.3 % K⁻¹ (15°C ~ 40°C)</td>
<td>-1.54 % K⁻¹ (20°C ~ 60°C)</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>-0.45% K⁻¹ (5°C ~ 65°C)</td>
<td>-0.25% K⁻¹ (6°C ~ 66°C)</td>
<td>+2.25% K⁻¹ (6°C ~ 66°C)</td>
</tr>
</tbody>
</table>
|                |                        | *Coppeta and Roger    | *Coppeta and Roger ...
|                |                        | -0.16 % K⁻¹ (20°C ~ 60°C) | +2.43 % K⁻¹ (20°C ~ 60°C) |
Some Limitations or Issues Using LIF Technique

• Some Limitations or Issues Using LIF Technique
  – Low temperature sensitivity:
    • Thermal flows with small temperature difference.

  – It is highly desirable to have an adjustable temperature sensitivity:
    • Temperature differences in thermal flows may change dynamically according to the operating condition.

  – Reflect light or scattering light may contaminate LIF signal:
    • Optical filters may not be able to filter out the reflecting laser light or scattering light completely.

• A novel molecular tagging thermometry technique is developed by using the long-lived laser induced phosphorescence of a specially-designed phosphorescent triplex (1-BrNp • Gβ-CD • ROH) to achieve temperature measurement with adjustable temperature sensitivity.
Long Lifetime Phosphorescent Molecular Tracers

**Phosphorescent triplex** \((1-\text{BrNp} \cdot \text{G}\beta\text{-CD} \cdot \text{ROH})\)

1. Bromonaphthalene \((1-\text{BrNp})\)
2. Cyclodextrin \((\text{G}\beta\text{-CD})\)
3. Alcohols \((\text{ROH})\)

Molecular structure of the phosphorescent triplex

Spectrophotometer Output vs Wavelength

- Phosphorescence
- Fluorescence

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 32.0°C</td>
<td>200 - 800</td>
</tr>
<tr>
<td>T = 25.4°C</td>
<td></td>
</tr>
<tr>
<td>T = 19.7°C</td>
<td></td>
</tr>
<tr>
<td>T = 14.5°C</td>
<td></td>
</tr>
<tr>
<td>T = 10.2°C</td>
<td></td>
</tr>
<tr>
<td>T = 3.40°C</td>
<td></td>
</tr>
</tbody>
</table>
Technical Basis for Temperature Measurement

- According to quantum theory, the decay of phosphorescence emission intensity \( I_{em} \) follows an exponential law:

\[
I_{em} = I_o e^{-t/\tau} = I_i C \varepsilon \Phi_p e^{-t/\tau}
\]

\( I_o \): Initial phosphorescence intensity:
\( I_i \): the local incident laser intensity
\( C \): concentration of phosphorescence dye
\( \varepsilon \): the absorption coefficient
\( \Phi_p \): phosphorescence quantum yield, temperature-dependant
\( \tau \): phosphorescence lifetime, which refers to the time when the intensity drops to 37\% (i.e. \( 1/e \)) of the initial intensity \( (I_o) \), temperature-dependant.

\[
\Phi = \Phi(T) \\
\tau = \tau(T)
\]  \( \Rightarrow \)  \[
I_o = I_o(T) \\
I_{em} = I_{em}(T)
\]
Technical Basis for Temperature Measurement

- Capturing the phosphorescence emission at time $t$ using a gated CCD detector:

$$S_p = \int_{t}^{t+\delta t} I_{em} dt = I_o(T) \cdot \tau(T) \left(1 - e^{-\frac{\delta t}{\tau(T)}}\right) \frac{t}{\tau(T)}$$

- At a prescribed temperature $T = T_o$

$$S_{p_o} = I_o(T_o) \cdot \tau(T_o) \left(1 - e^{-\frac{\delta t}{\tau(T_o)}}\right) \frac{t}{\tau(T_o)}$$

- Relative intensity:

$$R = \frac{S_p}{S_{p_o}} = \frac{I_o(T) \cdot \tau(T) \left(1 - e^{-\frac{\delta t}{\tau(T)}}\right)}{I_o(T_o) \cdot \tau(T_o) \left(1 - e^{-\frac{\delta t}{\tau(T_o)}}\right)} e^{-\left(\frac{1}{\tau(T)} - \frac{1}{\tau(T_o)}\right)t}$$

$= R(T, t)$

- Relative intensity $R$ is the function of temperature, $T$, and time delay after laser pulse, $t$ !!!

- The sensitivity for temperature measurement is adjustable by changing the time delay, $t$ !!!
Phosphorescence Lifetime vs. Temperature

- **Lifetime imaging technique:**

\[
\frac{S_2}{S_1} = e^{-\Delta t/\tau} \quad \Rightarrow \quad \tau = \frac{\Delta t}{\ln\left(\frac{S_2}{S_1}\right)} \quad \Rightarrow \quad \tau = \tau(T)
\]

- **Phosphorescence intensity**

\[
S_1 = I_i C \varepsilon \Phi_p \left(1 - e^{-\delta t/\tau}\right) e^{-t_0/\tau}
\]

\[
S_2 = I_i C \varepsilon \Phi_p \left(1 - e^{-\delta t/\tau}\right) e^{-(t_0+\Delta t)/\tau}
\]
Initial Phosphorescence Intensity vs. Temperature

Relative intensity vs. temperature graph showing initial intensity and experimental data with delays and exposures.
Calibration Profiles with Different Time Delay

Sensitivity for temperature measurement at 25 °C

<table>
<thead>
<tr>
<th>Time delay after laser pulse</th>
<th>Temperature sensitivity (K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delay=1 ms</td>
<td>5.8 %</td>
</tr>
<tr>
<td>Delay=2 ms</td>
<td>8.9 %</td>
</tr>
<tr>
<td>Delay=3 ms</td>
<td>13.0 %</td>
</tr>
<tr>
<td>Delay=5 ms</td>
<td>15.2 %</td>
</tr>
<tr>
<td>Delay=7 ms</td>
<td>21.5 %</td>
</tr>
<tr>
<td>LIF using Rhodamine B</td>
<td>2.2 %</td>
</tr>
</tbody>
</table>

- LIF of Rhodamine B
- Delay=2 ms, exposure time=1ms
- Delay=7 ms, exposure time=1ms
- Delay=5 ms, exposure time=1ms
- Delay=3 ms, exposure time=1ms
- Delay=1 ms, exposure time=1ms
- Initial intensity (200ns delay, 50us exposure)

Temperature (°C)

Relative intensity

Temperature (°C)
Demonstration Experimental Setup

Experimental setup

Heated cylinder

Present experimental parameters:

\( U_{in} = 0.034 \text{ m/s} \quad \text{D} = 4.76\text{mm} \)

\( T_{\text{fluid}} = 24.0 \degree \text{C} \quad T_{\text{cylinder}} = 57.0 \degree \text{C} \)

\( \text{Re} = 170 \)
Comparison of Raw Images with Different Time Delay

a. 1ms after laser pulse, exposure time 1ms

b. 3ms after laser pulse, exposure time 1ms

c. 5ms after laser pulse, exposure time 1ms

d. 7ms after laser pulse, exposure time 1ms
Demonstration Experiment

a. 7ms after laser pulse, exposure time 1ms

b. Background
A novel Molecular Tagging Thermometry was developed by taking advantage of the temperature dependence of laser induced phosphorescence of a specially-designed phosphorescent triplex \((\text{1-BrNp-G} \beta\text{-CD-ROH})\) to conduct temperature measurements in liquid.

**The advantages of the present technique:**

- **The temperature sensitivity of phosphorescence intensity is adjustable.**
  - changing the time delay between the laser excitation pulse and the phosphorescence image acquisition.

- **Much higher temperature sensitivity:**
  
  - Exposure time 1ms, time delay 1ms: 5.8% K\(^{-1}\) at 25 °C.
  - Exposure time 1ms, time delay 7ms: 21.5% K\(^{-1}\) at 25 °C.

- **Eliminate the effect of reflecting laser light or scattering light completely:**
  
  - The reflecting laser light and scattering light “live” only when the excitation laser is illuminating.
  - The time delay between the laser pulse and the phosphorescence image acquisition “kill” all the reflecting laser light and scattering light.

**The issues still need to be solved:**

- The effect of the non-uniformity of excitation laser intensity needs to be calibrated separately.
- A intensified camera may be required for the phosphorescence image acquisition with longer time delay after laser pulse.