Prof. Robert P. Lucht
Room 2204, Mechanical Engineering Building
School of Mechanical Engineering
Purdue University
West Lafayette, Indiana

Lucht@purdue.edu, 765-494-5623 (Phone)

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Outline of the Lecture

• Introduction to Laser-Induced Polarization Spectroscopy (PS)

• Theory of PS - Radiative Coupling of Zeeman States

• Applications of PS for Concentration Measurements
Laser-Induced Polarization Spectroscopy (LIPS)

Species-selective, spatially resolved, wide range of species, coherent signal, complicated physics
PS Signal Generation

Linear polarization can be regarded as a linear superposition of left- and right-circularly polarized light. The LCP RCP amplitudes are equal.

Because the circularly polarized pump beam, the LCP and RCP components of the probe beam experience different absorptions and phase shifts as they traverse the medium.
Polarization States of the Laser Field

For right-circularly polarized light:

\[
\vec{E}(\vec{r}, t) = \frac{1}{2} \hat{e} E_0 \exp\left[+i(\vec{k} \cdot \vec{r} - \omega t)\right] \\
+ \frac{1}{2} \hat{e}^* E_0 \exp\left[-i(\vec{k} \cdot \vec{r} - \omega t)\right] \\
= \frac{1}{2} \hat{e} E_0 \exp\left[+i(k z - \omega t)\right] \\
+ \frac{1}{2} \hat{e}^* E_0 \exp\left[-i(k z - \omega t)\right]
\]

\[
\hat{e} = \frac{\hat{x} - i \hat{y}}{\sqrt{2}}
\]

In terms of sines and cosines the expression above reduces to:

\[
\vec{E}(\vec{r}, t) = \hat{x} \frac{E_0}{\sqrt{2}} \cos(k z - \omega t) \\
+ \hat{y} \frac{E_0}{\sqrt{2}} \sin(k z - \omega t)
\]

For left-circularly polarized light:

\[
\hat{e} = \frac{\hat{x} + i \hat{y}}{\sqrt{2}}
\]
Polarization States of the Laser Field

For left-circularly polarized light:

\[ \hat{e} = \frac{\hat{x} + i \hat{y}}{\sqrt{2}} \]

In terms of sines and cosines, the expression for LCP light is given by:

\[ \vec{E}(\vec{r}, t) = \hat{x} \frac{E_0}{\sqrt{2}} \cos(kz - \omega t) - \hat{y} \frac{E_0}{\sqrt{2}} \sin(kz - \omega t) \]

The sum of LCP and RCP light is given by:

\[ \vec{E}(\vec{r}, t) = \hat{x} \frac{E_0}{\sqrt{2}} \cos(kz - \omega t) - \hat{y} \frac{E_0}{\sqrt{2}} \sin(kz - \omega t) \]

\[ + \hat{x} \frac{E_0}{\sqrt{2}} \cos(kz - \omega t) + \hat{y} \frac{E_0}{\sqrt{2}} \sin(kz - \omega t) \]

\[ = \hat{x} \frac{2E_0}{\sqrt{2}} \cos(kz - \omega t) \]
Polarization vectors for linearly polarized light:

\[ \hat{e} = \hat{x} \]

\[ \hat{e} = \frac{\hat{x} + \hat{y}}{\sqrt{2}} \]

\[ \hat{e} = \frac{\hat{x} - \hat{y}}{\sqrt{2}} \]

\[ \hat{e} = \hat{z} \]
The interaction term $V_{eg}$ (J) is given by

$$V_{eg} = -\vec{\mu}_{eg} \cdot \vec{E}_L(\vec{r},t)$$

$$\vec{\mu}_{eg} = \langle \psi_e | \vec{\mu} | \psi_g \rangle = \langle \psi_e | -e\vec{r} | \psi_g \rangle = -e\langle \psi_e | \vec{r} | \psi_g \rangle$$

Level $g$  Level $E$  Level $G$
The absorption coefficient \( \alpha_{eg}(\omega_L) \) \((m^{-1})\) between two Zeeman states is given by

\[
\alpha_{eg}(\omega_L) = \frac{2 \pi^2 g_H(\omega_L)}{\varepsilon_0 \hbar \lambda_L} \left( n_g - n_e \right) \left| \vec{\mu}_{eg} \cdot \hat{e}_L \right|^2
\]
Coupling of the Laser Field with Electric Dipole Transitions

The absorption coefficient is \( \alpha_{EG}(\omega_L) \) \((m^{-1})\)

summed over all Zeeman transitions is given by

\[
\alpha_{EG}(\omega_L) = \frac{2 \pi^2 g_H(\omega_L)}{\varepsilon_0 \hbar \lambda_L} \sum_e \sum_g \left[ (n_g - n_e) \left| \vec{\mu}_{eg} \cdot \hat{e}_L \right|^2 \right]
\]

Level E

Level G
Radiative Coupling of the Zeeman States

\[ P-\text{branch: } \Delta J = J_e - J_g = -1 \]

\[ \Delta M = M_e - M_g = -1 \]

\[ \tilde{\mu}_{eg} = \langle \alpha_e J_e M_e | \tilde{\mu} | \alpha_g J_g M_g \rangle = \langle \alpha_e J_e M_e | \tilde{\mu} | \alpha_g J_e + 1 M_e + 1 \rangle \]

\[ = -\frac{1}{2} \mu_R(\alpha_e J_e, \alpha_g J_e + 1) \sqrt{(J_e + M_e + 1)(J_e + M_e + 2)} (\hat{x} + i\hat{y}) \]

\[ \Delta M = +1 \]

\[ \langle \alpha_e J_e M_e | \tilde{\mu} | \alpha_g J_e + 1 M_e - 1 \rangle \]

\[ = \frac{1}{2} \mu_R(\alpha_e J_e, \alpha_g J_e + 1) \sqrt{(J_e - M_e + 1)(J_e - M_e + 2)} (\hat{x} - i\hat{y}) \]

\[ \Delta M = 0 \]

\[ \langle \alpha_e J_e M_e | \tilde{\mu} | \alpha_g J_e + 1 M_e \rangle = \mu_R(\alpha_e J_e, \alpha_g J_e + 1) \sqrt{(J_e + 1)^2 - M_e^2} \hat{z} \]
### Radiative Coupling of the Zeeman States

**P-branch**: \( \Delta J = J_e - J_g = -1 \)

\[
\Delta M = M_e - M_g = -1 \quad M_e = M_g - 1
\]

\[
\tilde{\mu}_{eg} = \left\langle \alpha_e J_e M_e | \tilde{\mu} | \alpha_g J_g M_g \right\rangle = \left\langle \alpha_e J_e M_e | \tilde{\mu} | \alpha_g J_e + 1 M_e + 1 \right\rangle
\]

\[
= -\frac{1}{2} \mu_R(\alpha_e J_e, \alpha_g J_e + 1) \sqrt{(J_e + M_e + 1)(J_e + M_e + 2)} \left( \hat{x} + i\hat{y} \right)
\]

\[
\mu_R(\alpha_e J_e, \alpha_g J_g) = \sqrt{\frac{A_{eg}}{\Gamma(J_e, J_g)} \frac{3 \varepsilon_0 \hbar \lambda_{eg}^3}{8\pi^2}} \quad \Gamma(J_e, J_e + 1) = (J_e + 1)(2J_e + 3)
\]

For this transition,

\[
-\tilde{\mu}_{eg} \cdot \hat{e}_{LCP} = -\tilde{\mu}_{eg} \cdot \left( \frac{\hat{x} + i\hat{y}}{\sqrt{2}} \right) = 0
\]

\[
-\tilde{\mu}_{eg} \cdot \hat{z} = 0
\]
Radiative Coupling of the Zeeman States

\( P \text{-branch}: \Delta J = J_e - J_g = -1 \)

\[
\Delta M = M_e - M_g = +1 \\
M_e = M_g + 1
\]

\[
\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e + 1 M_e - 1 \rangle
\]

\[
= \frac{1}{2} \mu_R(\alpha_e J_e, \alpha_g J_e + 1) \sqrt{(J_e - M_e + 1)(J_e - M_e + 2)} (\hat{x} - i\hat{y})
\]

\[
\mu_R(\alpha_e J_e, \alpha_g J_g) = \sqrt{\frac{A_{eg}}{\Gamma(J_e, J_g)}} \frac{3 \epsilon_0 \hbar \lambda_{eg}^3}{8\pi^2 \Gamma(J_e, J_g)} \frac{3 \epsilon_0 \hbar \lambda_{eg}^3}{8\pi^2} \Gamma(J_e, J_e + 1) = (J_e + 1)(2J_e + 3)
\]

For this transition,

\[
-\bar{\mu}_{eg} \cdot \hat{e}_{RCP} = -\bar{\mu}_{eg} \cdot \left( \frac{\hat{x} - i\hat{y}}{\sqrt{2}} \right) = 0
\]

\[
-\bar{\mu}_{eg} \cdot \hat{z} = 0
\]
Radiative Coupling of the Zeeman States

$Q$ – branch : $\Delta J = 0$

$\Delta M = -1$

$$\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e M_e +1 \rangle = \frac{1}{2} \mu_R(\alpha_e J_e,\alpha_g J_e) \sqrt{(J_e-M_e)(J_e+M_e+1)} (\hat{x} + i\hat{y})$$

$\Delta M = +1$

$$\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e M_e -1 \rangle = \frac{1}{2} \mu_R(\alpha_e J_e,\alpha_g J_e) \sqrt{(J_e+M_e)(J_e-M_e+1)} (\hat{x} - i\hat{y})$$

$\Delta M = 0$

$$\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e M_e \rangle = \mu_R(\alpha_e J_e,\alpha_g J_e) M_e \hat{z}$$
Radiative Coupling of the Zeeman States

$R-branch: \Delta J = +1$

$\Delta M = -1$

$$\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e -1 M_e +1 \rangle = \frac{1}{2} \mu_R(\alpha_e J_e, \alpha_g J_e -1) \sqrt{(J_e - M_e)(J_e - M_e -1)} \ (\hat{x} + i\hat{y})$$

$\Delta M = +1$

$$\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e -1 M_e -1 \rangle = -\frac{1}{2} \mu_R(\alpha_e J_e, \alpha_g J_e -1) \sqrt{(J_e + M_e)(J_e + M_e -1)} \ (\hat{x} - i\hat{y})$$

$\Delta M = 0$

$$\langle \alpha_e J_e M_e | \bar{\mu} | \alpha_g J_e -1 M_e \rangle = \mu_R(\alpha_e J_e, \alpha_g J_e -1) \sqrt{J_e^2 - M_e^2} \ \hat{z}$$
Laser radiation that is circularly polarized in the x-y plane couples very efficiently with superposition states with $M_J$ value that differ by +1 or -1.

circular dipole: $S(M=0) + P(M=\pm 1)$ states

$t = 0$  \hspace{1cm}  t = \frac{1}{4} \frac{h}{\Delta E}$  \hspace{1cm}  $t = \frac{1}{2} \frac{h}{\Delta E}$  \hspace{1cm}  $t = \frac{3}{4} \frac{h}{\Delta E}$  \hspace{1cm}  $t = \frac{h}{\Delta E}$
Laser radiation that is linearly polarized in the $z$-direction couples very efficiently with superposition states with the same $M_J$ value.
Modeling of the LIPS Process

Level 1: $J_g = 2$
- $M_g = -2$  -1 0 +1

Level 2: $J_e = 1$
- $M_e = -1$ 0 +1

Level 3: upper bath
- $\Gamma_{3 \rightarrow M_e}$
- $\Gamma_{M_e \rightarrow 3}$

Level 4: lower bath
- $\Gamma_{4 \rightarrow M_g}$
- $\Gamma_{M_g \rightarrow 4}$

Level 3
- $\Gamma_{34}$
Time-Dependent Density Matrix Equations for the Laser Interaction

Rate of change of population of state k:

$$\frac{\partial \rho_{kk}(\vec{r}, t)}{\partial t} = -\frac{i}{\hbar} \sum_m (V_{km} \rho_{mk} - \rho_{km} V_{mk}) - \Gamma_k \rho_{kk} + \sum_m \Gamma_{mk} \rho_{mm}$$

Time development of coherence between states k and j:

$$\frac{\partial \rho_{kj}(\vec{r}, t)}{\partial t} = -\rho_{kj}(i \omega_{kj} + \gamma_{kj}) - \frac{i}{\hbar} \sum_m (V_{km} \rho_{mj} - \rho_{km} V_{mj})$$

Coupling of laser radiation and dipole moment for states k and m:

$$V_{km} = -\vec{\mu}_{km} \cdot \vec{E}(\vec{r}, t) = -\vec{\mu}_{km} \cdot [\vec{E}_{pr}(\vec{r}, t) + \vec{E}_{pump}(\vec{r}, t)]$$
Theoretical Approach: Numerical Solution of the Time-Dependent Density Matrix Equations

• Time-dependent density matrix equations are manipulated for numerical solution, rotating wave approximation used.

• Doppler broadening effects included by dividing the state populations into velocity groups.

• Temporal profile of pump and probe lasers are input to code.
Different Absorption for Probe Components

The linearly polarized probe beam is the sum of equal quantities of left- and right-circularly polarized light:

$$\vec{E}_{probe}(z,t) = \frac{1}{2} \exp(-i\omega t + ikz) \left[ A_{02} \frac{(\hat{x} + i\hat{y})}{\sqrt{2}} + A_{03} \frac{(\hat{x} - i\hat{y})}{\sqrt{2}} \right] + c.c.$$  

The absorption and phase shift terms for the left- and right-circularly polarized components are different because of anisotropic pumping by the pump beam:

$$\alpha_2 = \left( \frac{2}{\varepsilon_0 \hbar \lambda_0 \Delta\omega_C} \right) \left( \frac{1}{1 + \left[ 2(\omega_2 - \omega_0) / \Delta\omega_C \right]^2} \right) \sum_e \sum_g \left[ (n_g - n_e) |\vec{\mu}_{eg} \cdot \hat{e}_2|^2 \right]$$
Experimental Schematic for Picosecond LIPS

PS Experiments with Short-Pulse (120 psec) Laser System

- Tunable laser system with 120-psec, near-Fourier-transform-limited pulses developed as facility laser at Sandia Livermore by Farrow and co-workers.

- Short OH PS experiments performed in a gas cell, OH produced by UV photodissociation of H₂O₂.

- PS signal dependence on pressure, laser intensity investigated.
Experimental Results for Picosecond PS of OH in Gas Cell

![Graph showing the relationship between PS Signal / [OH]^2 (arb. units) and Cell Pressure (torr).]

- Unsaturated (0.3 μJ pump)
- Saturated (170 μJ pump)
- Perturbative for 100-ps pulse
- Perturbative for 10-ns pulse
- DNI results
Polarization spectroscopy signal is generated mostly after the laser pulses are gone for $\tau_L < \tau_C$. 

- $\tau_C = 1$ psec
- $\tau_C = 1$ nsec
Time-Dependence of PS Signal for Saturating 100-psec Pulses

\( \tau_C = 1 \text{ nsec} \)

\( \gamma_c = 10^9 \text{ sec}^{-1} \)