ME 687 Lectures #24&25
Laser-Induced Fluorescence Spectroscopy: Two-Photon-Excited Fluorescence

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Outline of the Lecture

- Applications of TPEF
- Theory (Brief) of Two-Photon-Excited Fluorescence (TPEF)
Problem - First excited $n = 2$ electronic level for H lies at 82,200 cm$^{-1}$ above ground $n = 1$ level. One-photon excitation at 121.6 nm is impossible in flames because of VUV absorption, LIF cannot be observed except in near-vacuum conditions.

H-atom energy level diagram:

<table>
<thead>
<tr>
<th>Principal Quantum Number</th>
<th>$\varepsilon / hc$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>109,737</td>
</tr>
<tr>
<td>n=4</td>
<td>102,824</td>
</tr>
<tr>
<td>n=3</td>
<td>97,492</td>
</tr>
<tr>
<td>n=2</td>
<td>82,259</td>
</tr>
<tr>
<td>n=1</td>
<td>0</td>
</tr>
</tbody>
</table>

TPEF Measurements of the H-Atom
TPEF Measurements of the H-Atom

TPEF Measurements of the H-Atom

Fig. 4. Vertical number density profile of atomic hydrogen in the 72-Torr C\textsubscript{2}H\textsubscript{4}/O\textsubscript{2}/Ar flame at φ = 1.0. Also shown are the flame temperature and OH number density profiles.

Fig. 5. Vertical number density profile of atomic hydrogen in the 72-Torr C\textsubscript{2}H\textsubscript{4}/O\textsubscript{2}/Ar flame at φ = 1.7. Also shown are the flame temperature and OH number density profiles.

TPEF Measurements of the H-Atom

**Figure 1.** Multiphoton-excited fluorescence detection schemes used in this study for measuring atomic hydrogen concentration profiles in flames. The upward arrows indicate excitation wavelengths, and the downward arrows indicate fluorescence detection wavelengths.

Goldsmith, 22nd Combustion Symposium, pp. 1403-1411 (1988)
TPEF Measurements of the H-Atom

**TPEF Measurements of the H-Atom**

**Fig. 2.** Atomic hydrogen concentration profiles in flame A (72-Torr, $\phi = 0.6$ hydrogen-oxygen-argon flame). Symbols: Relative profiles measured using two-photon excitation (triangles), three-photon excitation (squares), and two-step excitation (circles). Solid curve: Absolute profile calculated using the flame model.

**Fig. 7.** Relative atomic hydrogen concentration profiles in flame F (25-Torr, $\phi = 2.0$ acetylene-oxygen, argon flame) measured using two-photon excitation (triangles), three-photon excitation (squares), and two-step excitation (circles). The profile in the inset (diamonds), plotted to the same scale as the main part of the figure, represents an interference observed using two-photon excitation with the 205-nm wavelength detuned slightly from the atomic hydrogen resonance.

TPEF Measurements of the H-Atom in Diamond-Forming Flames

H2 CARS measurements performed previously in the diamond-forming flames.

• Nd:YAG pumped narrowband dye laser generates 584 nm light
• KD*P crystal doubles dye laser output to 292 nm
• Spectrometer used as a narrow-band filter
• LIF signal detected by a photo-multiplier tube
• High-speed shutter prevents PMT saturation
TPEF Measurements of the H-Atom in Diamond-Forming Flames

• Calibration signal measured at $\Phi = 1.26$
• Calibration point uncertainty of $\pm 36\%$
  • Scatter due to flame instability and possibly some photochemical dissociation of water vapor

TPEF Measurements of the H-Atom in Diamond-Forming Flames

Substrate Temperature = 1040 K, Exit Velocity = 40 m/s

Base case measurement nearest to model conditions

Photoionization Loss-Controlled Spectroscopy (PICLS) H-atom Measurements

Photoionization Loss-Controlled Spectroscopy (PICLS) H-atom Measurements

Photoionization Loss-Controlled Spectroscopy (PICLS) H-atom Measurements

Stimulated Emission from Two-Photon-Excited Atomic Hydrogen

Fig. 1. Energy levels of atomic hydrogen (not to scale) relevant to 205-nm, two-photon-excited FL and SE.

Stimulated Emission from Two-Photon-Excited Atomic Hydrogen

Fig. 2. Apparatus used to observe atomic-hydrogen two-photon-excited FL and SE processes in low-pressure flames.
Stimulated Emission from Two-Photon-Excited Atomic Hydrogen


Fig. 4. Intensity dependences of two-photon-excited atomic-hydrogen SE (triangles) and FL (circles) recorded simultaneously in a lean (equivalence ratio 0.6), 72-Torr hydrogen–oxygen–argon flame. The dashed line is drawn with a slope of 2.
TPEF Schemes for Detection of Atomic Oxygen and Atomic Nitrogen


Fig. 1. States and wavelengths involved in the detection scheme. Fine state splittings are too small to show on this scale.

Fig. 2. Schematic diagram of the experiment. The wavelengths (nm) shown are those pertinent to O atoms, which are produced in the reaction NO + N → N₂ + O. Stokes beams (not shown) are also present in the Raman cell output.
Fig. 2. A schematic energy-level diagram showing the two-photon absorption and fluorescence wavelengths.

Fig. 8. The spatial distributions of scattered light intensities from CO molecules at different heights above the burner in a CH₄/air flame.
Schematic diagram of the three-state system and the two-photon absorption process for the case where the energy of state $c$ is much higher than the energy of state $b$.

TPEF Signal Levels

\[ n_b = \frac{\gamma_{ba}^2 \left( I^2 / I_{sat}^2 \right) \left[ (\omega_{cb} + \omega) n_a - (\omega_{ba} - 2\omega) n_c \right]}{(\omega_{cb} + \omega_{ba} - \omega) \left\{ \Delta_{ba}^2 + \gamma_{ba}^2 \left[ 1 + \left( I^2 / I_{sat}^2 \right) \right] \right\}} \]

\[ \Rightarrow \frac{\gamma_{ba}^2 \left( I^2 / I_{sat}^2 \right) (\omega_{cb} + \omega) n_a}{(\omega_{cb} + \omega_{ba} - \omega) \left\{ \Delta_{ba}^2 + \gamma_{ba}^2 \left[ 1 + \left( I^2 / I_{sat}^2 \right) \right] \right\}} \]

\[ I_{sat} = c \varepsilon_0 \hbar^2 \sqrt{\frac{2 \Gamma_b \gamma_{ba} (\omega_{cb} + \omega)^2}{|\vec{\mu}_{cb} \cdot \hat{e}|^2 |\vec{\mu}_{ac} \cdot \hat{e}|^2}} \]

where

\[ \omega_{ca} = \frac{(\varepsilon_c - \varepsilon_a)}{\hbar} \quad \omega_{ba} = \frac{(\varepsilon_b - \varepsilon_a)}{\hbar} \]

\[ \omega_{cb} = \frac{(\varepsilon_c - \varepsilon_b)}{\hbar} \quad \Delta_{ba} = (\omega_{ba} - 2\omega) \]

\[ \Gamma_b = \text{rate coefficient for population transfer from state } b \]
\[ \gamma_{ab} = \text{dephasing rate coefficient for state } b \]