Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 13: Laser-Induced Fluorescence: Two-Level Model

1. Introduction and background
2. Typical experimental setup
3. Signal level (steady & pulsed)
4. Two-level model
5. Detection limits (pulsed laser)
6. Characteristic times
7. Modifications to two-level model

Laser-Induced Fluorescence

Possible collisional change

Laser absorption

$\nu$ (spont. emission)
1. Introduction

- What is Laser-Induced Fluorescence (LIF)?
  - Laser-induced spontaneous emission
  - Multi-step process: absorption followed by emission (fluorescence)

Possible collisional change

2

Laser absorption (pulsed or CW laser)

\[ h\nu \text{ (spont. Emission)} \]

\[ = \text{LIF signal} \]

This is the laser-induced fluorescence

Notes

- May occur from multiple states
- Not instantaneous
1. Introduction

- Why is LIF of interest?
  - The LIF signal can be monitored at 90° to the exciting laser beam, thereby gives spatial resolution to the absorption measurement.
  - The signal rides on a dark background, rather than being based on signal differences as in absorption.
  - Species specific, and much stronger than Raman scattering.

- Signal for scanned-\( \lambda \) LIF

![Diagram of LIF setup with volume element and collection optics](image)
1. Introduction

- LIF can be used to monitor multiple gas properties including
  - $n_i (n, v, J)$ number density of species $i$ in a state described by $n$, $v$, and $J$
  - $T$ temperature (from the Boltzmann fraction)
  - $\chi_i$ species concentration
  - $P$ pressure (from line broadening)
  - $\vec{v}$ velocity (from the Doppler shift of the absorption frequency)

- And species including
  - **Radicals:** OH, C$_2$, CN, NH, …
  - **Stable diatoms:** O$_2$, NO, CO, I$_2$, …
  - **Polyatomics:** NO$_2$, NCO, CO$_2$, Acetone (CH$_3$COCH$_3$), Biacetyl ((CH$_3$CO)$_2$), Toluene (C$_7$H$_8$), and other carbonyls and aromatic compounds

- **As well as many atoms….**
## 1. Introduction

### Absorption vs. LIF

<table>
<thead>
<tr>
<th>Absorption</th>
<th>LIF</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Laser absorption" /></td>
<td><img src="image" alt="Possible collisional change" /></td>
</tr>
<tr>
<td>Instantaneous</td>
<td>NOT instantaneous</td>
</tr>
<tr>
<td>Single-step process</td>
<td>Multi-step process: absorption followed after some delay by spontaneous emission</td>
</tr>
<tr>
<td>Line-of-sight</td>
<td>Typically 90° to the excitation laser beam</td>
</tr>
<tr>
<td>Based on incident/transmitted signal difference</td>
<td>Rides on a dark background</td>
</tr>
</tbody>
</table>

- Absorption and LIF can be performed with either CW or pulsed lasers
1. Introduction

- **History & Some Key Accomplishments**
  - Flash-lamp pumped dye laser (Schafer, 1966)
  - Tunable CW dye laser (1970)
  - CW-doubled ring dye laser (1980)
  - Nd-YAG and excimer-pumped dye lasers (1980)
  - CW $\lambda$-scanned LIF (1980s)
  - Identification of ketone tracers for PLIF imaging (1991)
  - Extension of PLIF to high pressure/temperature (1993-2005)
  - PLIF with vibrational transitions (IR-PLIF) (2000)
  - Pulse-burst PLIF (2000)
  - UV- PLIF of CO$_2$ (2004)
  - High-speed PLIF (2005)
  - CW PLIF (2009)
2. Typical Experimental Setup

- Typical experimental setup for LIF systems
  - Excitation $\lambda_{ex}$
  - Volume element ($\sim 1\text{mm}^3$)
  - Experiment (e.g. flame, flow, plasma)
  - Laser
  - Collection optics
  - Pulsed laser
  - PMT with spectral filter to record emission at $\lambda_{ex}$ or at $\lambda_{det}$ ($\neq \lambda_{ex}$), or grating monochromator to disperse the spectrum

- Recording modes
  1. Emission intensity at a fixed detection wavelength
  2. Fluorescence spectrum (spectrometer)
  3. Excitation spectrum (scanned laser)
  4. Can be extended to 2-d with CCD array detector (PLIF)
  5. Can also measure temporal behavior
2. Typical Experimental Setup

- Measurement volume

Pathlength: \( L \approx 0.5 \text{ – } 5 \text{mm} \)

Solid angle of collection: \( \Omega \equiv \frac{\text{lens area}}{l^2} \)

\[ = \frac{\pi d^2 / 4}{l^2} \approx \frac{1}{(f\#)^2} \]

f # of collection: \( f\# \equiv \frac{l}{d} \)

Note:
At \( f\# = 2.5 \), \( \Omega/4\pi = 0.01 \), or 1%. Collection process is relatively inefficient, even for fast lenses.
3. Signal Level

Spontaneous emission corresponds to a decay in energy

\[ S_2^{21}[\text{# photons/sec}] = N_2 \times A_{21} \times \frac{\Omega}{4\pi} = n_2 \times V \times A_{21} \times \frac{\Omega}{4\pi} \]

- \( N_2 \) = # molecules in the measurement volume in state 2
- \( n_2 \) = number density of molecules (#/cc) in state 2
- \( V \) = volume (cc)
- \( A_{21} \) = probability/sec of emission from state 2 to state 1
- \( \Omega/4\pi \) = collection fraction

\[ S_F[\text{power collected}] = (S_2^{21}[\text{# photons/sec}])h\nu \]

- \( S_F \) = The LIF signal \( S_F^{21} \) depends on constants and \( n_2 \). Hence, the challenge of LIF is to find a way of specifying \( n_2 \) quantitatively.
3. Signal Level

- Spontaneous emission corresponds to a decay in energy

\[ n_2(t) \text{ depends on the laser and the collision process (further explained later)} \]

- Pulsed conditions

For unsteady conditions (e.g., short times or pulsed excitation):

\[ S_F^{21}[\# \text{photons}] = \left\{ \int_0^\tau n_2(t) dt \right\} \times V \times A_{21} \times \frac{\Omega}{4\pi} \]

\( n_2(t) \) depends on the laser and the collision process (further explained later)
4. Two-level Model

- Entry-level model for LIF (two levels)

\[ n_1 W_{12} \quad n_2 W_{21} \quad n_1 Q_{12} \quad n_2 Q_{21} \quad n_2 A_{21} \]

Induced Absorption  Induced Emission  Collisional Excitation  Collisional De-Excitation  Fluorescence

Energy

Energy levels:

1. \( n_1 \)
2. \( n_2 \)

Negligible "quenching" of induced emission.

Einstein theory:

\[ \text{prob/sec}^{v \to v + d\nu}_{1 \to 2} = B_{12}^{\rho} \rho(v) \phi(v) d\nu \]

\[ \rho(v) = I_v / c \]

\[ \int \phi(v) d\nu = 1 \]

Let \( B_{12} = B_{12}^{\rho} / c \)
4. Two-level Model

Entry-level model for LIF (two levels)

- Induced Absorption
- Induced Emission
- Collisional Excitation
- Collisional De-Excitation
- Fluorescence

Most pulsed lasers are spectrally broad compared with absorption lines ⇒ \( I_\nu \approx \text{constant over abs. line} \)

\[
\text{Rate}_{1\rightarrow 2} = n_1 \int_{\text{line}} B_{12} I_\nu \phi(\nu) d\nu = n_1 B_{12} I_\nu = n_1 W_{12}
\]

Rate (s\(^{-1}\)) that individual molecules in state 1 undergo the transition to state 2

Rate analysis

\[
\dot{n}_2 = n_1 (I_\nu B_{12}) - n_2 (I_\nu B_{21} + Q_{21} + A_{21}) \quad \text{S.S.} \quad n_2 \approx 0
\]

\[
\frac{n_2}{n_1} = \frac{W_{12}}{W_{21} + Q_{21} + A_{21}}
\]

So now we have a solution for \( n_2 \)!
4. Two-level Model

- Entry level model for LIF (two levels)

\[
(n_2)_{SS} = n_1 \frac{W_{12}}{W_{21} + Q_{21} + A_{21}}
\]

Two limits emerge from the steady-state analysis for \(n_2\):

- Weak excitation ("linear LIF")
- Strong excitation ("saturated LIF")

**Weak excitation limit:**

Induced emission from level 2 much weaker than the sum of collisional and spontaneous decay processes

\[
W_{21} = B_{21}I_v \ll A_{21} + Q_{21}
\]

Then \(n_2 \ll n_1\), and \(n_1 \approx n_1^0\) (usually \(n_1^0 \approx n^0\) where \(n^0\) is the conserved total number density, \(n^0 = n_1 + n_2\))
4. Two-level Model

Weak excitation limit

Fluorescence signal in weak excitation limit

\[ S_F = n_2 \times V \times A_{21} \times \frac{\Omega}{4\pi} \quad \text{(photons/s)} \]

\[ = \left( n_1^0 V \right) W_{12} = B_{12} I_\nu \left( \frac{A_{21}}{A_{21} + Q_{21}} \right) \left( \frac{\Omega}{4\pi} \right) \]

Notes:

1. To find \( n_1^0 \), need to know \( Q_{21} \) (rate of the electronic quenching, a collisional process), \( A_{21}, I_\nu, \nu \) and \( \Omega \)

2. \( S_F \propto n_1^0 = n_i f_{v,J}(T) \)
   LIF is directly proportional to the population density in the lower quantum level ➤ LIF is typically viewed as a species diagnostic

3. Alternative view:

   \[ \text{# of absorptions/sec} = \left( \text{# molec in 1} \right) \left( \text{prob/s of abs} \right) = \left( n_1^0 V \right) B_{12} I_\nu \]
4. Two-level Model

Consider the saturation limit

Induced emission rate $\gg$ collisional and spontaneous emission rates

$$W_{21} \gg A_{21} + Q_{21}$$

$$n_2 = n_1 \frac{W_{12}}{W_{21}} = n_1 \frac{B_{12}}{B_{21}} = n_1 \frac{g_2}{g_1}$$

Notes:

1. If $g_2 = g_1$, then $n_2 = n_1$, when the transition is “saturated”

2. $n_1^0 = \text{total} = n_1 + n_2 \Rightarrow n_2 = \frac{n_1^0}{1 + g_1 / g_2} = \frac{n_1^0}{2}$ when $g_2 = g_1$

Fluorescence signal in saturation limit

$$S_F = n_1^0 \left( \frac{g_2}{g_1 + g_2} \right) \times V \times A_{21} \times \frac{\Omega}{4\pi} \quad \text{(photons/s)}$$

Virtue: does not depend on $Q_{21}$, laser intensity

Complication: may be difficult to reach the saturation limit in all parts of the laser beam

*If intensity not sufficiently high, may reach intermediate situation between weak excitation and saturation*
4. Two-level Model

- Intermediate result

\[
(n_2)_{SS} = n_1 \frac{W_{12}}{W_{21} + Q_{21} + A_{21}}
\]

with \( n_1 + n_2 = n_1^0 \)

\[
1 + B_{12} + B_{21} \left\{ \frac{Q_{21} + A_{21}}{(B_{12} + B_{21})I_v} \right\}^{-1}
\]

\[
\frac{S_F}{S_{F,sat}} = \frac{n_2}{n_{2,sat}} = \frac{1}{1 + \frac{Q_{21} + A_{21}}{(B_{12} + B_{21})I_v}}
\]

at small \((B_{12} + B_{21})I_v\),

\[
\frac{S_F}{S_{F,sat}} = \frac{(B_{12} + B_{21})I_v}{(Q_{21} + A_{21})}
\]
4. Two-level Model

Typical values for A and Q in electronic transitions

1. \( A_{21} \approx 10^5 \sim 10^8 \text{ s}^{-1} \) (\( 10^6 \text{ s}^{-1} \) for NO, OH; \( 10^8 \text{ s}^{-1} \) for Na)

2. \( Q_{21} \approx Z(\text{collision frequency}) \)
   \[ = n \times \pi \sigma^2 \times \left( \bar{c} = \sqrt{8kT / \pi \mu} \right) \]
   \[ \propto \sigma^2 P / \sqrt{T} \]
   \[ Q_{21} \approx 10^9 - 10^{10} \text{ s}^{-1} \text{ at STP} \]

   \[ \text{Note: } \left( A_{21} / Q_{21} \right)_{P=\text{atm,comb.T}} \]
   \[ \approx 10^6 \text{ s}^{-1} / 10^{10} \text{ s}^{-1} \]
   \[ \approx 10^{-4} \]
   \[ \Rightarrow \text{A small number!} \]

3. Fluorescence yield = \( A_{21} / (A_{21} + Q_{21}) \ll 1 \) except at low P
   \[ \Rightarrow \text{LIF is an inefficient process!} \]

4. Spontaneous emission for IR is much weaker (smaller \( A_{21} \)) than UV
   \[ \Rightarrow \text{LIF is weaker in the IR, unless } Q_{21} \text{ is small (as may be the case!)} \]

   \[ A_{21,\text{IR}} / A_{21,\text{UV}} \ll 1 \]
   \[ Q_{21,\text{IR}} / Q_{21,\text{UV}} = ? \]
4. Two-level Model

- Typical values for A and Q in electronic transitions

5. What is $I_\nu$ for $B_{21}I_\nu >> A_{21} + Q_{21}$? Call this ($I_\nu)_\text{sat}$

   - For low $Q_{21}$, $I_\nu,\text{sat} >> A_{21}/B_{21}$
   - For high $Q_{21}$, $I_\nu,\text{sat} >> Q_{21}/B_{21}$ so that $I_\nu,\text{sat} \propto \left( P / \sqrt{T} \right) (1 / B_{21})$

   $B_{21}^\rho = A_{21} \left( \lambda^3 / 8h\pi \right) \Rightarrow B_{21} = B_{21}^I = \frac{B_{21}^\rho}{c} = A_{21} \frac{\lambda^3}{8hc\pi}$

   @ $\lambda = 500$nm, $B_{21} = 25A_{21} \text{cm}^2/\text{erg} \cdot \text{s}$

   - Assume $Q_{21} \approx 10^4A_{21}$ (e.g., $Q_{21} = 10^{10}\text{s}^{-1}$, $A_{21} = 10^6\text{s}^{-1}$)

   $I_\nu,\text{sat} >> 10^4 A_{21} / 25A_{21}$

   $$= 400 \begin{bmatrix} \text{ergs/cm}^2 = \frac{\text{erg/s}}{\text{cm}^2 \cdot \text{Hz}} \end{bmatrix}$$

   $$= 0.4 \text{ J/m}^2$$
4. Two-level Model

Typical values for A and Q in electronic transitions - continued

5. What is $I_{\nu}$ for $B_{21}I_{\nu} \gg A_{21} + Q_{21}$? Call this $(I_{\nu})_{\text{sat}}$

- But $I_{\nu} = \frac{\text{Power}}{\text{Area} \cdot \Delta \nu_{\text{laser}}}$; let $d = 1\text{mm}$, $\Delta \nu_L = 0.5\text{cm}^{-1} = 1.5 \times 10^{10}\text{s}^{-1}$

then $I_{\nu} = \frac{P(W) \cdot 10^7 \text{ergs/J}}{2 \times 10^{-2} \text{cm}^2 \left(1.5 \times 10^{10} \text{s}^{-1}\right)} = P(W) \left(0.08 \frac{\text{ergs}}{\text{cm}^2 \text{W}}\right)$

$P_{\text{sat}}[W] \gg \frac{400 \left[\text{ergs/cm}^3\right]}{0.08} = 5 \times 10^3 \text{W} = 5\text{kW}$!

- Far too high for a CW laser, but...

- Note: Nd:YAG-pumped dye lasers give 1-10mJ per 10nsec pulse at 225 or 300nm, giving $10^5$-$10^6\text{W}$!

- Therefore, it’s easy to saturate within the limits of a 2-level model! In fact, with atoms it’s easy to reach full saturation; with molecules it is not so easy get full saturation, owing particularly to population exchanges with adjacent rotational states, but saturation is feasible at $P \leq 1\text{atm}$
4. Two-level Model

- Typical values for $A$ and $Q$: Vibrational transitions (IR)

1. $A_{21} \approx 10^1 \sim 10^2 \text{ s}^{-1}$ (30 s$^{-1}$ for CO, $\Delta v = 1$) for strong IR bands

2. $Q_{21}$ is either the vibration-translation (V-T) de-excitation rate or vibrational-vibrational (V-V) transfer rate (to another species). The dominant process is usually V-V. 

   e.g., $Q_{\text{V-V}} \approx 10^5 \text{ s}^{-1}$ for CO with N$_2$ near STP

3. Therefore, the fluorescent yield is typically in the range $10^{-3} \sim 10^{-5}$. This is sufficient for IR LIF to be a useful diagnostic, providing a means of imaging many species not accessible via electronic transitions.
5. Detection Limits (Pulsed Laser)

Fluorescence signal level in the weak excitation limit

\[ S_F = \int S_F(t)dt \quad (\text{photons}) \]

\[ = n_1^0 V \times \int I_v dt \times B_{12} \frac{A_{21}}{A_{21} + Q_{21}} \frac{\Omega}{4\pi} \]

\[ n_1^0 = n X_i f_{v,J} \]

\( n = \) total number density

\( X_i = \) mole fraction

\( f_{v,J} = \) fraction of molecules initially in \( v \) and \( J \)

\[ \int I_v dt = \frac{E_p}{\Delta \nu_L \cdot A_c} = \frac{\text{laser pulse energy}}{(\text{laser linewidth})(\text{cross-sectional area of the exciting beam})} \]

\[ S_F \approx n_1^0 L \frac{E_p}{\Delta \nu_L} B_{12} \frac{A}{Q} \frac{\Omega}{4\pi} \]

assuming \( A_{21} << Q_{21} \)

Length of the measurement zone \( L = V/A_c \)
5. Detection Limits (Pulsed Laser)

- Fluorescence signal level in the weak excitation limit: Example
  - Laser pulse energy \( E_P = 10^{-5} \text{J} (10\mu\text{J}) = 10^2 \text{ ergs} \)
  - Pulse length \( \tau_L = 10^{-8} \text{ s} \)
  - Pulse linewidth \( \Delta \nu_L = 1 \text{ cm}^{-1} \)
  - Number density \( n = 5 \times 10^{18} \text{ molecules/cc} \) (at 1 atm, 1620K)
  - Boltzmann fraction \( f_{\nu,J} = 0.01 \) (1% of the species is in the absorbing state)
  - Measurement volume \( V = A_c \times L = (10^{-2} \text{ cm}^2)(10^{-1} \text{cm}) = 0.001 \text{ cc} \)
  - Collection angle \( \Omega/4\pi = 10^{-3} \) (for optics with \( f \# = 8 \))
  - Einstein coefficients \( A/Q \approx 10^{-4}, B_{12} \approx 20 \cdot A_{21} \text{ [cm}^2/\text{erg} \cdot \text{s}], A_{21} = 10^6 \text{ s}^{-1} \)

Using these values:

\[
S_F = \left(\frac{5 \times 10^{18} \cdot X_i \cdot 10^{-2}}{n_i^0}\right) \left(\frac{10^{-1}}{1 \cdot 10^{-1}}\right) \left(\frac{10^{-1}}{10^2}\right) \left(\frac{20 \times 10^6}{B_{12}}\right) \left(10^{-4}\right) \left(10^{-3}\right)
\]

\[
= 10^{16} \cdot X_i \cdot \frac{E_P[\text{ergs}]}{1 \text{cm}^{-1} \cdot 3 \times 10^{10} \text{ cm/s}}
\]

\[
= 3 \times 10^7 \cdot X_i
\]

\( X_i = \text{mole fraction of the absorber i} \)
5. Detection Limits (Pulsed Laser)

Fluorescence signal level in the weak excitation limit: Example

Quantum efficiency

\[ \eta = \frac{\text{# of } e^- \text{ produced}}{\text{# of photons input}} \]

Total photoelectrons produced by photons incident on a quantum detector

\[ S_F \eta \]

For ideal, shot-noise-limited detection

\[ \text{SNR} = \sqrt{S_F \eta} \]

\[ S_F = 3 \times 10^7 \cdot X_i \]

\[ \eta = 0.1 \]

\[ \text{SNR} = \sqrt{3 \times 10^6 \cdot X_i} \]

SNR = 1.7 for \( X_i = 1 \text{ ppm} \)

\( X_i = 0.3 \text{ ppm for SNR = 1} \)

Impressive for a non-intrusive measurement made in a 1 mm\(^3\) volume in 10 nsec and with only 10 \( \mu J \) of laser energy!
5. Detection Limits (Pulsed Laser)

Saturation limit

\[ S_F = n_i^0 V \frac{g_2}{g_1 + g_2} A_{21} \frac{\Omega}{4\pi} \left( \int_0^{\tau_{\text{laser}}} dt = \tau_L \right) \] [photons]

For the same typical conditions

\[ S_F = \left(5 \times 10^{18} \cdot X_i \cdot 10^{-2}\right)\left(10^{-3} \text{cc}\right)0.5 = \frac{g_2}{g_1 + g_2}\left(10^6 \text{s}^{-1}\right)\left(10^{-3}\right)\left(10^{-8} \text{s}\right) = 2.5 \times 10^8 \cdot X_i \]

\[ \eta = 0.1 \quad \text{SNR} = \sqrt{2.5 \times 10^7 \cdot X_i} \quad \text{SNR} = 5 \text{ for } X_i = 1 \text{ ppm} \]

\[ X_{i,\text{min}} = 0.04 \text{ ppm for SNR} = 1 \]

Thus, if we can saturate, the minimum detection limit \( \approx 0.04 \text{ppm}! \)

But in molecules, the dominant collisional rate (in the rate equation analysis) tends to be rotational transfer, and because this rate is typically larger than \( Q_{\text{elec}} \), saturation is difficult to achieve except at reduced pressures.
6. Characteristic Times

- Pulsed excitation

Laser pulse \( \tau_{\text{laser}} \approx 5-20\,\text{ns} \)

Recall: \( S_F(t)[\text{# photons/s}] = n_2(t) \times V \times A_{21} \times \frac{\Omega}{4\pi} \) at any time \( t \)

hence we need expressions for \( n_2 \)

- \( (n_2)_{\text{SS}} = n_1 \frac{W_{12}}{W_{21} + A_{21} + Q_{21}} \) for any \( I_\nu \)

- \( (n_2)^{\text{weak}}_{\text{SS}} = n_1^0 \frac{W_{12}}{A_{21} + Q_{21}} \)

Applicable to pulsed experiments IF there is time to reach steady-state, i.e., \( \tau_{\text{SS}} < \tau_{\text{Laser}} \)
6. Characteristic Times

- Pulsed excitation: what is $\tau_{SS}$

\[
(n_2)_{SS} = n_1 \frac{W_{12}}{W_{21} + A_{21} + Q_{21}} = n_1^0 \frac{W_{12}}{W_{12} + W_{21} + A_{21} + Q_{21}}
\]

\[
(n_2)_{SS}^{\text{weak}} = n_1^0 \frac{W_{12}}{A_{21} + Q_{21}}
\]

Consider idealized step changes in $I_v$.

Define $\tau_{SS}$ (characteristic time to reach steady-state)

\[
\tau_{SS} = \frac{(n_2)_{SS}}{(n_2)_{\text{initial}}}
\]

\[
\tau_{SS} = \frac{1}{W_{12} + W_{21} + A_{21} + Q_{21}}
\]

\[
\tau_{\text{decay}} = \frac{1}{A_{21} + Q_{21}}
\]
6. Characteristic Times

Two cases:

**Weak Excitation**

$W_{12} \ll Q_{21}, A_{21} \ll Q_{21} \Rightarrow \tau_{SS} \approx 1/Q_{21}$

E.g., $Q_{21} \approx 10^9 - 10^{10} \text{ s}^{-1}$, $\tau_{SS} \approx 0.1 - 1\text{ ns}$

SS relation applies at virtually all values of time in the laser pulse for pulses $\sim 10\text{ ns}$ and longer

**Strong Excitation**

$W_{12} \gg Q_{21} \gg A_{21}$

$\Rightarrow \tau_{SS} \approx 1/(W_{12} + W_{21}) \ll 1/Q_{21}$

For typical $Q_{21}$, $\tau_{SS} \ll 10^{-9}\text{ s}$, SS approximation is good on most time scales of interest for strong excitation (except, perhaps, for ultrafast lasers)
7. Modifications of the Two-level Model

Recall: Entry level two-level model

\[ \frac{(n_2)_{SS}}{n_1} = \frac{W_{12}}{W_{21} + Q_{21} + A_{21}} \]

Weak excitation limit
\[ S_F = n_1^0 \left( \frac{g_2}{g_1 + g_2} \right) \times V \times A_{21} \times \frac{\Omega}{4\pi} \]

Saturation limit
\[ \text{(photons/sec)} \]
7. Modifications of the Two-level Model: Two Issues

- Hole-burning effects
  - Inhomogeneous (velocity) broadening
  - “Hole” burning (saturation due to depletion of a certain velocity class) can occur with intense, spectrally narrow lasers

- Multi-level effects
  - Upper and lower levels are really manifold states

Let’s consider multi-level effect
7. Modifications of the Two-level Model

- Multi-level effects
  - Upper and lower levels are really manifold states

LIF signal and fluorescence quantum yield depend on collisional transfer rates among upper levels and the number of these monitored by the detection system.

- Two limits: narrowband detection and broadband detection

  - Narrowband detection: emission is collected only from \( v', J' \)

\[
\dot{n}_2 = n_1 B_{12} I_v - n_2 \left( B_{21} I_v + A_{21} + Q_{\text{elec}} + Q_{\text{rot}} + Q_{\text{vib}} \right)
\]

Weak excitation

\[
(n_2)_{SS} = n_1 \frac{B_{12} I_v}{A_{21} + \sum Q} \quad \Rightarrow \quad S_F = n_1 I_v B_{12} \left( \frac{A_{21}}{A_{21} + \sum Q} \right) \frac{\Omega}{4\pi}
\]

The effective loss or “quenching” rate includes \( Q_{\text{rot}}, Q_{\text{vib}}, Q_{\text{elec}} \) (i.e., all processes removing molecules from the upper state observed by fluorescent emission)
7. Modifications of the Two-level Model

- Multi-level effects
  Upper and lower levels are really manifold states

LIF signal and fluorescence quantum yield depend on collisional transfer rates among upper levels and the number of these monitored by the detection system.

- Two limits: narrowband detection and broadband detection

- **Broadband detection**: from \( v' \) and all \( J' \); i.e., the "2" state includes all rotational levels in \( v' \) (could also include collection from all \( v' \) & \( J' \))

  In weak excitation limit

  \[
  (n_2)_{SS} = n_1 \frac{B_{12} I_v}{A_{21} + \Sigma Q} \\
  S_F = n_1 \cdot V^0 \cdot I_v B_{12} \cdot \frac{A_{21}}{A_{21} + \Sigma Q} \cdot \frac{\Omega}{4\pi}
  \]

  Includes only \( Q_{\text{elec}} \), i.e., those collisions that preclude emission in collection bandwidth
7. Modifications of the Two-level Model

- Multi-level effects
  - Upper and lower levels are really manifold states

- Conclusion: collection bandwidth defines “2”!

LIF signal and fluorescence quantum yield depend on collisional transfer rates among upper levels and the number of these monitored by the detection system.

- Two limits: narrowband detection and broadband detection

\[ S_F = n_1 \cdot V^0 \cdot I_v B_{12} \cdot \frac{A_{21}}{A_{21} + Q_{eff}} \cdot \frac{\Omega}{4\pi} \]

- Effective average of emitting states “2”
- Effective transfer rate from states “2” defined by the collection wavelength region
7. Modifications of the Two-level Model: Example Multi-Level Effects (OH)

- Fluorescence spectrum of OH LIF in a 30-torr flame at two different time delays relative to the beginning of the laser (Lucht et al., 1986)

The $P_1(5)$ line of the OH $\chi^2\Pi - A^2\Sigma^+(0,0)$ band was directly excited by the laser. The fluorescence lines labeled $P_{12}(5)$, $P_1(5)$, $Q_1(4)$, $Q_{12}(4)$, $R_1(3)$ all have the same upper level (Dicke and Crosswhite, 1962)

- Note the evolution of fluorescence spectrum at different delays

![Fluorescence spectra for different delays](image)
7. Modifications of the Two-level Model

Simple Models

- Fluorescence yield: multi-level models

- “Narrowband collection” (single line)

Fluorescence yield (FY)

= fraction of absorbed photons emitted into the collection bandwidth, e.g., to capture $A_P$

\[
FY = \frac{\text{probability or rate of desired process}}{\text{sum rate of all removal processes}}
\]

\[
FY = \frac{A_P}{(A_P + A_Q + A_R) + Q_{\text{rot}} + Q_{\text{el}}} \approx \frac{A_P}{Q_{\text{rot}}} \quad (\text{usually})
\]

$Q_{\text{rot}}$ is usually $> Q_{\text{el}} >> A_P, A_Q, A_R$

But signal is weak!
7. Modifications of the Two-level Model

Fluorescence yield: multi-level models

A<sub>P</sub>, A<sub>Q</sub>, and A<sub>R</sub> = A-coefficients (in s<sup>-1</sup>) for P, Q, R branch emission from v', J' of an atom or molecule

Q<sub>el</sub> = electronic quench rate [s<sup>-1</sup>]
Q<sub>rot</sub> = rotational transfer rate [s<sup>-1</sup>]

Assume these rates are the same for all J'

“Broadband collection”; i.e., from P, Q & R of all J' in v'

Consider a sequence of time steps, each with 1 of 3 outcomes: A, Q<sub>el</sub>, or Q<sub>rot</sub>, and let A = A<sub>P</sub>+A<sub>Q</sub>+A<sub>R</sub>

Absorption

\[
\alpha = \frac{A}{A + Q_{rot} + Q_{el}}
\]

\[
\beta = \frac{Q_{rot}}{A + Q_{rot} + Q_{el}}
\]

Success rate for remaining in v'

\[\text{FY} = \sum_{n=0}^{\infty} \beta^n = \frac{\alpha}{1 - \beta} = \frac{A}{A + Q_{el}}\]

Note: Stimulated emission not included ⇒ “weak excitation” limit or linear LIF regime

Conclusion: (1) Strong signals; (2) FY is the same as 2 level model!
7. Modifications of the Two-level Model: A way to avoid $Q_{\text{coll}}$

Two ways: (1) Internal conversion (same multiplicity)
(2) Intersystem crossing (change multiplicity)

Here (1) leading to predissociation

- **New decay path**: $Q_{\text{pre}}$
  
  where $Q_{\text{pre}} >> Q_{\text{rot}} > Q_{\text{vib}}$

  E.g., for $O_2$, $Q_{\text{pre}} \approx 10^{11} - 10^{12}$ s$^{-1}$

  ➞ recover two-level result, with $Q_{\text{eff}} = Q_{\text{pre}}$

- **Advantage**: $Q_{\text{pre}}$ is independent of composition, pressure and temperature, so the fluorescence yield is more readily quantified

- **Disadvantage**: $A/Q_{\text{pre}}$ may be small! (i.e., low fluorescence yield)

- **Rate analysis**

  $\dot{n}_2 = n_1 B_{12} I_{\nu} - n_2 \left( B_{21} I_{\nu} + A_{21} + Q_{\text{elec}} + Q_{\text{rot}} + Q_{\text{vib}} + Q_{\text{pre}} \right)$

  $\left( n_2 \right)_{SS} = \frac{n_1 W_{12}}{Q_{\text{pre}}}$
Next Lecture – LIF/PLIF of Small Molecules

- LIF is spatially-resolved with signal from a point or a line
- Excite LIF with the laser expanded into a narrow sheet and collect the fluorescence with a camera:
  Planar Laser-Induced Fluorescence or PLIF

- Applications of PLIF to small (diatomic) radicals (e.g., OH & NO)