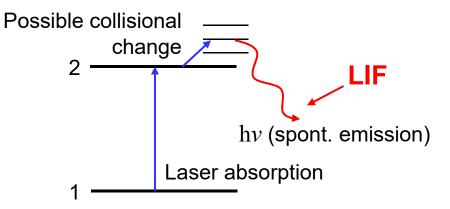# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 13: Laser-Induced Fluorescence: Two-Level Model
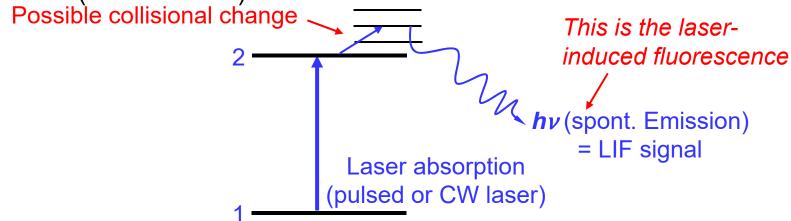
1. Introduction and background

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

*L*aser-*I*nduced *F*luorescence

1. Introduction

- What is *L*aser-*I*nduced *F*luorescence (LIF)?
  - Laser-induced <u>spontaneous emission</u>
  - Multi-step process: absorption followed by emission (fluorescence)
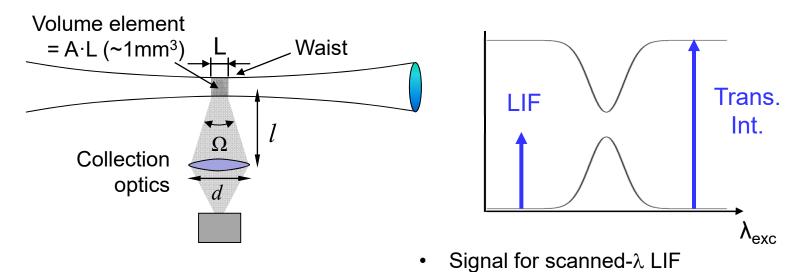
Possible collisional change

This is the laser-induced fluorescence

2

$h\nu$ (spont. Emission)
= LIF signal

Laser absorption
(pulsed or CW laser)

1

- Notes
  - May occur from multiple states
  - Not instantaneous

2

1. Introduction

- Why is LIF of interest?

  - The LIF signal can be monitored at 90° to the exciting laser beam, thereby <u>gives spatial resolution to the absorption measurement</u>

  - The <u>signal rides on a dark background</u>, rather than being based on signal differences as in absorption

  - <u>Species specific</u>, and much <u>stronger</u> than Raman scattering

Volume element = A·L (~1mm³) L Waist

l

Ω

Collection optics

d

LIF

Trans. Int.

λ_{exc}

- Signal for scanned-λ LIF

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)
    - X_i species concentration
    - P pressure (from line broadening)
    - $\vec{v}$ velocity (from the Doppler shift of the absorption frequency)

- And species including
    - <u>Radicals</u>:   OH, C_2, CN, CH, NH, …
    - <u>Stable diatoms</u>: O_2, NO, CO, I_2, …
    - <u>Polyatomics</u>: NO_2, NCO, CO_2, Acetone (CH_3COCH_3), Biacetyl (($CH_3CO)_2$), Toluene (C_7H_8), and other carbonyls and aromatic compounds
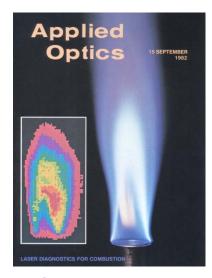
    - ***As well as many atoms….***

1. Introduction

Absorption	LIF
Instantaneous Single-step process	**NOT** instantaneous Multi-step process: absorption followed after some delay by spontaneous emission
Line-of-sight	Typically 90° to the excitation laser beam
Based on incident/transmitted signal difference	Rides on a dark background

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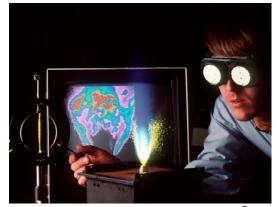
1. Introduction

- 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 λ-scanned LIF (1980s)
    - First PLIF imaging in laminar combustion (1982), turbulent (1984)
    - Single-laser-pulse PLIF imaging of NO, T, and velocity (1989)
    - Identification of ketone tracers for PLIF imaging (1991)
    - M>1 Combustion: NO, T imaging (1993), OH imaging (1996)
    - 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)
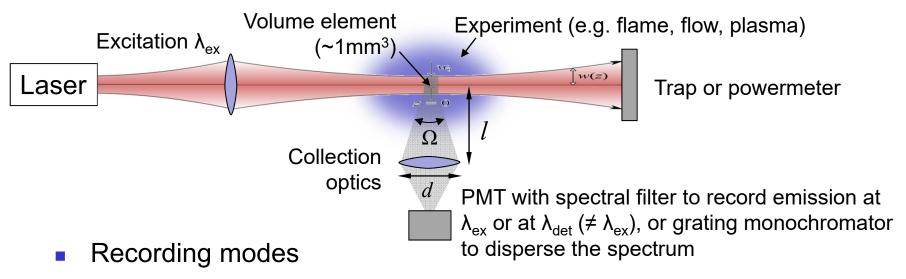   - High-speed PLIF (2005)
    - CW PLIF (2009)

OH PLIF in
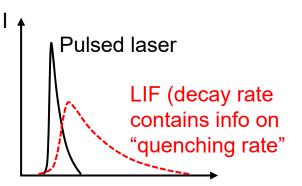laminar flame

OH PLIF in
spray flame

2. Typical Experimental Setup

- Typical experimental setup for LIF systems

Excitation λ_{ex}
Volume element (~1mm³)
Experiment (e.g. flame, flow, plasma)
Laser
Trap or powermeter
$w(z)$
Ω
l
Collection optics
d
PMT with spectral filter to record emission at λ_{ex} or at λ_{det} ($\neq \lambda_{ex}$), or grating monochromator to disperse the spectrum

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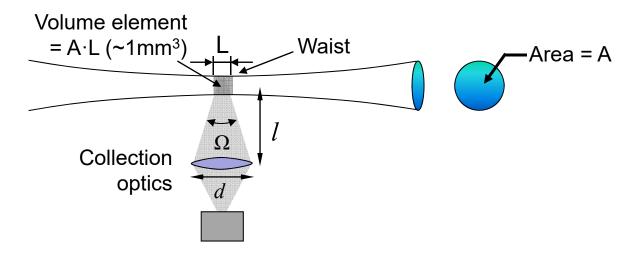 1. Emission intensity at a fixed detection wavelength
  2. Fluorescence spectrum (spectrometer)
  3. Excitation spectrum (scanned laser)
  4. Can be extended to 2-d with CCD array detector (PLIF)
  5. Can also measure temporal behavior

I
Pulsed laser
LIF (decay rate contains info on "quenching rate")

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2. Typical Experimental Setup

- Measurement volume

Volume element = A·L (~1mm³) L Waist Area = A

Ω

l

Collection optics

d

- Pathlength: $L \approx 0.5 - 5mm$

- Solid angle of collection: $\Omega \equiv \dfrac{\text{lens area}}{l^2}$

$$= \frac{\pi d^2 / 4}{l^2} \approx \frac{1}{\left(f\#\right)^2}$$

- f # of collection: $f\# \equiv \dfrac{l}{d}$

✏ 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

2 ——————————————

Spontaneous
Emission

A_{21}

1 ——————————————

- Steady conditions

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

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
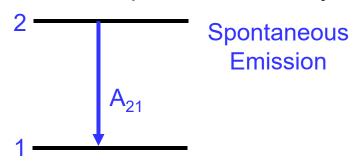
$\Omega/4\pi$ = collection fraction

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

- ∴ The LIF signal S_F^{21} depends on <u>constants</u> and n_2. Hence, the challenge of LIF is to find a way of specifying n_2 quantitatively

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3. Signal Level

- Spontaneous emission corresponds to a decay in energy

2 ——————

Spontaneous
Emission

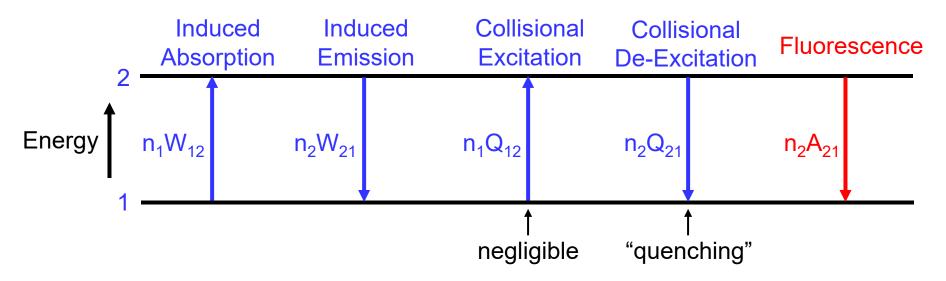A_{21}

1 ——————

- Pulsed conditions

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

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

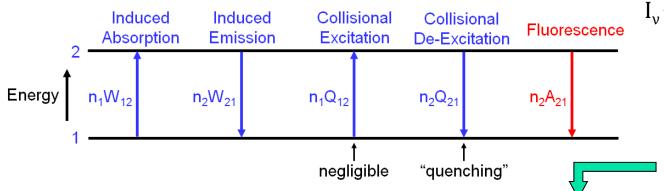$n_2(t)$ depends on the laser and the collision process (further explained later)

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4. Two-level Model

- Entry-level model for LIF (two levels)

$$\text{Einstein theory} \Rightarrow \text{prob/sec}_{1\to 2}^{v \to v+dv} = \overbrace{B_{12}^{\rho}\rho(v)}^{B_{12}I_v}\phi(v)dv = W_{12}(v \to v+dv), \text{ s}^{-1}$$

$$\rho(v) = I_v / c \qquad \int \phi(v)dv = 1$$

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
$n_1 W_{12}$	$n_2 W_{21}$	$n_1 Q_{12}$	$n_2 Q_{21}$	$n_2 A_{21}$

Energy (axis, levels 2 and 1)

negligible   "quenching"

I_ν — Laser (~0.5cm^{-1} FWHM) for typical pulses

ν_0 ν

Absorption line (~0.1cm^{-1} at STP)

Most pulsed lasers are spectrally broad compared with absorption lines ➡ $I_\nu \approx$ constant over abs. line

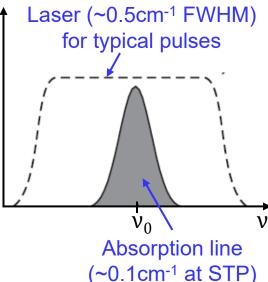$$\text{Rate}_{1\rightarrow 2} = n_1 \int_{\text{line}} B_{12} I_\nu \phi(\nu)\, d\nu = n_1 B_{12} I_\nu = n_1 W_{12}$$

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

Probability per second of absorption per unit spectral intensity: $B_{12} = B_{12}^\rho / c$

Rate analysis ➡
$$\dot{n}_2 = n_1(I_\nu B_{12}) - n_2(I_\nu B_{21} + Q_{21} + A_{21})$$
$$= n_1 W_{12} - n_2(W_{21} + Q_{21} + A_{21})$$

S.S. $\dot{n}_2 \approx 0$

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

So now we have a solution for n_2!

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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

$$W_{21} = B_{21}I_v << A_{21} + Q_{21}$$

$$g_1 B_{12} = g_2 B_{21}$$
$$g_1 W_{12} = g_2 W_{21}$$

Then $n_2 << n_1$, and $n_1 \approx n_1^0$ (usually $n_1^0 \approx n^0$ where n^0 is the conserved total number density, $n^0 = n_1 + n_2$)

$$n_2 = n_1^0 \frac{W_{12}}{A_{21} + Q_{21}}$$

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4. Two-level Model

- Weak excitation limit

Fluorescence signal in weak excitation limit

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

$$= \underbrace{(n_1^0 V)(W_{12} = B_{12} I_\nu)}_{\text{photons absorbed/sec}} \underbrace{\left(\frac{A_{21}}{A_{21} + Q_{21}}\right)}_{\text{"fluor. yield"}} \underbrace{\left(\frac{\Omega}{4\pi}\right)}_{\text{fraction collected}}$$

✎ Notes:

1. To find n_1^0, need to know Q_{21} (rate of the electronic quenching, a collisional process), A_{21}, I_ν, ν and Ω

2. $S_F \propto n_1^0 = n_i f_{\nu,J}(T)$

   LIF is directly proportional to the population density in the lower quantum level ➡ LIF is typically viewed as a species diagnostic

3. Alternative view:

$$\text{\# of absorptions/sec} = (\text{\# molec in 1})(\text{prob/s of abs})$$
$$= (n_1^0 V)(B_{12} I_\nu)$$

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4. Two-level Model

- Consider the saturation limit

Induced emission rate >> collisional and spontaneous emission rates

$$W_{21} >> A_{21} + Q_{21}$$

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

- Recall:

$$g_1 B_{12} = g_2 B_{21}$$

so $g_1 W_{12} = g_2 W_{21}$

✎ Notes:

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

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

➡ Fluorescence signal in saturation limit

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

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

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4. Two-level Model
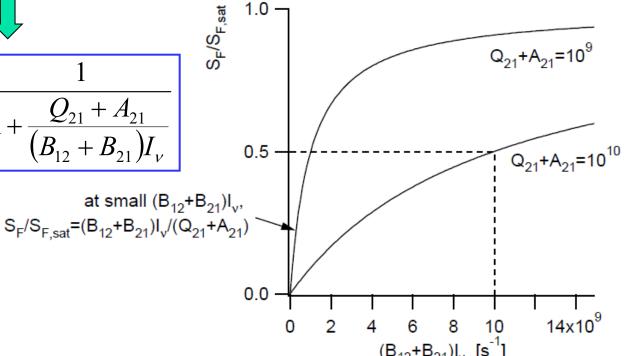
- Intermediate result

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

$$\text{with } n_1 + n_2 = n_1^0$$

$$\Rightarrow \quad n_2 = n_1^0 \frac{B_{12}}{B_{12} + B_{21}} \left\{ 1 + \frac{Q_{21} + A_{21}}{(B_{12} + B_{21})I_v} \right\}^{-1}$$

$$g_1 B_{12} = g_2 B_{21}$$

$$B_{12}/(B_{12} + B_{21}) = g_2/(g_1 + g_2)$$

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

at small $(B_{12}+B_{21})I_v$,
$S_F/S_{F,sat} = (B_{12}+B_{21})I_v/(Q_{21}+A_{21})$

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4. Two-level Model

■ Typical values for A and Q in electronic transitions

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

2. $Q_{21} \approx Z(\text{collision frequency})$

$$= n \times \pi\sigma^2 \times \left(\overline{c} = \sqrt{8kT/\pi\mu}\right)$$

$$\propto \sigma^2 P / \sqrt{T}$$

$$Q_{21} \approx 10^9 - 10^{10}\left[\text{s}^{-1}\right] \text{at STP}$$

✎Note: $\left(A_{21}/Q_{21}\right)_{P=1\text{atm,comb. T}}^{\text{OH}}$

$$\sim 10^6\,\text{s}^{-1}/10^{10}\,\text{s}^{-1}$$

$$\sim 10^{-4}$$

➡ A small number!

3. Fluorescence yield = $A_{21}/(A_{21}+Q_{21})$ << 1 except at low P

➡ LIF is an inefficient process!

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

$$A_{21,\text{IR}} / A_{21,\text{UV}} << 1$$

$$Q_{21,\text{IR}} / Q_{21,\text{UV}} = ?$$

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4. Two-level Model

- Typical values for A and Q in electronic transitions

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

     - For low Q_{21}, $I_{\nu,sat} \gg A_{21}/B_{21}$

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

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

       @ λ = 500nm, $B_{21} = 25\ [cm^2/erg]\ A_{21}\ [s^{-1}]$

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

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

       $$= 400\left[ergs/cm^2 = \dfrac{erg/s}{cm^2 \cdot Hz}\right]$$

       $$= 0.4\ [J/m^2 = W/m^2/Hz] \quad J/s/m^2/Hz = W/m^2/Hz$$

4. Two-level Model

- Typical values for A and Q in electronic transitions - continued

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

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

$$\text{then } I_\nu = \frac{P(\text{W}) \cdot 10^7 \text{ergs/J}}{(.8\times10^{-2}\,\text{cm}^2)(1.5\times10^{10}\,\text{s}^{-1})} = P(\text{W})\left(0.08\,\frac{\text{ergs}}{\text{cm}^2\,\text{W}}\right)$$

$$\Rightarrow P_{sat}[\text{W}] \gg \frac{400\left[\text{ergs/cm}^2\right]}{0.08} = 5\times10^3\,\text{W} = \underline{5\text{kW}!}$$

- 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 10^5-10^6W!

- Therefore, it's easy to saturate within the limits of a 2-level model! In fact, with <u>atoms</u> it's easy to reach full saturation; with <u>molecules</u> it is not so easy to get full saturation, owing particularly to population exchanges with adjacent rotational states, but saturation is feasible at P ≤ 1atm

4. Two-level Model

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

  1. $A_{21} \approx 10^1 \sim 10^2$ 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., $Q_{V-V} \approx 10^5$ s^{-1} for CO with N_2 near STP

  3. Therefore, the fluorescent yield is typically in the range 10^{-3} – 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

$$S_F = \int S_F(t)\,dt \quad (photons)$$

$$= n_1^0 V \times \int I_\nu\,dt \times B_{12} \frac{A_{21}}{A_{21}+Q_{21}} \frac{\Omega}{4\pi}$$

$n_1^0 = nX_i f_{v,J}$

n = total number density

X_i = mole fraction

$f_{v,J}$ = fraction of molecules initially in v and J

but $\int I_\nu\,dt = \dfrac{E_p}{\Delta\nu_L \cdot A_c} = \dfrac{\text{laser pulse energy}}{(\text{laser linewidth})(\text{cross-sectional area of the exciting beam})}$

$$\boxed{S_F \approx n_1^0 L \frac{E_p}{\Delta\nu_L} B_{12} \frac{A}{Q} \frac{\Omega}{4\pi}}$$ assuming $A_{21} \ll Q_{21}$

Length of the measurement zone L = V/A_c

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5. Detection Limits (Pulsed Laser)

- Fluorescence signal level in the weak excitation limit: Example

- Laser pulse energy $E_P = 10^{-5}J$ (10μJ) = 10^2 ergs

- Pulse length $\tau_L = 10^{-8}$ s

- Pulse linewidth $\Delta\nu_L = 1$ cm^{-1}

- Number density n = 5 x 10^{18} molecules/cc (at 1 atm, 1620K)

- Boltzmann fraction $f_{v,J} = 0.01$ (1% of the species is in the absorbing state)

- Measurement volume $V = A_c \times L = (10^{-2}$ cm$^2)(10^{-1}$cm$) = 0.001$ cc

- Collection angle $\Omega/4\pi = 10^{-3}$ (for optics with f # = 8)

- Einstein coefficients $A/Q \approx 10^{-4}$, $B_{12} \approx 20 \cdot A_{21}$ [cm^2/erg·s], $A_{21} = 10^6$ s^{-1}

Using these values:

$$S_F = \underbrace{\left(5\times10^{18} \cdot X_i \cdot 10^{-2}\right)}_{n_1^0}\left(10^{-1}\right)\left(\frac{E_P[\text{ergs}]}{\Delta v_L[\text{s}^{-1}]}\right)\underbrace{\left(20\times10^6\right)}_{B_{12}}\left(10^{-4}\right)\left(10^{-3}\right) \qquad \text{(photons)}$$

$$= 10^{16} \cdot X_i \cdot \frac{E_P[\text{ergs}]}{1\text{cm}^{-1} \cdot 3\times10^{10}\text{cm/s}}$$

X_i = mole fraction of the absorber i

$$= 3\times10^7 \cdot X_i$$

5. Detection Limits (Pulsed Laser)

- Fluorescence signal level in the weak excitation limit: Example

Quantum efficiency $\qquad \eta = \dfrac{\# \text{ of } e^- \text{ produced}}{\# \text{ of photons input}}$

Total photoelectrons produced by photons incident on a quantum detector $\qquad S_F \eta$

For ideal, shot-noise-limited detection $\qquad \text{SNR} = \sqrt{S_F \eta}$

$S_F = 3 \times 10^7 \cdot X_i$

$\eta = 0.1$

$\longrightarrow \quad \text{SNR} = \sqrt{3 \times 10^6 \cdot X_i} \quad \Longrightarrow$

SNR = 1.7 for X_i = 1 ppm

X_i = 0.3 ppm for SNR = 1

Impressive for a non-intrusive measurement made in a 1 mm^3 volume in 10 nsec and with only 10 µJ of laser energy!

5. Detection Limits (Pulsed Laser)

■ Saturation limit

$$S_F = n_1^0 V \frac{g_2}{g_1 + g_2} A_{21} \frac{\Omega}{4\pi} \left(\int_0^{\tau_{laser}} dt = \tau_L \right) \quad [\text{photons}]$$

For the same typical conditions

$$S_F = \left(5\times10^{18} \cdot X_i \cdot 10^{-2}\right)\left(10^{-3}\,\text{cc}\right)\left(0.5 = g_2 /(g_1 + g_2)\right)\left(10^6\,\text{s}^{-1}\right)\left(10^{-3}\right)\left(10^{-8}\,\text{s}\right)$$

$$= 2.5\times10^8 \cdot X_i$$

$$\eta = 0.1$$

$$\xrightarrow{} \quad \text{SNR} = \sqrt{2.5\times10^7 \cdot X_i} \quad \Longrightarrow \quad \text{SNR} = 5 \text{ for } X_i = 1 \text{ ppm}$$
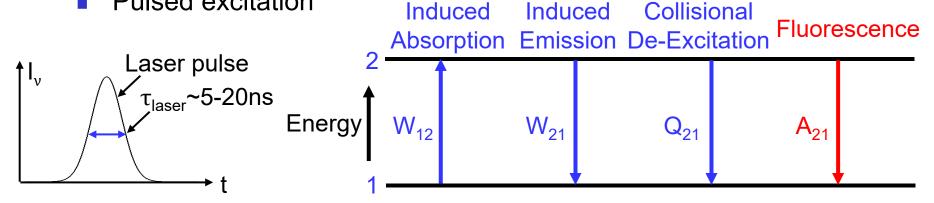
$$X_{i,min} = 0.04 \text{ ppm for SNR} = 1$$

Thus, <u>if</u> we can saturate, the minimum detection limit ≈ 0.04ppm!

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

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6. Characteristic Times

- Pulsed excitation

Laser pulse

τ_{laser}~5-20ns

I_ν

t

Energy

2

1

Induced Absorption W_{12}

Induced Emission W_{21}

Collisional De-Excitation Q_{21}

Fluorescence A_{21}

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

hence we need expressions for n_2

- $(n_2)_{SS} = n_1 \dfrac{W_{12}}{W_{21} + A_{21} + Q_{21}}$ for any I_ν

$= n_1^0 \dfrac{W_{12}}{W_{12} + W_{21} + A_{21} + Q_{21}}$

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

Applicable to pulsed experiments IF there is time to reach steady-state, i.e., $\tau_{SS} < \tau_{Laser}$

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6. Characteristic Times

- Pulsed excitation: what is τ_{SS}

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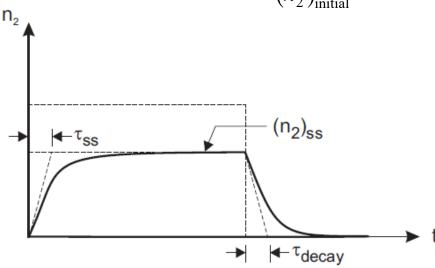
$$\left(n_2\right)_{SS}^{\text{weak}} = n_1^0 \frac{W_{12}}{A_{21} + Q_{21}}$$

Consider idealized step changes in I_ν.

Define τ_{SS} (characteristic time to reach steady-state) $\tau_{SS} = \dfrac{\left(n_2\right)_{SS}}{\left(\dot{n}_2\right)_{\text{initial}}}$

$$\Rightarrow \quad \tau_{SS} = \frac{1}{W_{12} + W_{21} + A_{21} + Q_{21}}$$
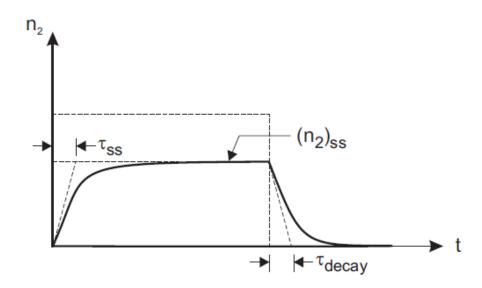
$$\tau_{\text{decay}} = \frac{1}{A_{21} + Q_{21}}$$

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6. Characteristic Times

- Two cases:

Weak Excitation

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

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

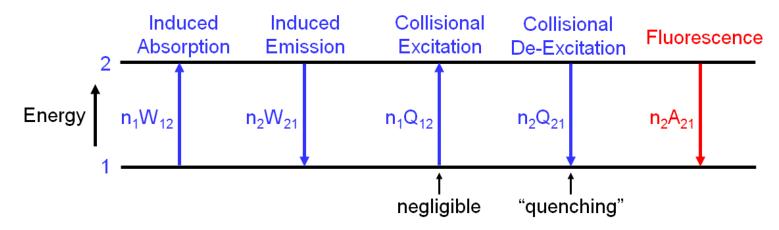SS relation applies at virtually all values of time in the laser pulse for pulses ~ 10ns and longer
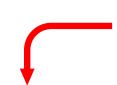
Strong Excitation

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

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

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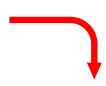
7. Modifications of the Two-level Model

- Recall: Entry level two-level model

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

Weak excitation limit

$$S_F = \underbrace{(n_1^0 V)(W_{12} = B_{12}I_\nu)}_{\text{photons absorbed/sec}} \underbrace{\left(\frac{A_{21}}{A_{21} + Q_{21}}\right)}_{\text{"fluor. yield"}} \underbrace{\left(\frac{\Omega}{4\pi}\right)}_{\text{fraction collected}}$$

$$(\text{photons/s})$$

Saturation limit

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

$$(\text{photons/s})$$

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7. Modifications of the Two-level Model: Two Issues
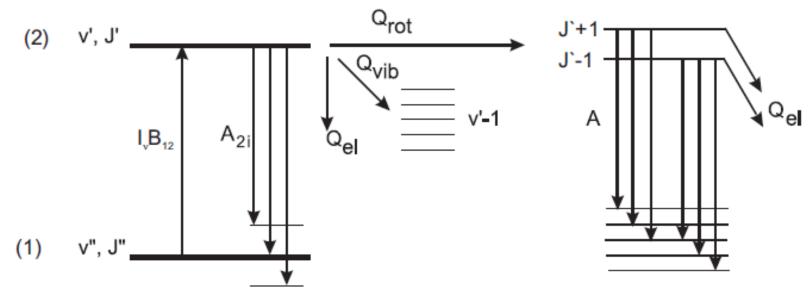
- Hole-burning effects

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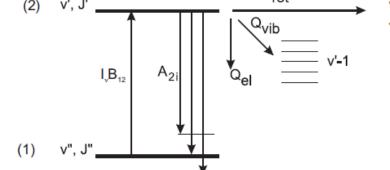
- Multi-level effects

    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.
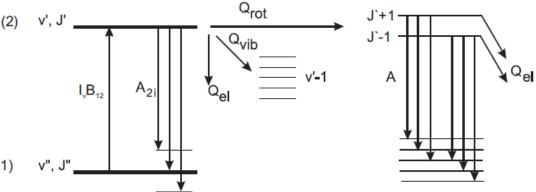
■ Two limits: <u>narrowband</u> detection and <u>broadband</u> detection

　■ <u>Narrowband detection</u>: emission is collected *only* from v', J'

┌─Sum of A_{2i} for allowed and collected transitions

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

Weak excitation ⟹ $(n_2)_{SS} = n_1 \dfrac{B_{12} I_v}{A_{21} + \underline{\Sigma Q}}$ ⟹ $S_F = n_1 \cdot V^0 \cdot I_v B_{12} \cdot \dfrac{A_{21}}{A_{21} + \Sigma Q} \cdot \dfrac{\Omega}{4\pi}$

In weak excitation limit

The effective loss or "quenching" rate includes Q_{rot}, Q_{vib}, Q_{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: <u>narrowband</u> detection and <u>broadband</u> detection

■ <u>Broadband detection</u>: 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

$$\left(n_2\right)_{SS} = n_1 \frac{B_{12}I_\nu}{A_{21} + \underline{\Sigma Q}} \qquad \Rightarrow \qquad S_F = n_1 \cdot V^0 \cdot I_\nu B_{12} \cdot \frac{A_{21}}{A_{21} + \Sigma Q} \cdot \frac{\Omega}{4\pi}$$

Includes only Q_{elec}! i.e., those collisions that preclude emission in <u>collection bandwidth</u>

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.
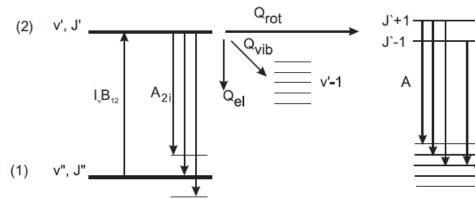
- Two limits: <u>narrowband</u> detection and <u>broadband</u> detection

  - <u>Conclusion</u>: collection bandwidth defines "2"!

$$S_F = n_1 \cdot V^0 \cdot I_v B_{12} \cdot \frac{A_{21}}{\overline{A}_{21} + Q_{eff}} \cdot \frac{\Omega}{4\pi}$$
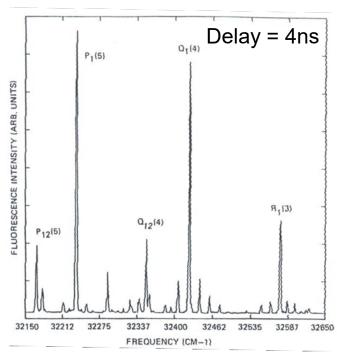
Effective average of emitting states "2"

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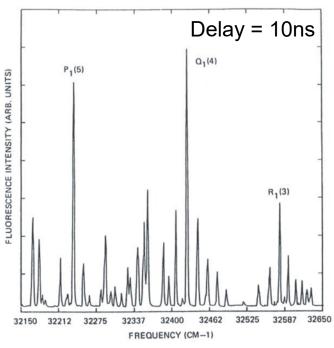
7. Modifications of the Two-level Model: Example Multi-Level Effects (OH)

■ 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 $X^2\Pi-A^2\Sigma^+(0,0)$ 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

7. Modifications of the Two-level Model
Simple Models

- Fluorescence yield: multi-level models

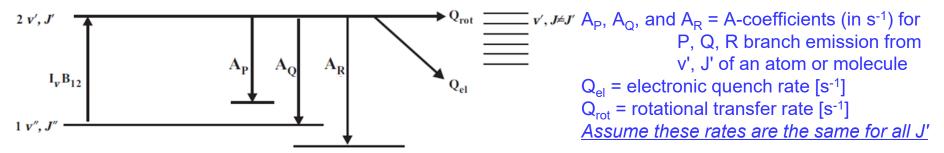A_P, A_Q, and A_R = A-coefficients (in s^{-1}) for P, Q, R branch emission from v', J' of an atom or molecule

Q_{el} = electronic quench rate [s^{-1}]
Q_{rot} = rotational transfer rate [s^{-1}]
Assume these rates are the same for all J'

- "Narrowband collection" (single line)

Fluorescence yield (FY)
= fraction of absorbed photons emitted into the collection bandwidth, e.g., to capture A_P

$$FY = \frac{\text{probability or rate of desired process}}{\text{sum rate of all removal processes}}$$
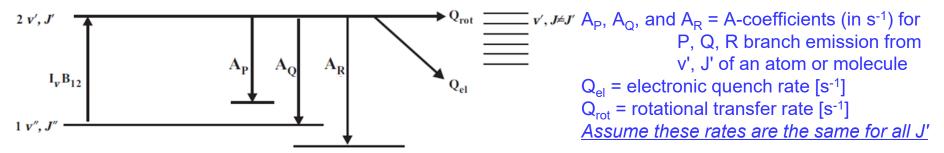
$$FY = \frac{A_P}{\left(A_P + A_Q + A_R\right) + Q_{rot} + Q_{el}} \approx \frac{A_P}{Q_{rot}}\left(\text{usually}\right)$$
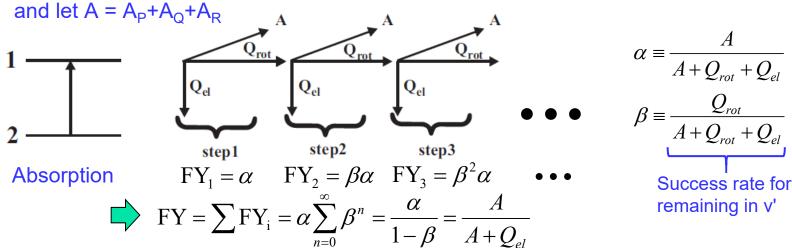
$$Q_{rot} \text{ is usually} > Q_{el} >> A_P, A_Q, A_R$$

But signal is weak!

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- Fluorescence yield: multi-level models

$2\ v', J'$

$I_v B_{12}$

$1\ v'', J''$

A_P A_Q A_R

Q_{rot}

Q_{el}

$v', J \neq J'$

A_P, A_Q, and A_R = A-coefficients (in s^{-1}) for P, Q, R branch emission from v', J' of an atom or molecule

Q_{el} = electronic quench rate [s^{-1}]

Q_{rot} = rotational transfer rate [s^{-1}]

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_{el}, or Q_{rot}, and let $A = A_P + A_Q + A_R$

1

2

A   A   A

Q_{rot} Q_{rot} Q_{rot}

Q_{el} Q_{el} Q_{el}

step1   step2   step3

Absorption

$$\alpha \equiv \frac{A}{A + Q_{rot} + Q_{el}}$$

$$\beta \equiv \frac{Q_{rot}}{A + Q_{rot} + Q_{el}}$$

Success rate for remaining in v'

$$FY_1 = \alpha \quad FY_2 = \beta\alpha \quad FY_3 = \beta^2\alpha \quad \cdots$$

$$FY = \sum FY_i = \alpha \sum_{n=0}^{\infty} \beta^n = \frac{\alpha}{1-\beta} = \frac{A}{A + Q_{el}}$$

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!

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)