ME 687  Lecture #17
Laser-Induced Fluorescence Spectroscopy: Theory II

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Outline of the Lecture

• Effects of Multi-Level Structure of Molecules and Atoms: The Three-Level Model

• Linear LIF Techniques for Concentration Measurements
LIF in a Three-Level System

Define:

\[ T_{21} = A_{21} + Q_{21} \]
\[ T_{31} = A_{31} + Q_{31} \]
\[ T_{32} = A_{32} + Q_{32} = Q_{32} \]
\[ T_{23} = A_{23} + Q_{23} \]
LIF in a Three-Level System

\[ \frac{dn_3}{dt} = 0 = n_2 T_{23} - n_3 (T_{31} + T_{32}) \quad \Rightarrow \quad \frac{n_3}{n_2} = \frac{T_{23}}{(T_{31} + T_{32})} \]

\[ \frac{dn_2}{dt} = 0 = n_1 W_{12} - n_2 (T_{23} + T_{21} + W_{21}) + n_3 T_{32} \]

\[ = n_1 W_{12} - n_2 (T_{23} + T_{21} + W_{21}) + n_2 \left( \frac{n_3}{n_2} \right) T_{32} \]

\[ = n_1 W_{12} - n_2 (T_{23} + T_{21} + W_{21}) + n_2 \frac{T_{23} T_{32}}{(T_{31} + T_{32})} \quad \Rightarrow \]

\[ \frac{n_1}{n_2} = \frac{T_{23} + T_{21} + W_{21}}{W_{12}} - \left[ \frac{T_{23} T_{32}}{(T_{31} + T_{32})} \right] \]

\[ \frac{n_1}{n_2} = \frac{T_{23} (1 - \alpha) + T_{21} + W_{21}}{W_{12}} \quad \text{where} \quad \alpha = \frac{T_{32}}{T_{31} + T_{32}} \]
LIF in a Three-Level System

\[
\frac{n_1}{n_2} + \frac{n_2}{n_2} + \frac{n_3}{n_2} = \frac{n_1^0}{n_2} = \frac{T_{23}(1-\alpha) + T_{21} + W_{21}}{W_{12}} + 1 + \frac{T_{23}}{T_{31} + T_{32}}
\]

\[
\Rightarrow \quad \frac{n_2}{n_1^0} = \frac{1}{\left[ \frac{T_{23}(1-\alpha) + T_{21} + W_{21}}{W_{12}} + 1 + \frac{T_{23}}{T_{31} + T_{32}} \right]}
\]

\[
\frac{n_3}{n_1^0} = \left( \frac{n_3}{n_2} \right) \left( \frac{n_2}{n_1^0} \right) = \frac{T_{23}}{(T_{31} + T_{32})} \frac{n_2}{n_1^0}
\]
Linear LIF in a Three-Level System

Now let's look at this solution in the limit of low laser irradiance, the linear LIF limit. In this limit $W_{12}, W_{21} \ll T_{21}, T_{23}$

$$\frac{n_2}{n_1} = \frac{W_{12}}{T_{23}(1-\alpha) + T_{21} + W_{12} + W_{21} + \frac{W_{12}T_{23}}{T_{31} + T_{32}}} = \frac{W_{12}}{T_{23}(1-\alpha) + T_{21}}$$

$$\frac{n_2 + n_3}{n_1} = \frac{n_2}{n_1} \left[1 + \frac{T_{23}}{T_{31} + T_{32}}\right] = \frac{W_{12}}{T_{23}(1-\alpha) + T_{21}} \left[\frac{T_{31} + T_{32} + T_{23}}{T_{31} + T_{32}}\right]$$

$$= \frac{W_{12}}{T_{23}\left(1 - \frac{T_{32}}{T_{31} + T_{32}}\right) + T_{21}} \left[\frac{T_{31} + T_{32} + T_{23}}{T_{31} + T_{32}}\right]$$
Linear LIF in a Three-Level System

\[
\frac{(n_2 + n_3)}{n_1^0} = \frac{W_{12} (T_{31} + T_{32} + T_{23})}{T_{23} (T_{31} + T_{32}) - T_{23} T_{32} + T_{21} (T_{31} + T_{32})}
\]

At this point our solution still looks quite messy. Let’s assume though, that the upper levels 2 and 3 have the same quenching and spontaneous emission coefficients to the ground level, i.e.,

\[T_{21} = T_{31}\]

In this case the above expression reduces immediately to

\[
\frac{(n_2 + n_3)}{n_1^0} = \frac{W_{12}}{T_{21}} = \frac{W_{12}}{T_{31}}
\]
Linear LIF in a Three-Level System

For the two-level system in the linear LIF regime we obtained

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

For the three-level system in the linear LIF regime we obtained

\[
\frac{(n_2 + n_3)}{n_1} = \frac{W_{12}}{T_{21}} = \frac{W_{12}}{T_{31}}
\]

If we assumed that \( T_{21} = T_{31} \).

In general, linear LIF for a multi-level system can be analyzed using the two-level model result provided that the (quenching + spontaneous emission) rate coefficient from each upper level is the same.
Linear LIF Techniques

• Quenching-corrected measurements – use another technique to measure major species and temperature, calculate the quenching rate coefficient from this information

• Picosecond laser excitation – use laser with pulse length much shorter than the characteristic collision time, measure quenching rate coefficient directly

• Excitation to strongly predissociating state
Time-Resolved LIF with a Picosecond Laser

Analyze a two level system for a laser pulse with length

$$\Delta t_L \ll Q_{21} + A_{21}$$

The rate equation for the system is

$$\frac{dn_2}{dt} = n_1 W_{12} - n_2 W_{21} - n_2 (Q_{21} + A_{21})$$

where the laser-induced rates are proportional to laser irradiance $I_L$. The solution for a laser turned on to a constant $I_L$ at time $t = 0$ is

$$n_2(t) = \frac{n_1^0 W_{12}}{\beta} \left(1 - e^{-\beta t}\right) , \quad \beta = W_{12} + W_{21} + Q_{21} + A_{21}$$
Time-Resolved LIF with a Picosecond Laser

For time $t << 1/\beta$,

$$e^{-\beta t} \approx 1 - \beta t \quad \Rightarrow \quad n_2(t) = \frac{n_1^0 W_{12}}{\beta} \beta t = n_1^0 W_{12} t$$
So for a laser pulse of length $\Delta t_L << Q_{21} + A_{21}$

$$n_2^{\text{init}} = n_1^0 W_{12} \Delta t_L \propto n_1^0 E_L$$

For times $t > \Delta t_L$, $W_{12} = W_{21} = 0$

$$S_f(t) \propto n_2(t) A_{21} = n_2^{\text{init}} e^{-(Q_{21} + A_{21})(t - \Delta t_L)} A_{21}$$

$$\cong n_2^{\text{init}} e^{-(Q_{21} + A_{21})t} A_{21}$$

The quantity $Q_{21} + A_{21}$ is found from the time-resolved fluorescence trace.
Time-Resolved LIF with a Picosecond Laser

The integrated fluorescence signal detected is given by

\[ \int_0^\infty S_f(t) \, dt \propto \int_0^\infty n_2(t) \, dt = - \frac{n_2^{\text{init}} \, A_{21}}{Q_{21} + A_{21}} \left[ e^{-(Q_{21} + A_{21})t} \right]_0^\infty \]

\[ = \frac{n_2^{\text{init}} \, A_{21}}{Q_{21} + A_{21}} \propto \frac{n_1^0 \, E_L \, A_{21}}{Q_{21} + A_{21}} \]

However, remember the laser and resonance line shape factors - need to be careful about picosecond excitation of the resonance. It is not simple to calculate the initial excited state population due to picosecond laser excitation.
Time-Resolved LIF with a Picosecond Laser

\[ S_f(t) \]

\[ Q_{21} + A_{21} \] from shape of decay curve

\[ \int_0^\infty S_f(t) \, dt \]
Collisionless-Decay-Dominated LIF Spectroscopy

\[
\frac{dn_2}{dt} = n_1^0 W_{12} - n_2 \left( W_{12} + W_{21} + Q_{21} + A_{21} + D_{2c} \right)
\]
Collisionless-Decay-Dominated LIF Spectroscopy

For \( n_1^0 W_{12} \Delta t_L \ll n_1^0 \), \( n_1 \approx n_1^0 \) during the laser pulse, and we obtain

\[
n_2 = \frac{n_1^0 W_{12}}{W_{12} + W_{21} + Q_{21} + A_{21} + D_{2c}}
\]

For weak laser excitation

\[
n_2 = \frac{n_1^0 W_{12}}{Q_{21} + A_{21} + D_{2c}}
\]

If predissociation is fast compared to quenching \( (D_{2c} \gg Q_{21} + A_{21}) \)

\[
n_2 = \frac{n_1^0 W_{12}}{D_{2c}} \quad \Rightarrow \quad S_f \propto \frac{n_1^0 W_{12} A_{21}}{D_{2c}}
\]