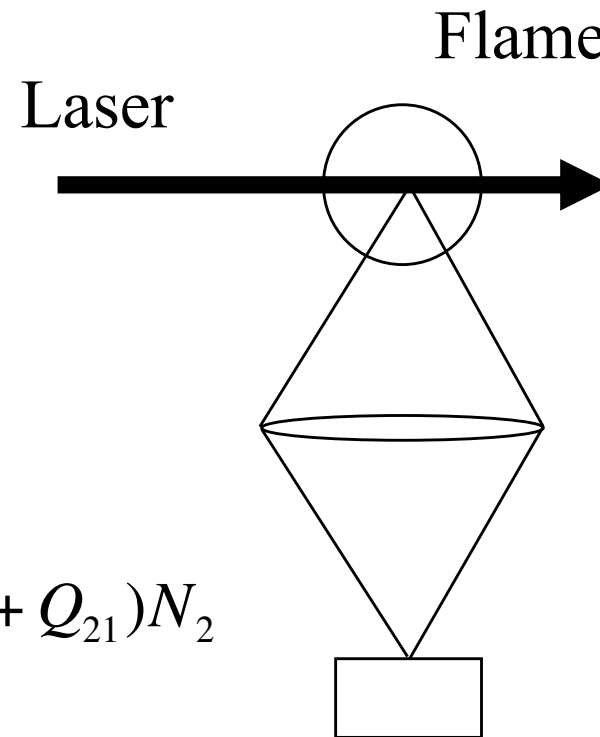
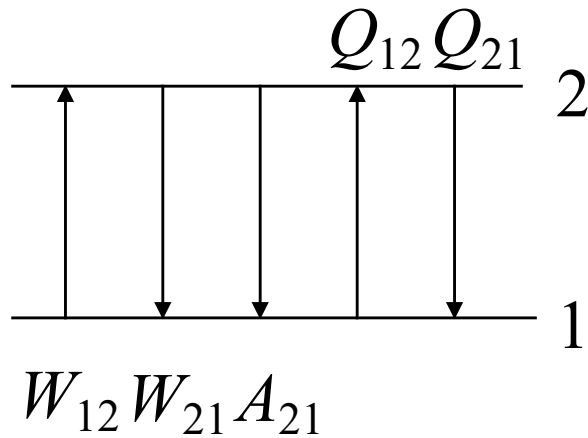


Laser Induced Fluorescence Spectroscopy

John W. Daily



The Simple Picture



$$\frac{dN_2}{dt} = (W_{12} + Q_{12})N_1 - (W_{21} + A_{21} + Q_{21})N_2$$

$$S_F = \epsilon h\nu \left(\frac{A_{21}}{4\pi} \right) \Omega_c \int_{\nu} \int_{V_c} N_2 \phi(\nu) dV_c d\nu$$

Detector

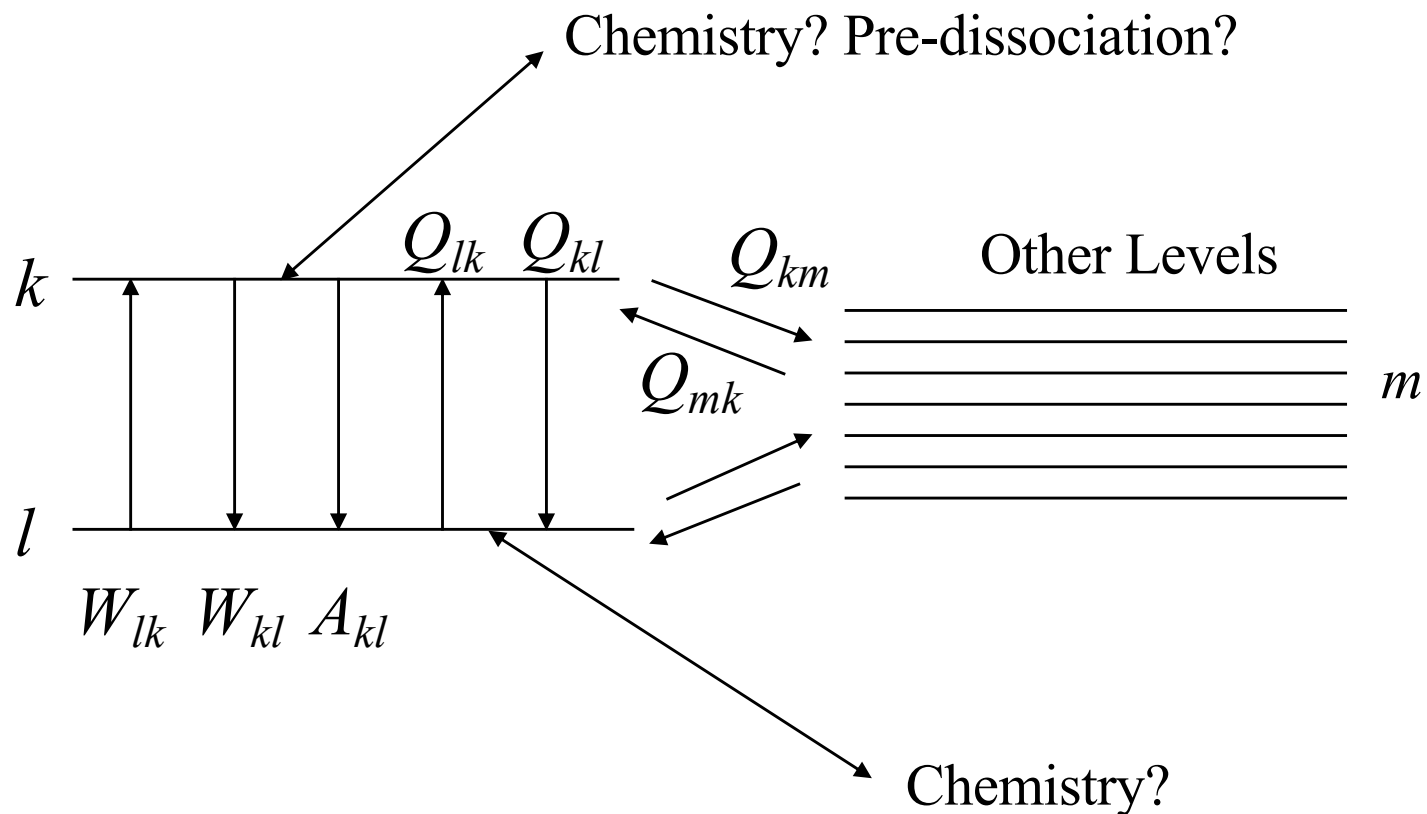
Reality

- What one measures directly is the excited state concentration, and indirectly the ground state population.
- To infer thermodynamic state properties or total concentrations requires understanding the excitation dynamics.
- Because LIF is an inherently transient process, described by a set of rate equations:

$$\begin{aligned} \frac{dN_i}{dt} = & \sum_{j \neq i, W_{ij} \neq 0} (W_{ji}N_j - W_{ij}N_i) + \sum_{j > i} A_{ji}N_j \\ & + \sum_{j \neq i} (Q_{ji}N_j - Q_{ij}N_i) \\ & + \text{Chemical Source and Sink Terms} \end{aligned}$$



- The laser only couples one transition, k - l in this diagram, but spontaneous radiation and collisions involve many other quantum states.
- Typically laser light sources involve very short pulses of light.



Linear Limit

- In the so called “linear” or “weak” limit, one can assume that the excitation laser intensity is small enough that populations are not greatly perturbed.
- In which case a simple relation between the total population and the LIF signal can be written.

$$S_F = C \frac{\alpha}{\beta} Y \frac{W_{12}}{A_{21}} N_T$$

- C is a calibration factor, α and β represent the fraction of population in the ground and excited states, respectively, that are tied up in the laser coupled states. Y is the fluorescence yield:

$$Y = \frac{A_{21}}{Q_{21} + A_{21}}$$



Basic Strategy

- Structure
 - Observe and Interpret Position of LIF Spectra
- Dynamics
 - Track Populations of Laser Excited States
- Concentration
 - Measure excited state population and relate to total population
- Temperature
 - Use Boltzmann Ratio or measure line shape if Doppler dominated.
- Pressure
 - Relate pressure to measured temperature using ideal gas law
 - If line shape dominated by collisions can recover pressure.



NO LIF

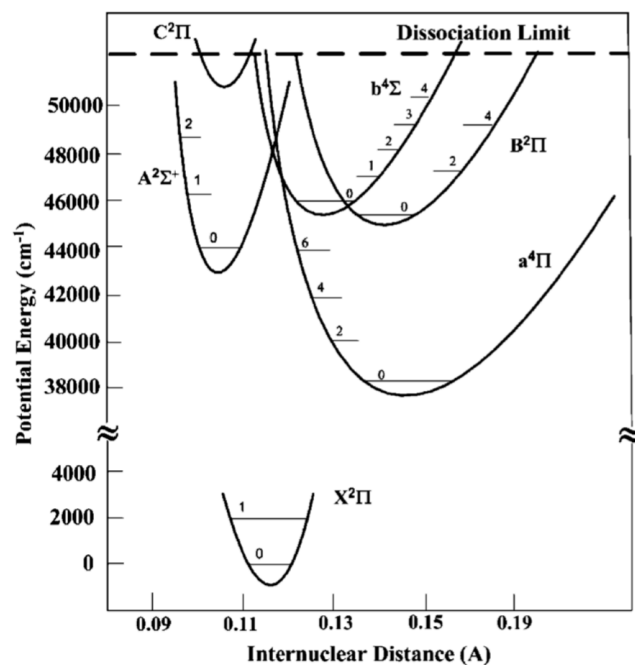


Fig. 1 NO energy level diagram.

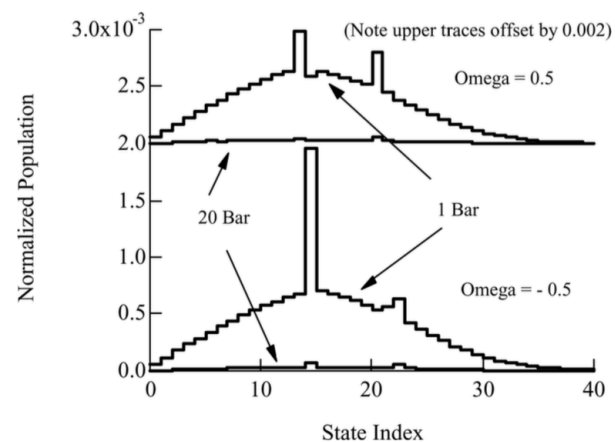


Fig. 3 A-state rotational population distribution (4 ns); EET all lost.

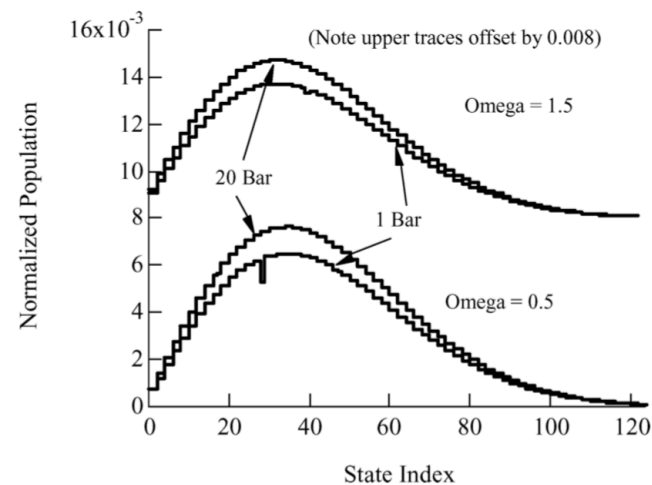


Fig. 4 X-state rotational population distribution (4 ns); EET all lost.

