Chapter 3

Molecular Detection

3.1 Laser Induced Fluorescence Detection

Potentially, background-free laser induced fluorescence (LIF) is a highly sensitive technique for detecting small numbers of molecules. In analytical chemistry and biology, resonance fluorescence is used extensively for efficient detection and identification of single molecules. The sensitivity of the fluorescence detection technique depends upon the characteristics of the decay channels of the excited states, namely that the radiative branching ratios are favorable and quenching processes are not significant. Further, for maximum detected signal, the decay photons should be collected over as large a solid angle as possible; in our experiment, intra-vacuum optics provide solid angle efficiencies of 0.5-4.5%, depending on the specific spatial location. With quantum efficiencies in the range of 10% for the cathode surfaces of modern photomultiplier tubes (PMT), one then expects a photoelectron event for every $\sim$1000 fluorescent decays. The dark current of the quantum detector is a few to a few tens of counts per second. However, various phenomena may degrade the signal-to-noise ratio. Even with careful baffling and shielding, the most severe limitation on the detection sensitivity is often the scattered excitation laser photons, which may dominate stray background light, even after careful imaging and spatial filtering.

To combat this scattered light noise, we have developed several useful techniques. The most substantial of these is a PMT whose gain can be suppressed by 10^4 in 100 ns.

The key to switching the PMT's gain is to reverse-bias several of the dynodes in the electron multiplier chain. Experimentally, we have found that for most PMTs (circular and linear geometries) reverse biasing the dynodes 1, 3, and 5 by -20 V provided the most suppression (see Fig. 3.1). Note, that because of the tube geometry linear PMTs usually exhibit a larger gain suppression. Another advantage of switching a small number of dynodes is that the capacitive load of the switches is greatly reduced, thus speeding up the attainable switching time. Typically, the gated photo-multiplier, which is normally in the suppressed gain state, is turned 'on' $\sim$100 ns after the excitation laser fires and remains on for 5 to 20 μs, depending on the molecule's fluorescence lifetime. Thus, the PMT and subsequent electronics do not 'see' the majority of the scattered excitation laser light. This is particularly advantageous in situations when the scattered light noise dominates over the LIF signal, *e.g.* imaging within the decelerator array which consist of highly polished stainless steel rods. Also, because the PMT is gated 'on' only for a few microseconds the contribution of dark counts is completely negligible. Another useful technique for suppressing scattered light has been to coat the inside of the vacuum chamber with a flat-black vacuum compatible paint, originally developed for use in satellites [2]. This paint prevents multiple reflections of the scattered light and can decrease the stray light signal as much as an order of magnitude, while still allowing vacuum pressures of 10^{-9} torr. One final useful technique, which is often over-looked in LIF detection experiments, is the use of a 'red' filter. The typical LIF experiment utilizes an optical filter whose goal is to attenuate at the excitation laser frequency as much as possible (typically OD $\geq$ 5), while transmitting as much as possible at the fluorescence wavelength (typically 50%). However, when using an ultra-violet wavelength for the excitation frequency, as is required for most molecular detection schemes, the scattered light can cause objects in its path (windows, vacuum chamber walls, etc.) to fluoresce. This fluorescence is almost always red-shifted and can usually passes through the filter used to block the excitation laser, leading to substantial noise backgrounds. By placing

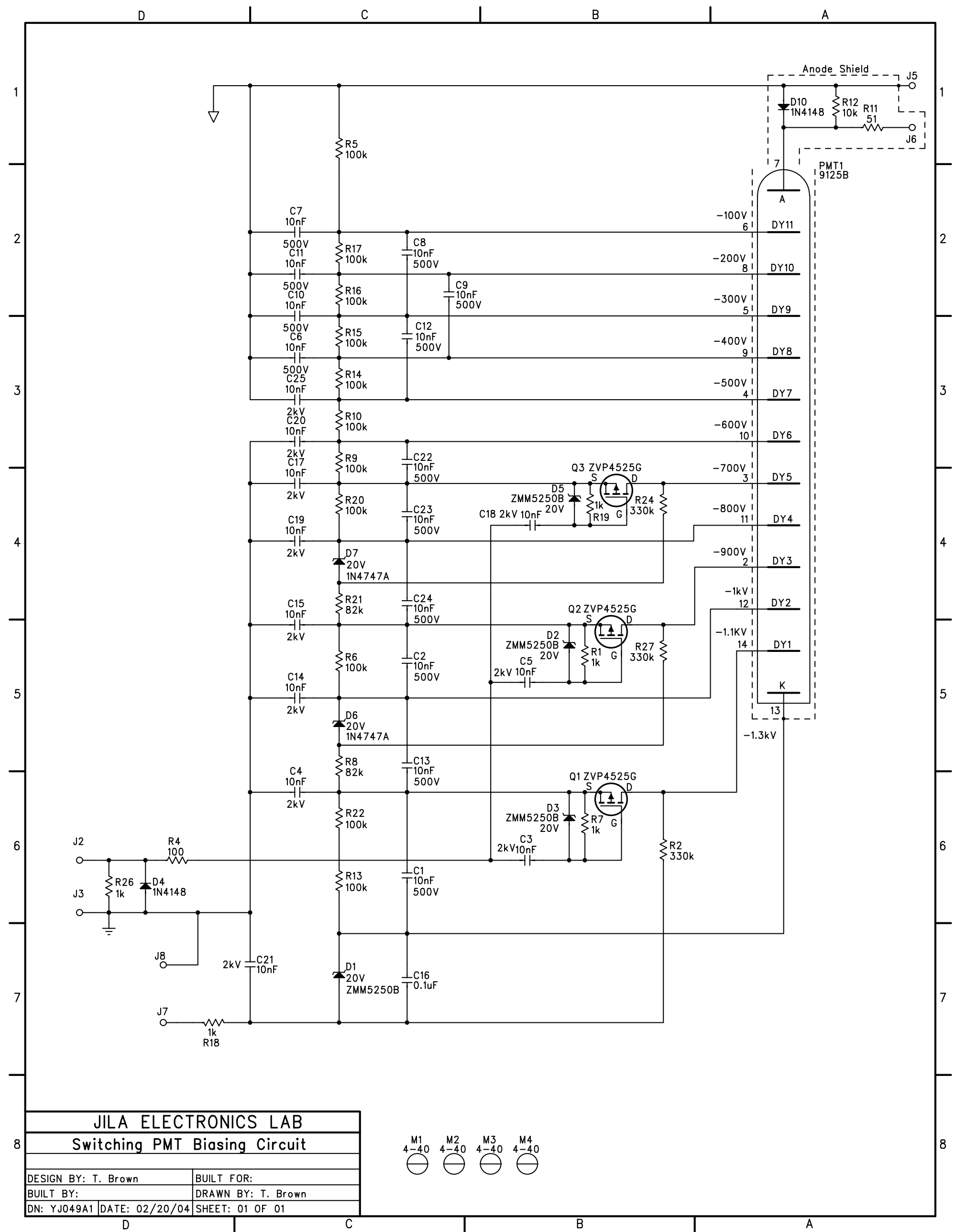

Figure 3.1: Gated photomultiplier schematic. The voltages on dynodes 1, 3, and 5 are reverse biased by -20 V shutting off the electron cascade.

a filter in the fluorescence collection path, which blocks frequencies to the red of the laser (but obviously not the fluorescence wavelength) this source of noise can be completely eliminated.

Using these three techniques, along with careful imaging and spatial filtering of the collected fluorescence, we reduce the noise signal due to scattered/stray light to a negligible level. In optimum situations, we register ∼0.03 noise photons per pulse of the excitation laser, while a typical bunching peak, containing of order 10^6 molecules, registers 10 signal photons in a single pulse.

A key benefit of utilizing fluorescence detection, besides its relative ease of implementation, is, as opposed to a spatially fixed ionization-based scheme, the ability to detect in situ molecules at multiple locations within the decelerator, greatly increasing the experimental flexibility and level of understanding. OH signals are measured within the decelerator during the actual slowing process, giving insight into the active longitudinal phase-space manipulation of the molecules by the pulsed, inhomogeneous electric fields. Specifically, in the experiment we employ LIF detection to monitor the molecules after the valve, observe the focusing effects of the hexapole on the molecules, measure the molecular packet spectra at various positions within the Stark decelerator, and finally, detect the molecules at the decelerator exit.

3.2 Hydroxyl Radical Detection

A relatively favorable branching ratio (∼70%), a large difference between the excitation and decay wavelengths, and a reasonable quantum efficiency in fluorescence detection make laser induced fluorescence (LIF) a versatile approach for detecting the hydroxyl radical. The excitation source is tuned resonant with the $A^2\Sigma^+_{1/2}$ (v = 1) $\leftarrow$ $^2\Pi_{3/2}$ (v = 0) electronic transition at 282 nm for subsequent detection of the red-shifted radiative decay around 313 nm $A^2\Sigma^+_{1/2}$ (v = 1) $\rightarrow$ $^2\Pi_{3/2}$ (v = 1). The separation in wavelength allows effective optical filtering to reduce the background scattering. The

characteristic fluorescence 750 ns decay lifetime provides a distinctive signature of the presence of OH molecules.

Using a beta barium borate (BBO) crystal to frequency-double a 564 nm dye laser output ($\sim$10 ns pulse duration) creates the ultraviolet excitation light at 282 nm with high peak intensity. The excitation laser is counter-propagated to the molecular pulse traveling down the central axis of the Stark decelerator. The relatively spectrally broad light source ($\sim$2 GHz) encompasses any Doppler-induced frequency shifts in the OH resonance as the molecular longitudinal velocity changes during the deceleration process. As aforementioned, reduction of the laser scatter is paramount for optimized signal collection. First, due to the separation of the excitation and fluorescence wavelengths, the carefully selected photomultiplier tube (PMT) has a photocathode responsivity that is severely reduced at the laser wavelength versus the fluorescence wavelength. Next, an interference filter selectively inhibits the laser light (10^5 suppression) versus the fluorescent photons (70% transmission). We also utilize a switched PMT whose dynode voltages are quickly arranged during the laser pulse so as to actively repel photoelectrons liberated by the scattered UV light on the cathode material.

The OH molecular signal is measured as a function of time at a particular spatial location in the following manner. First, immediately prior to the measurement ($\sim$1 μs), all high voltage electrodes within the vacuum chamber are grounded to avoid Stark shifting of the OH transition frequency. Subsequently, before the molecules have had an opportunity to exit the specific detection region, the excitation laser pulse fires, generating the OH fluorescence signal. The detected photoelectrons from the PMT are then either counted with a photon counter or amplified, averaged, and integrated over a 5 μs time window to fully encompass the appropriate state decay lifetime. The laser is stepped later in time relative to when the valve opens, and the entire measurement is repeated. In this iterative manner, a spectrum consisting of the OH signal as a function of time is generated.

3.3 Formaldehyde Molecule Detection

Laser induced fluorescence detection of the formaldehyde molecule is extremely similar to the hydroxyl radical case. The molecules are excited from the $|1_1 1\rangle$ ground state by photons at 353 nm generated from a frequency-doubled, pulsed-dye laser (PDL) pumped by a Nd:YAG laser to the $\widetilde{A}^1 A_2$ electronically excited state with one quantum in the ν_4 out-of-plane bending vibrational mode. Approximately 40% of the excited H_2CO decays non-radiatively [57], while the remaining molecules emit distributed fluorescence from 353 nm to 610 nm [109]. This fluorescence is collected, filtered, and imaged onto a photo-multiplier tube. The output of the photomultiplier tube is sent to a multi-channel scalar/averager, which serves as a gated photon counter. Operating the decelerator at 5 Hz and the PDL system at 10 Hz allows a “lock-in” type data-collection, such that every other signal is subtracted from the total photon counts. By scanning the delay between the PDL system and the triggering of the valve, a time-of-flight (ToF) curve is generated. A single data point is generated by collecting photon counts for 30 s to 2400 s (depending on required signal to noise).