

The two beams are aligned such that they cross in a near right angle in the sample. To avoid accumulation of reaction products a flow-through cuvette can be used for experiments in solution. The reservoir can be purged with a gas (usually nitrogen or oxygen) during the whole experiment, to control the oxygen concentration in the sample and thus enable or suppress oxygen quenching. In the case of the sample being a film, the quartz window, on which the film is applied, is rotated during the experiment (see figure 2.2).⁴ Thus, the beams constantly encounter a fresh region of the film. Here, control of oxygen concentration is not possible. The probe beam is dispersed in a monochromator, with variable entry- and exit-slits. By adjusting the slits, the spectral resolution of the monochromator can be controlled. In this work, the resolution was usually chosen to be between 2 and 2.5 nm. The spectral range available is limited on the high energy side by the xenon lamp, whose intensity is too weak below 280 nm; and on the low energy side by the photomultiplier, which does not exhibit enough sensitivity for wavelengths above 750 nm.

1.2 Transient Emission

The spectrometer described in the previous section can also be used to investigate the emission of transient species. Therefore the setup has to be changed in only one point, as no probe beam is required (see figure 1.4).

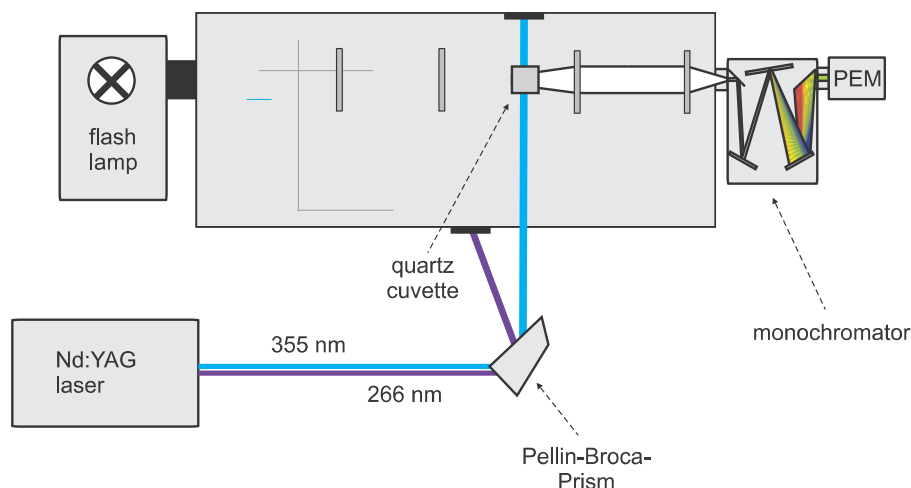


Figure 1.4: Setup for transient emission measurements in solution

As described above, excitation of the ground state molecule to the S_n state molecule is followed by fast IC into the S_1 state. Then, if the transition is allowed, fluorescence from the S_1 state can occur. Analogous to the transient absorption experiment, the emission at distinct wavelengths is detected for several nanoseconds. The signal-to-noise ratio of the kinetic trace can be enhanced by integration over the whole spectral range, if only one species is emitting. The time-resolved