

AD-A057 081

WASHINGTON STATE UNIV PULLMAN DEPT OF CHEMISTRY
CHEMICAL MEASUREMENTS IN THE PICOSECOND AND SHORTER TIME RANGE.(U)
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Fig. 2.1.6 Ippen and Shank's adaptation of Weber's technique for pulse-width measurements of pulses from a modelocked CW dye laser ^(Laser Focus, July, 1977). λ Second harmonic output is at an angle to the fundamental frequency and eliminates the need for filters to separate ν from 2ν . One of the input pulse trains is chopped, and the lock-in amplifier provides synchronous detection of 2ν at the chopping frequency. This increases signal to noise dramatically, and weak (second harmonic) signals are more easily measured.

Fig. 2.1.7 Two photon fluorescence (TPF) method. Pulsewidths are generally determined from a microdensitometer trace of the photographed fluorescence image.

Fig. 2.1.8 Streak tube from an Imacon II streak camera (Hadland Photonics, Ltd.)

Fig. 2.3.1 Spatial extent of laser pulses relative to same size: A) pulsewidth = 1 ns; B) pulsewidth = 10 ps.

Fig. 2.3.2 Malley-Rentzepis crossed beam technique (51). The interrogating pulse is passed through a Ronchi ruling, about a meter from the ruling, to smooth its cross-sectional intensity profile. In this way homogeneous illumination of the sample cell is accomplished. This assures reasonably accurate determination of decay kinetics from optical wake profiles.

Fig. 2.3.3 Echelon technique developed by Topp, Rentzepis, and Jones (52). If the bleaching pulse uniformly illuminates the sample, a microdensitometer trace of the photograph of the interrogating pulse will resemble a histogram

(of intensity bands) reflecting decay of excited state absorbance or return of ground state absorbance. If a spectrograph is used, a photographic record will also include spectral information and allow the calculation of rate constants at several wavelengths.

Fig. 2.3.4 Picosecond flash photolysis apparatus developed by Magde and Windsor (55,56). See text for detailed description.

Fig. 2.3.5 Photographic record of excited state decay of BDN in iodoethane using the Magde-Windsor technique (56). The film plate is moved and the delay time between excitation pulse and monitoring pulse is changed between exposures. The dark central portion of each image is due to absorbance of the continuum by the excited state.

Fig. 2.3.6 Photographic record of excited state decay of [(OEP)SnCl₂] in 1,2-dichloroethane showing both S₁ and T₁ absorption as studied by Magde *et al.*, (57). The persistent excited state absorbance due to the T₁ state is particularly evident in the 500 and 2,000 ps exposures.

Fig. 2.3.7 Photographic record of excited state decay of DODCI in ethanol as studied by Magde and Windsor (55). Bleaching of ground state absorbance can be seen between 560 and 590 nm as a light central band in the shorter-time exposures.

Fig. 2.3.8 Kinetics of one of the electron transfer steps in bacterial photosynthesis measured at three different wavelengths in reaction centers isolated from the photosynthetic bacterium, *Rps. viridis*. Figure 2.3.9 shows the spectra of the states before and after this step. From the paper by Holten *et al.*, (196).

Fig. 2.3.9 Absorbance changes at room temperature for reaction centers of *Rps. viridis*, measured after time delays of 20 ps (open circles) and 1 ns (closed circles). The change in the difference spectrum between the two time delays reflects the transfer of an electron from a molecule of bacteriopheophytin to ubiquinone. The kinetics of this process are shown in Figure 2.3.8. From the paper by Holten et al., (196).

Fig. 2.3.10 Schematic of the method used to measure transient kinetics by the decay of a grating (interference pattern) produced when two coherent pulses cross in a sample cell. The interference pattern is a spatial modulation in the ratio of ground to excited states and persists with a lifetime dependent on excited state relaxation or decay of induced orientational anisotropy (64).

Fig. 2.4.1 Kerr shutter used in measuring fluorescence lifetimes. The photomultiplier detects the signal that passes through the Kerr cell coincident with the gating pulse. By delaying the arrival of the gating pulse, the intensity of the fluorescence signal can be measured and plotted versus the delay time. The resolution of the Kerr shutter is a function of the width of the gating pulse (~ 5 ps). Consequently, this method works best when lifetimes are ≥ 50 ps (69,70).

Fig. 2.4.2 Kerr shutter used to measure short fluorescence lifetimes (≤ 50 ps) in a single pulse: A) Kinetic data are obtained from OMA output of from a microdensitometer trace of the photographic image; B) Kinetic and spectral data are both available in this design P_1 and P_2 are crossed polarizers (72).

Fig. 2.4.3 ^{B)} Kerr shutter incorporating a colinear gating pulse and fluorescence signal: A) Detail of transmitting echelon. (55).

Fig. 2.4.4 Streak camera technique for measurement of fluorescence lifetimes.

Fig. 2.5.1 Folded cavity configuration characteristic of the modelocked CW dye laser systems developed by Ippen and Shank (*Laser Focus*, July, 1977).

Fig. 3.1.1 Envelope of vectors reflecting the $\cos^2\theta$ distribution of ground state moments remaining after absorption of a pulse linearly polarized in the Y direction (θ is the angle off the X axis). The excitation pulse is travelling into the page along the z-axis. Molecules with transition moments perpendicular to Y remain unexcited, whereas the ensemble of molecules with moments nearly parallel with Y is maximally disturbed. The induced anisotropic distribution of moments will influence the relative transmission of the polarized light and will persist with a lifetime characteristic of excited state decay or orientational redistribution.

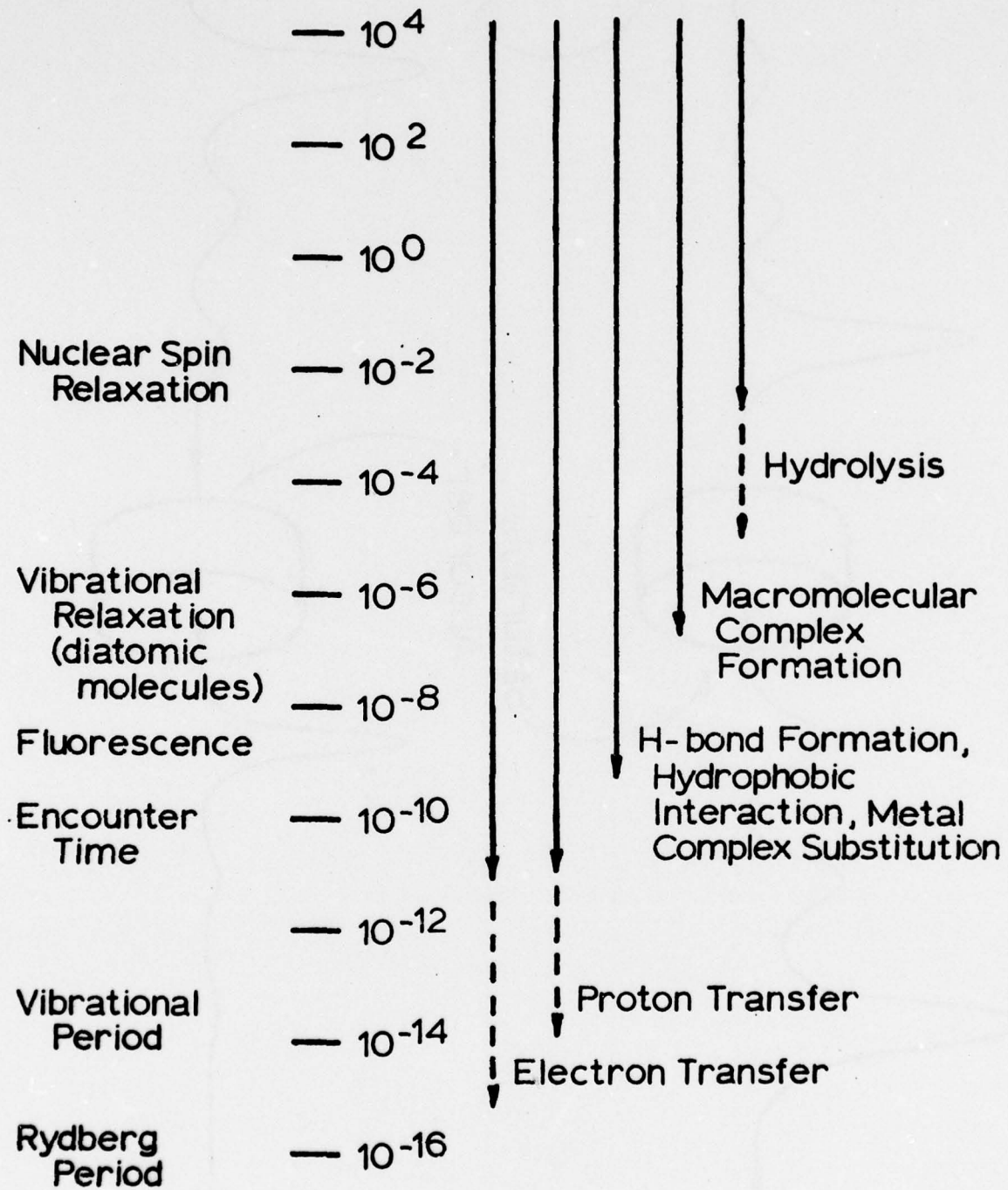
Fig. 3.1.2 Orientation relaxation times versus solution viscosity for R-6G in different solvents (93).

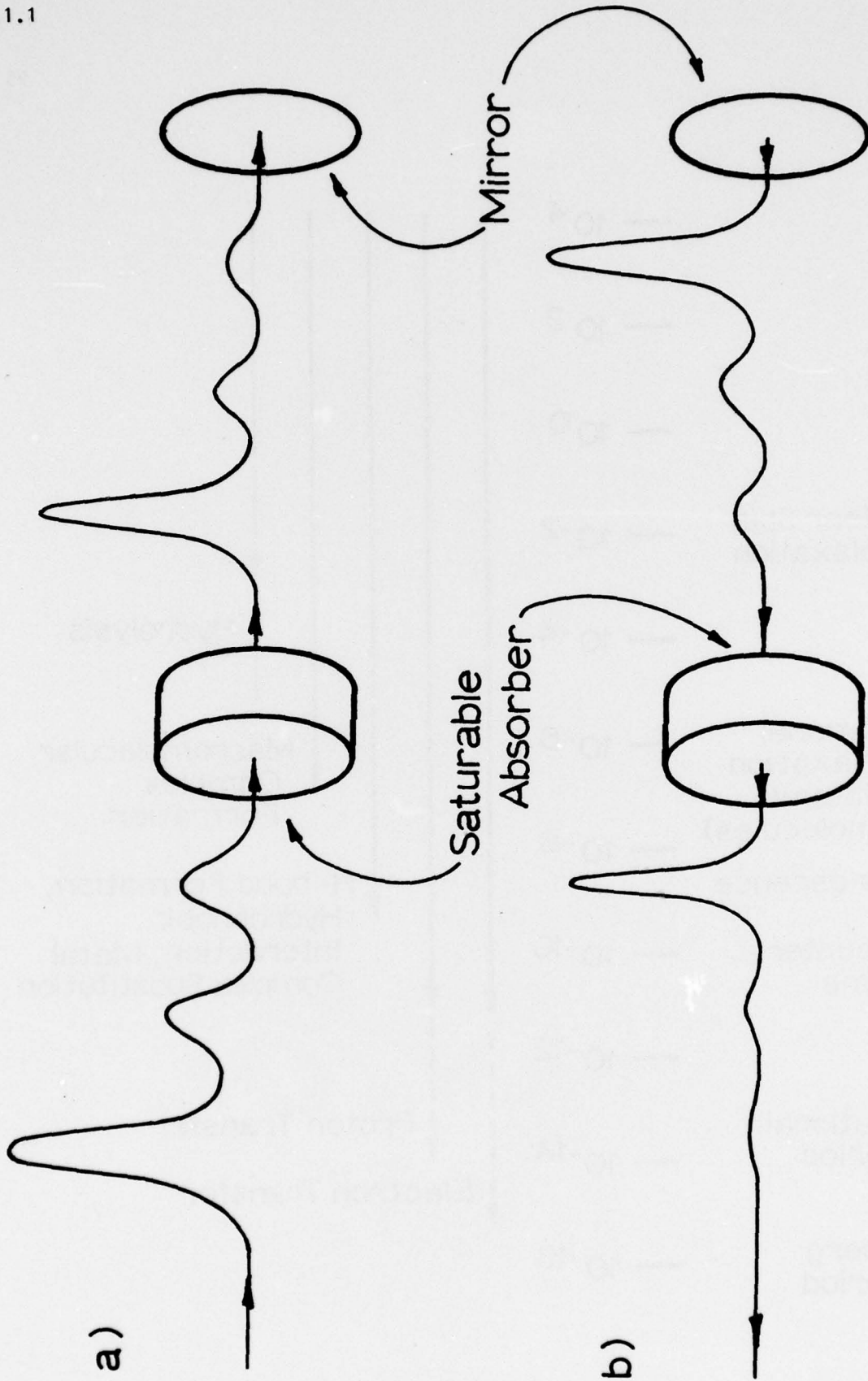
Fig. 3.1.3 Structure of the triphenylmethane dye crystal violet. Symmetry is D_3 with the phenyl groups at an angle to the molecular plane giving the molecule a propeller-like conformation. The structures of other triphenylmethane dyes are similar.

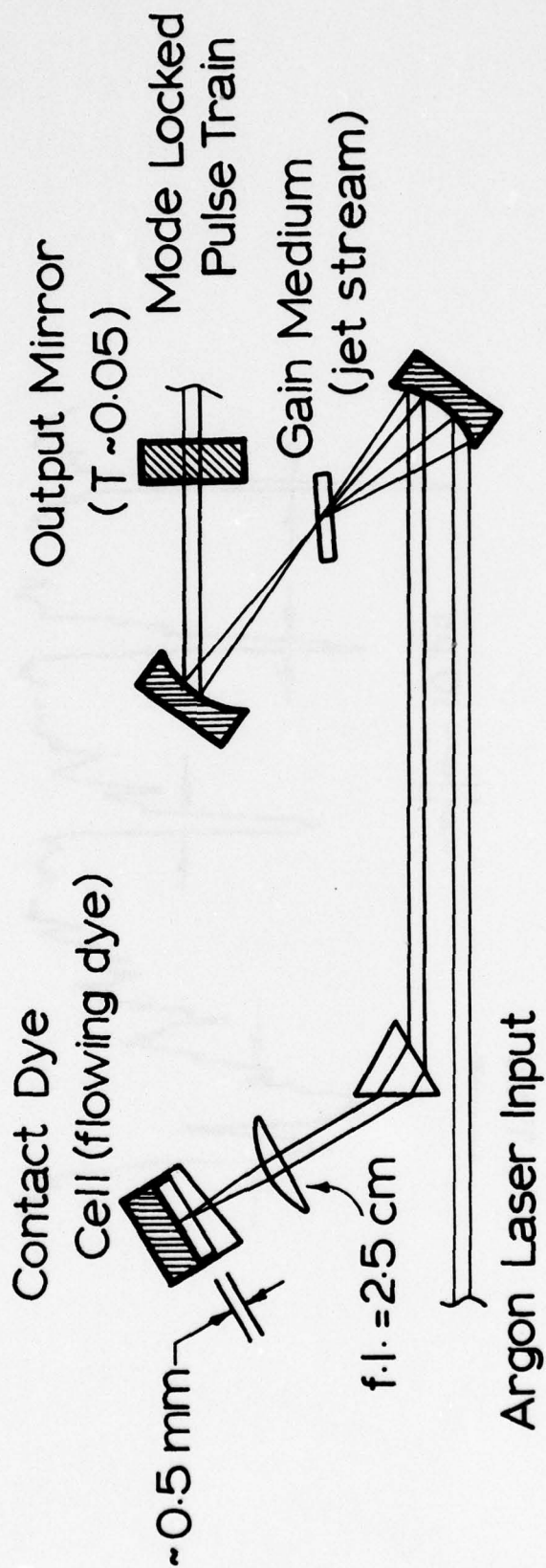
Fig. 3.1.4 A) Driven rotation kinetic model requires the difference in ground and excited state potential energy minima to be large. The viscosity dependence of the ring rotation rate $K\theta$ accounts for the variation of the fluorescence quantum yield with viscosity. B) Results of ground state repopulation experiments can

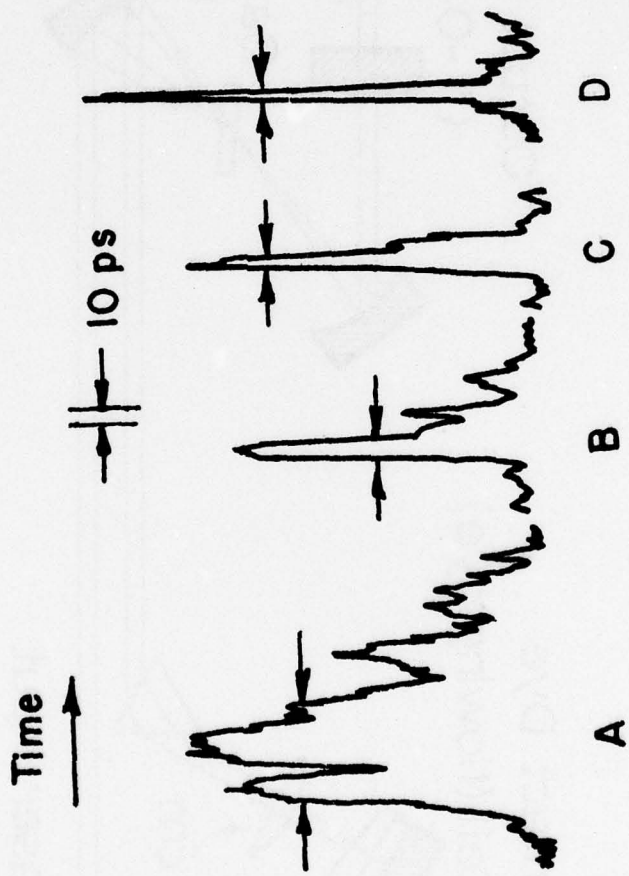
be explained by considering the potential surfaces to be shallow, with the excited state surface somewhat shallower than that of the ground state.

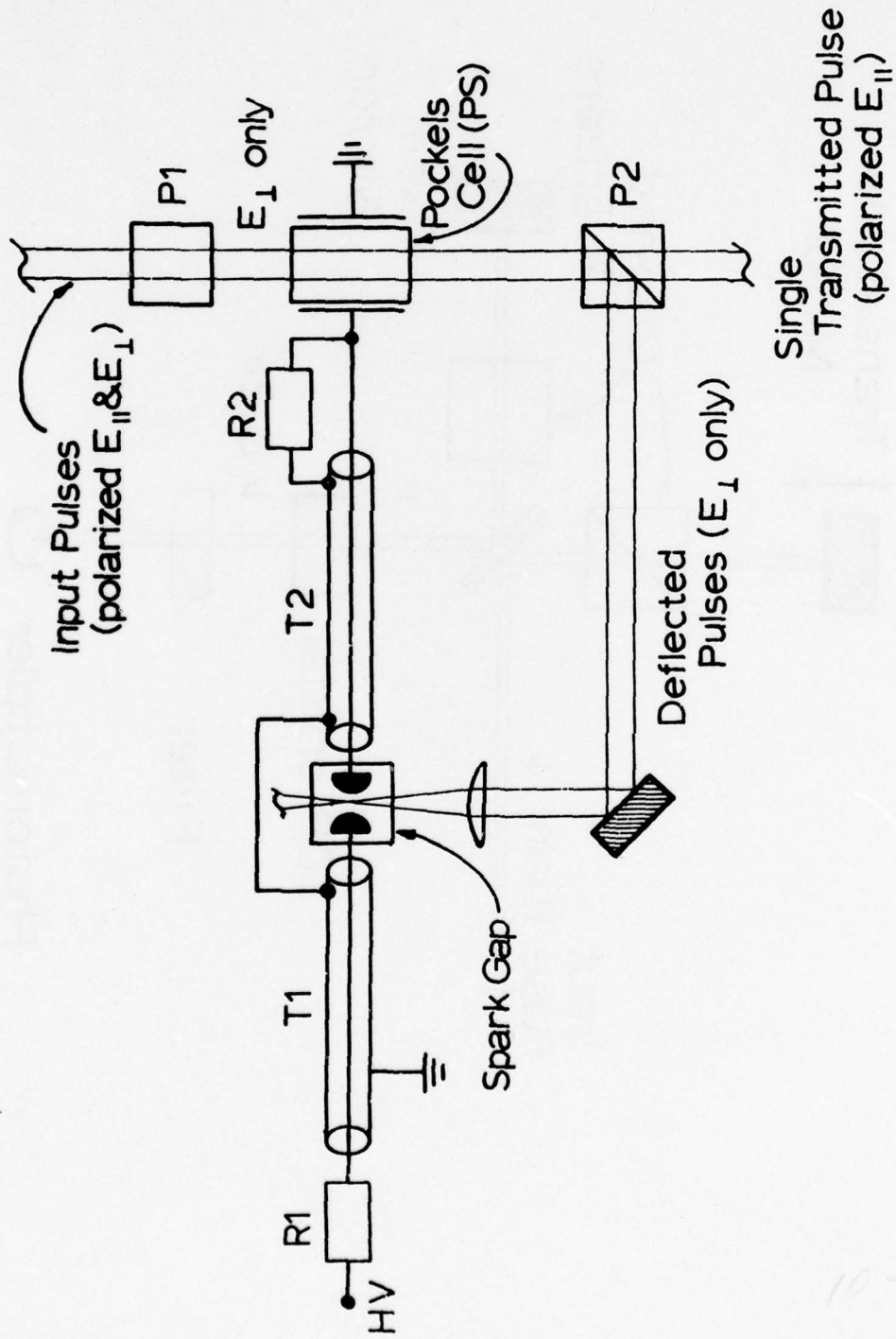
This results in excited molecules having distinct decay rates over a wide range of values. Observed viscosity dependence of kinetics results from ring rotation in low viscosity solvents.

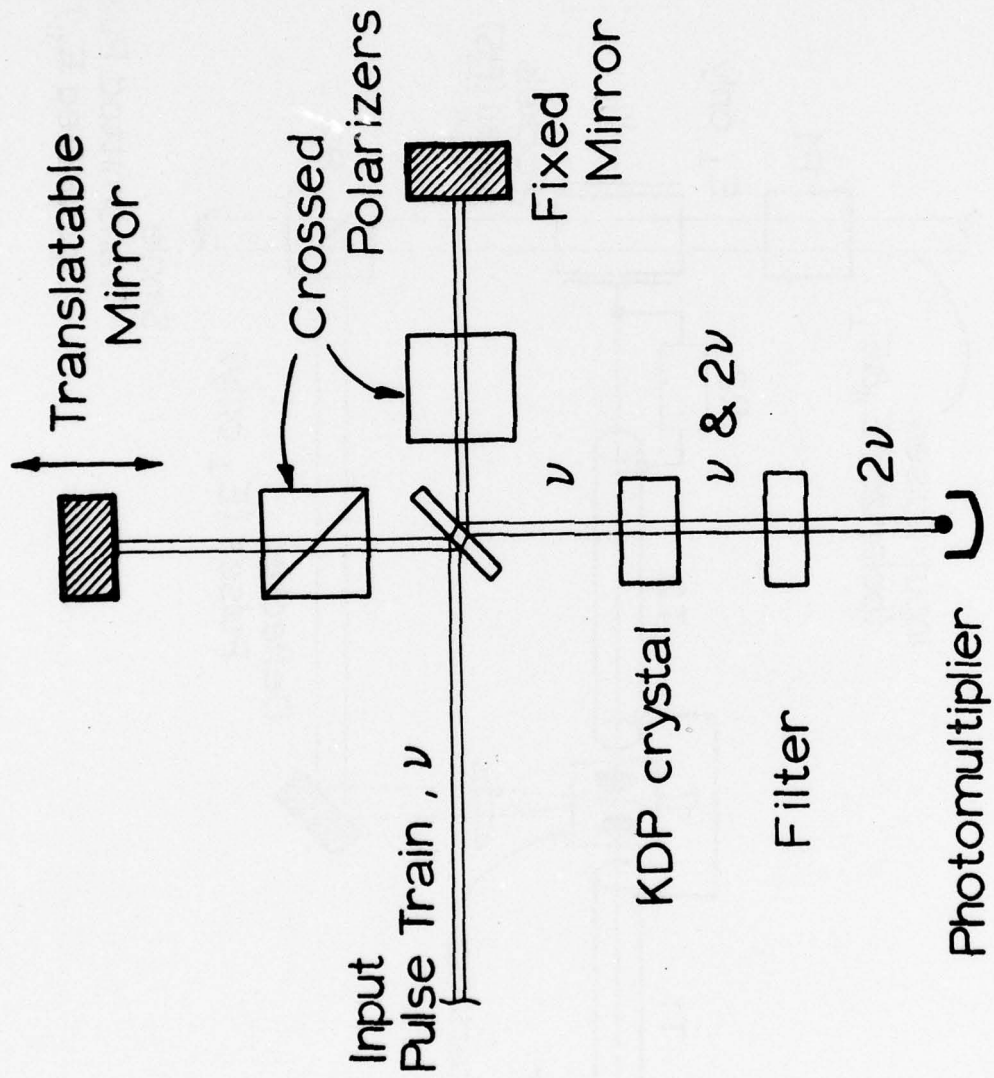


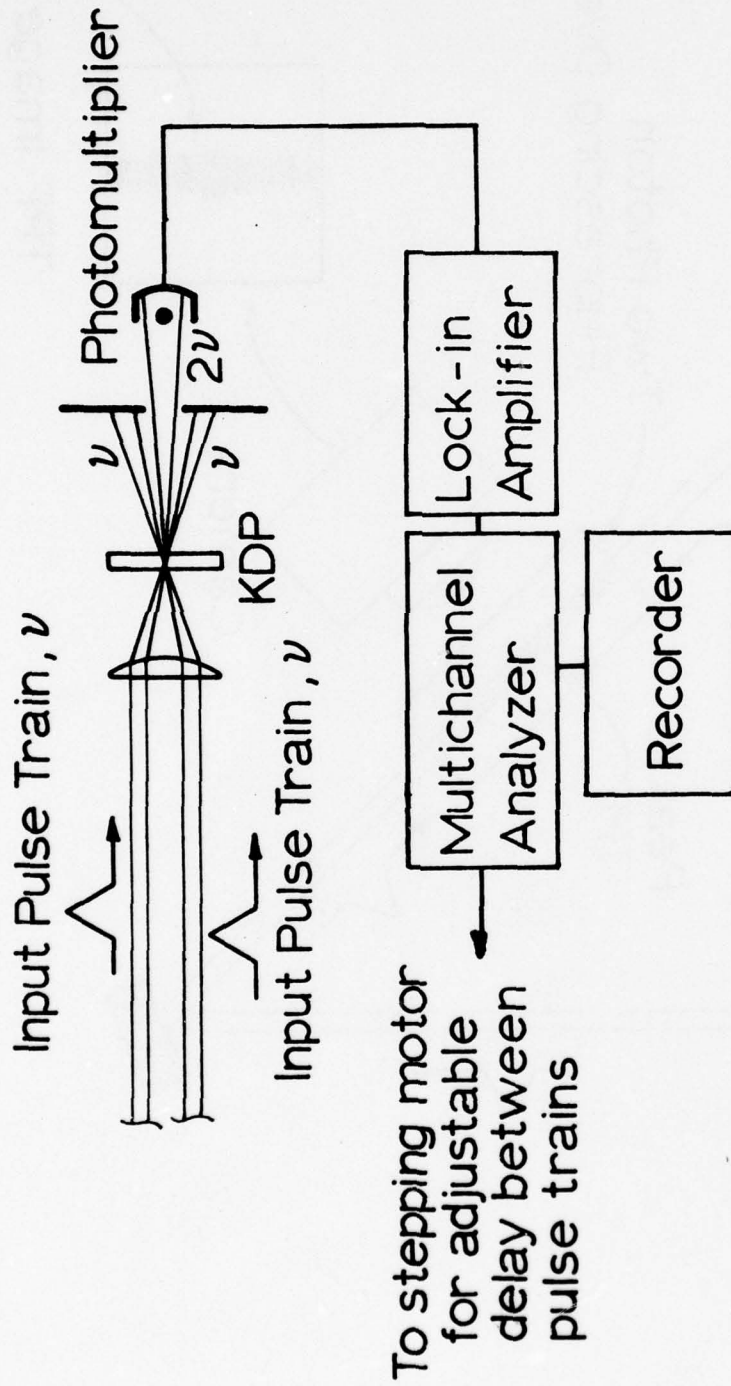












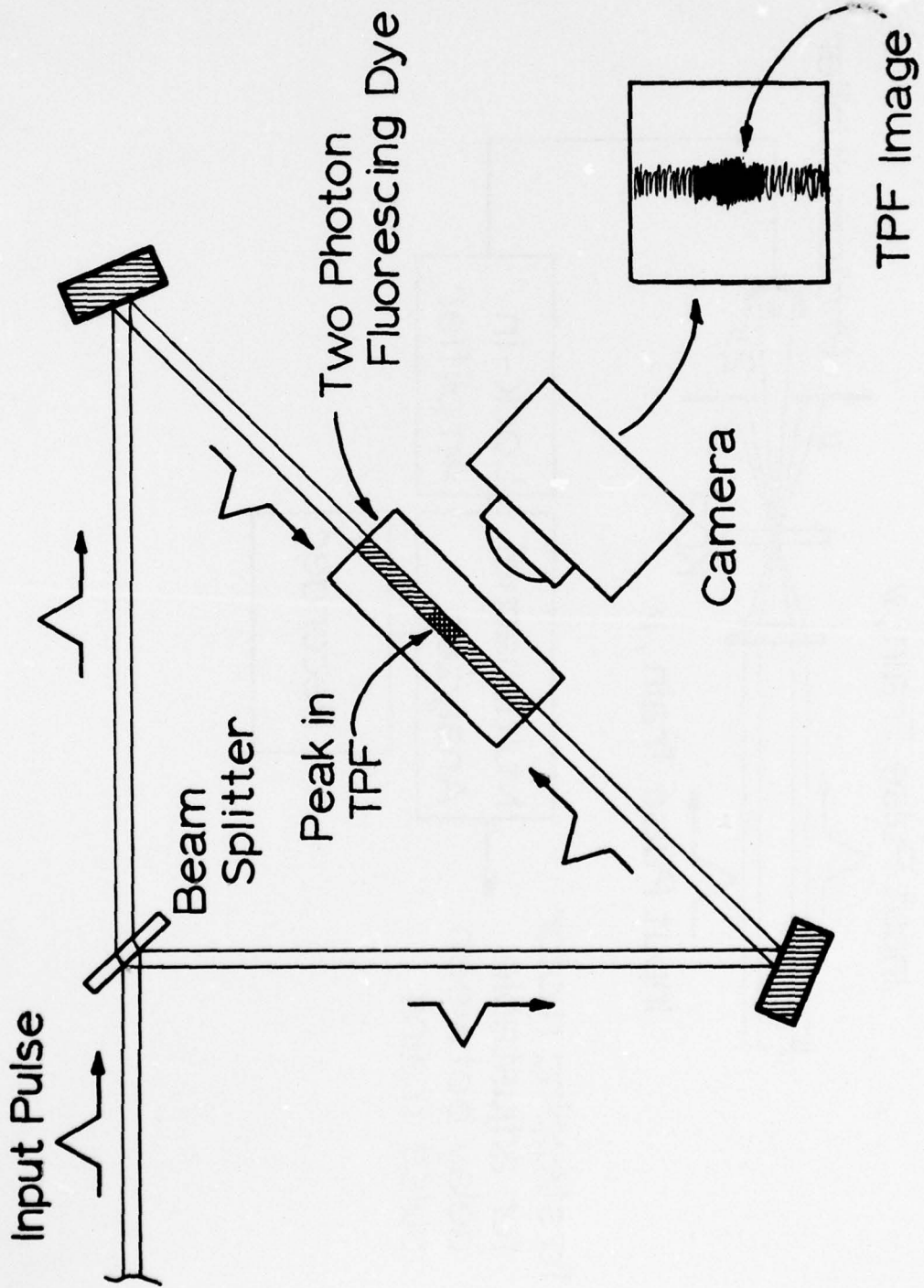


Image Intensifier,
Camera or OMA

Extraction Mesh
Electrode

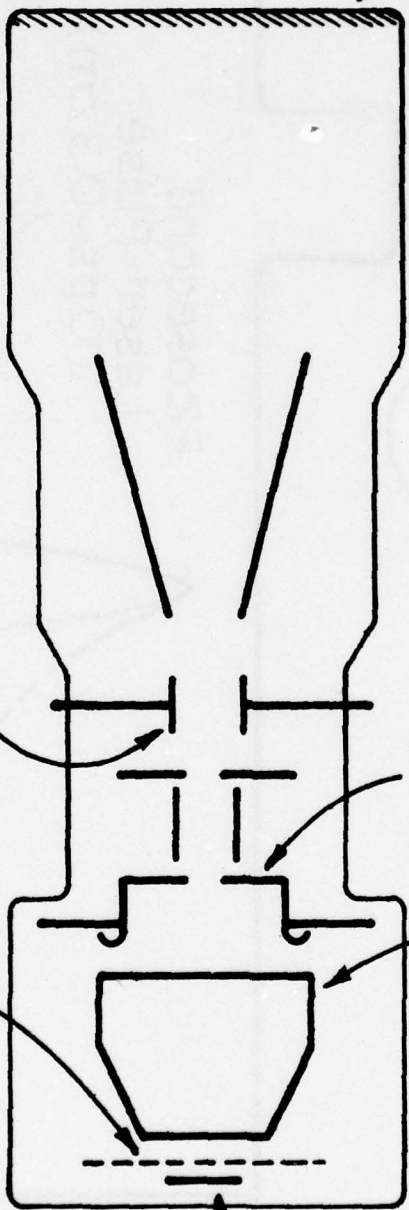
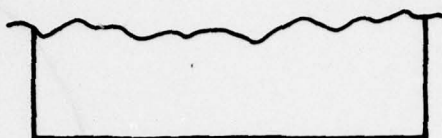
Sweep Plates

Anode

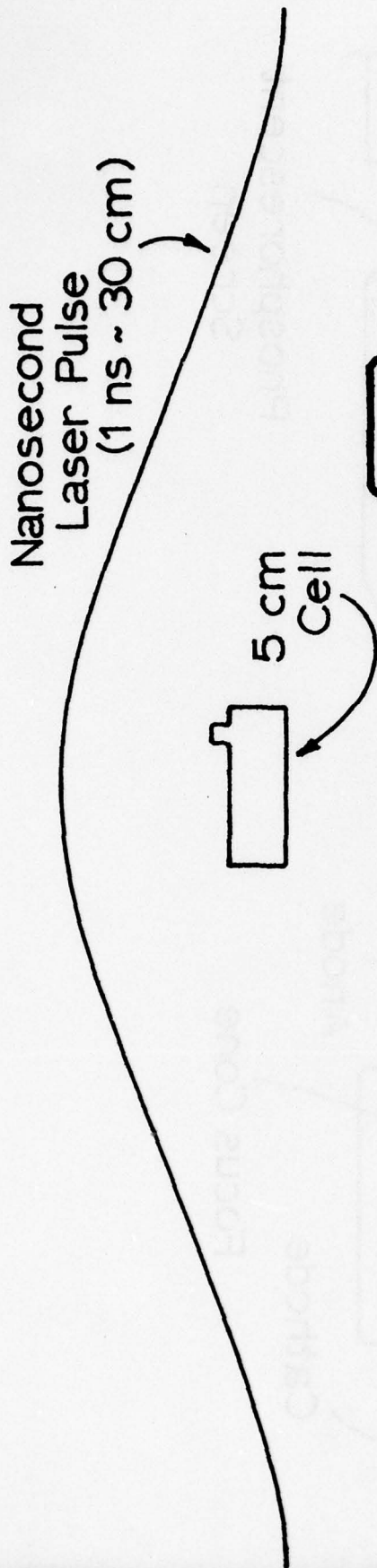
Cathode

Focus Cone

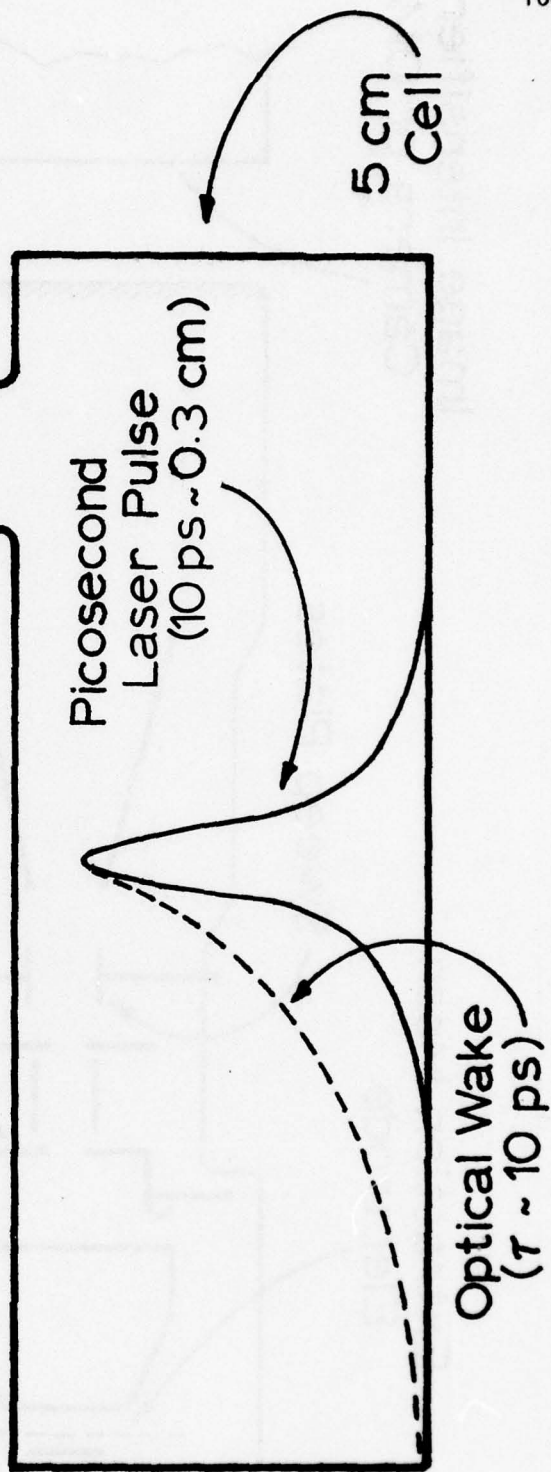
Phosphorescent
Screen

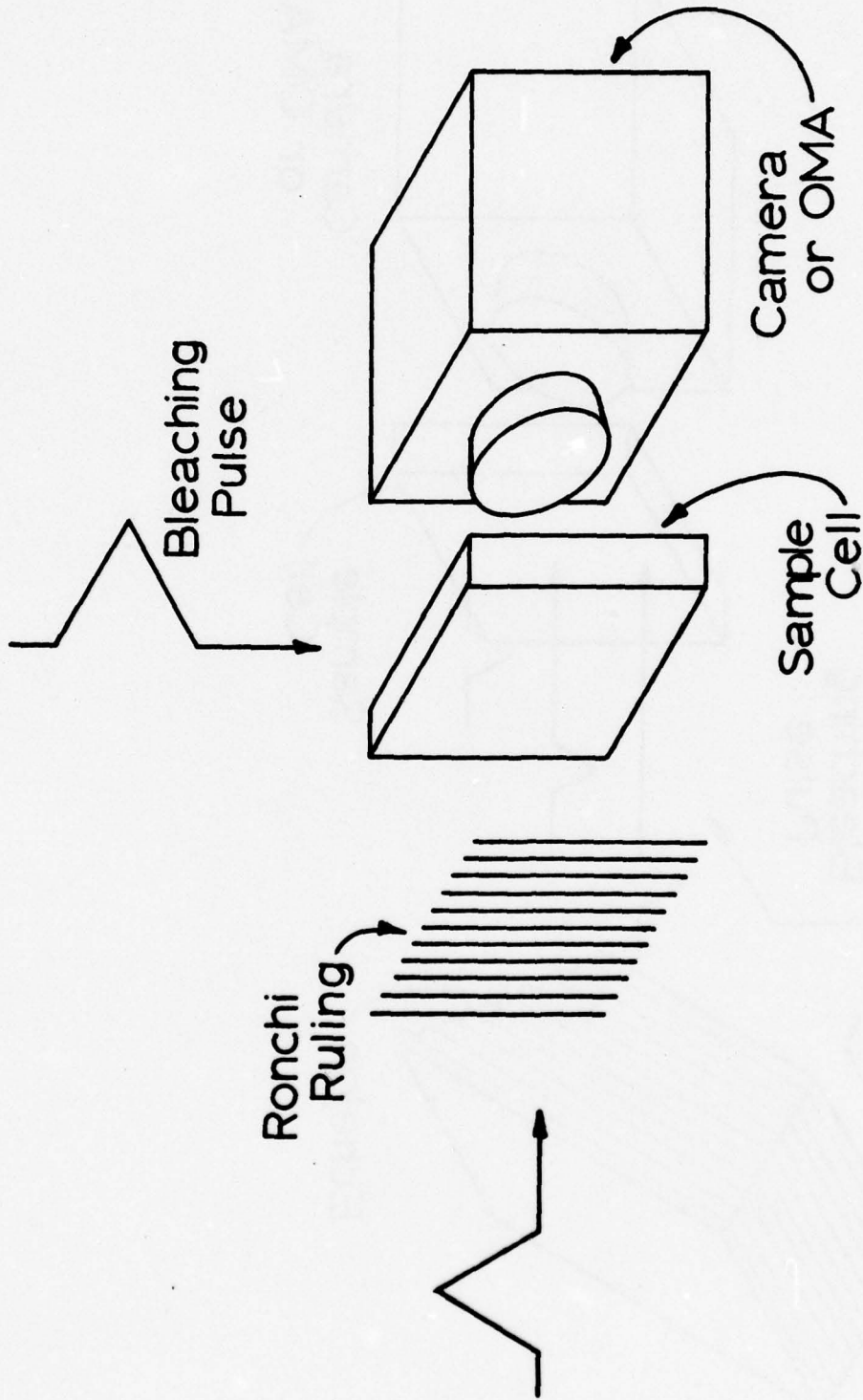


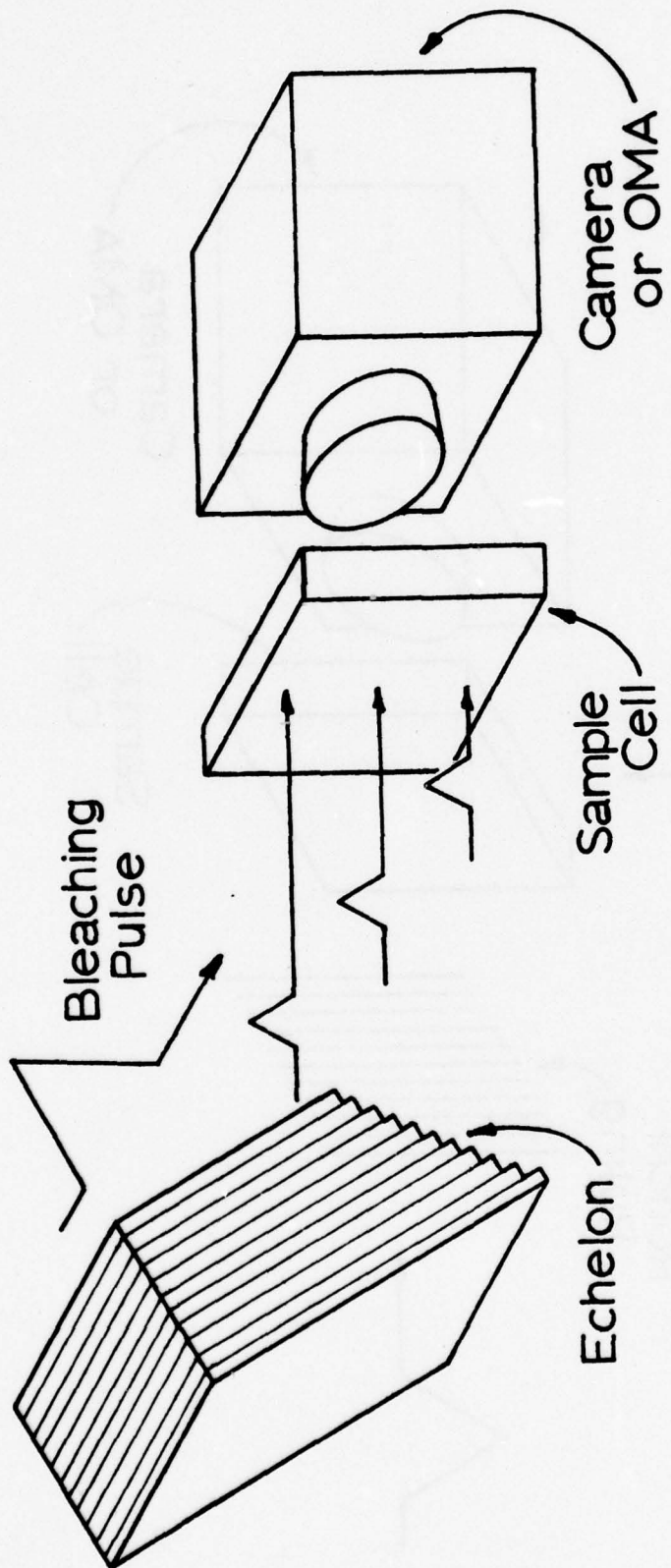
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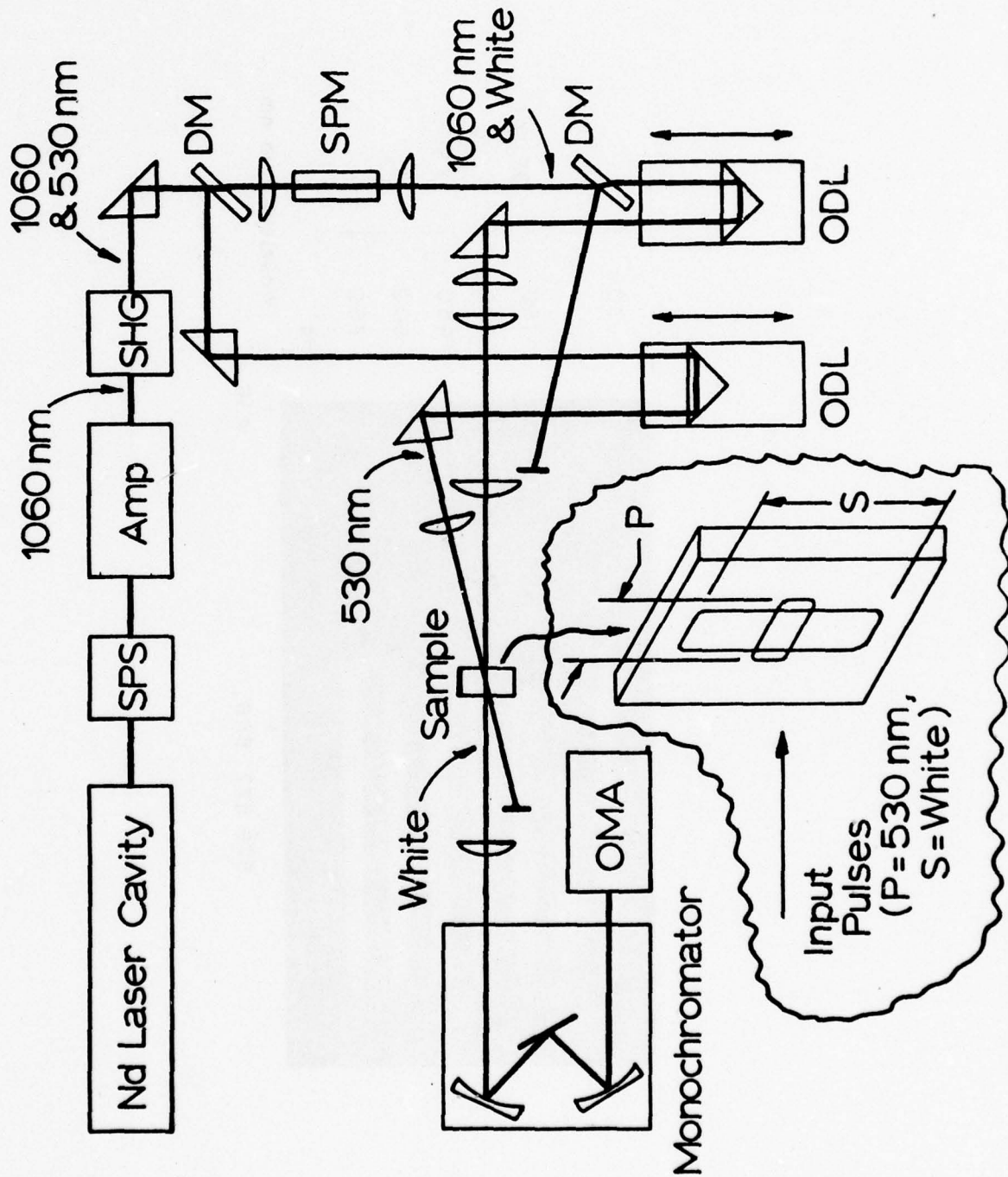


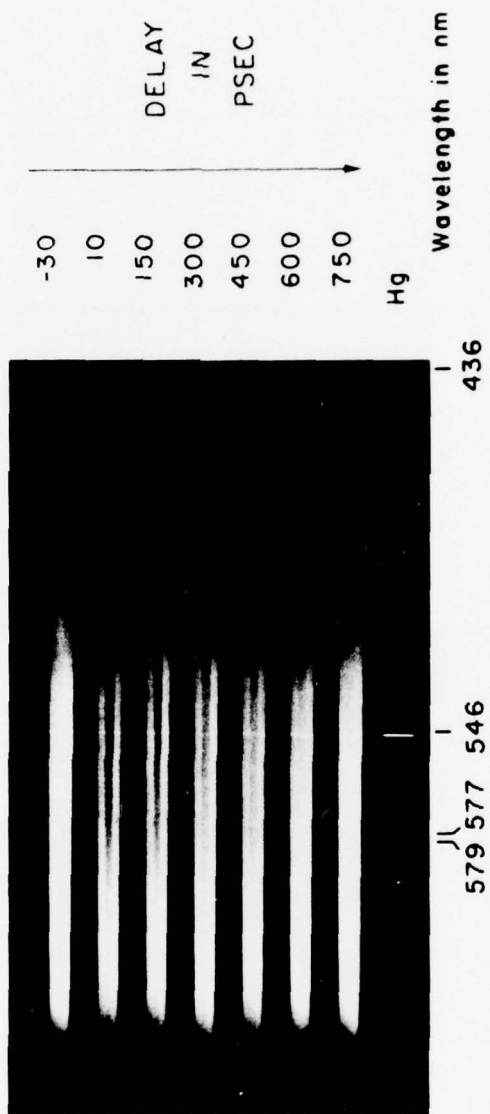
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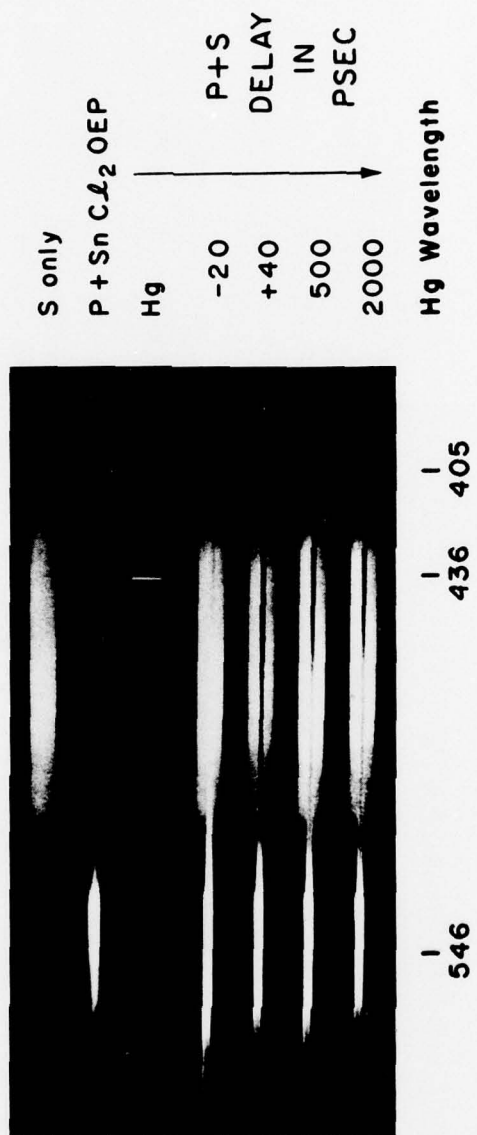


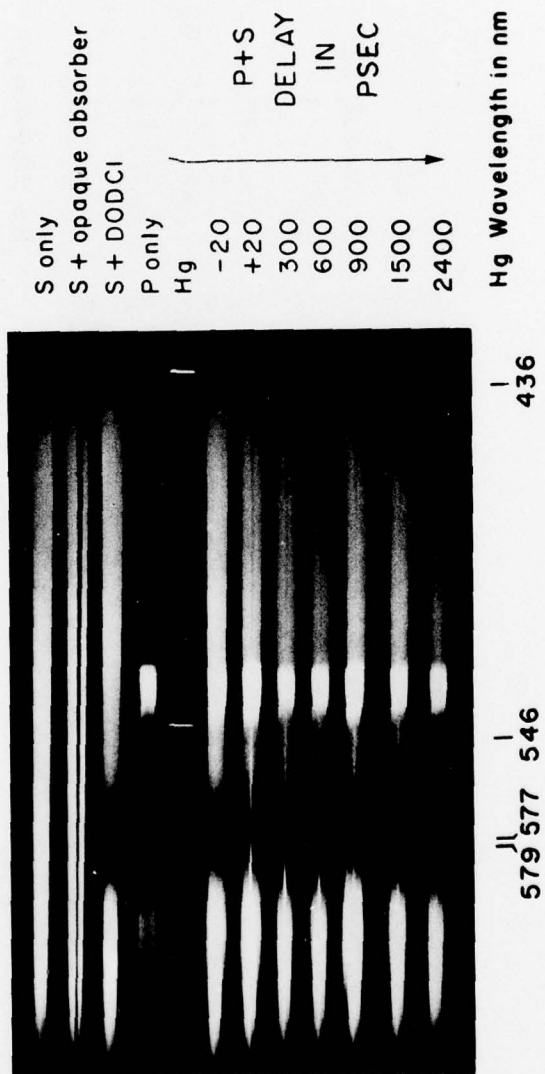


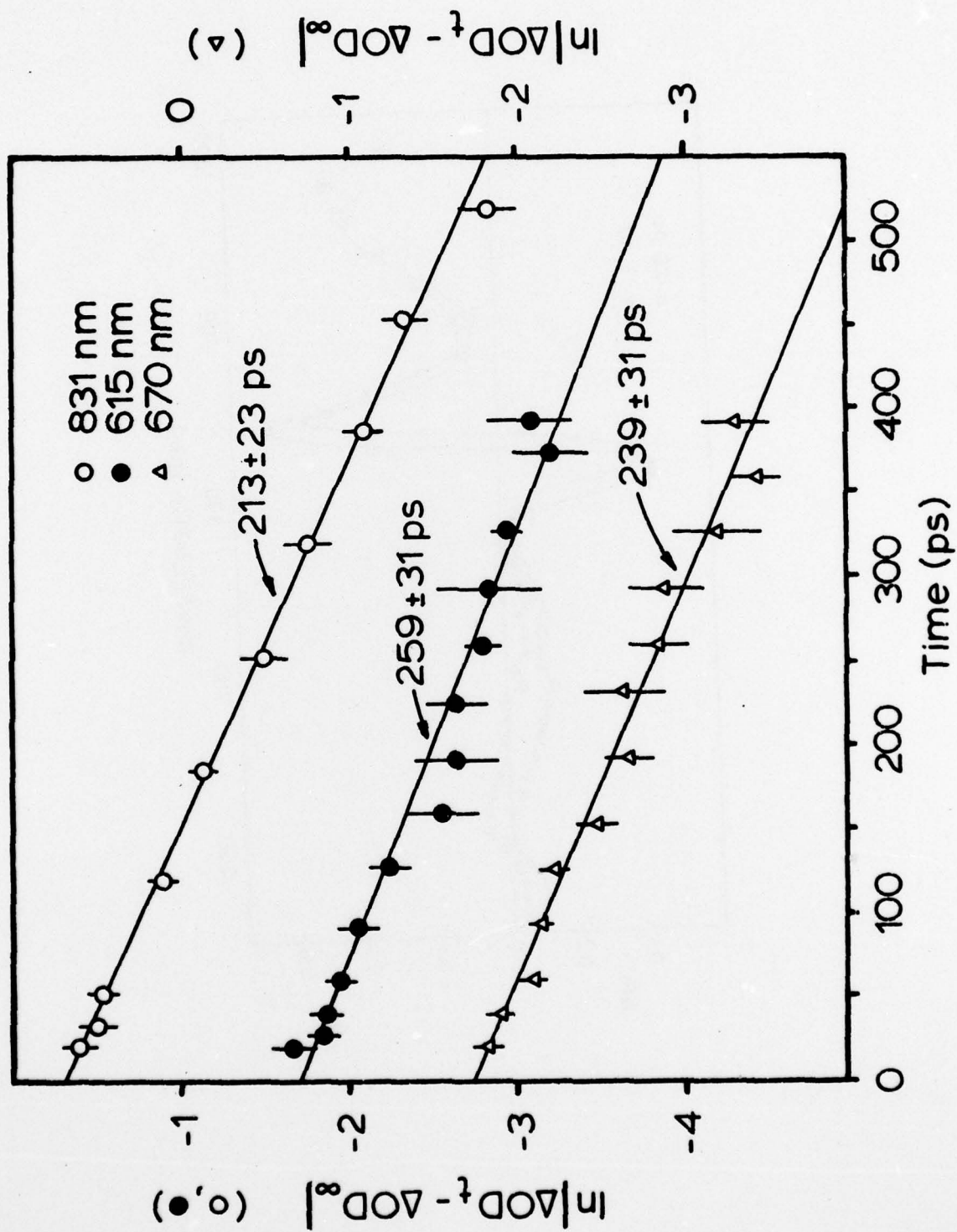


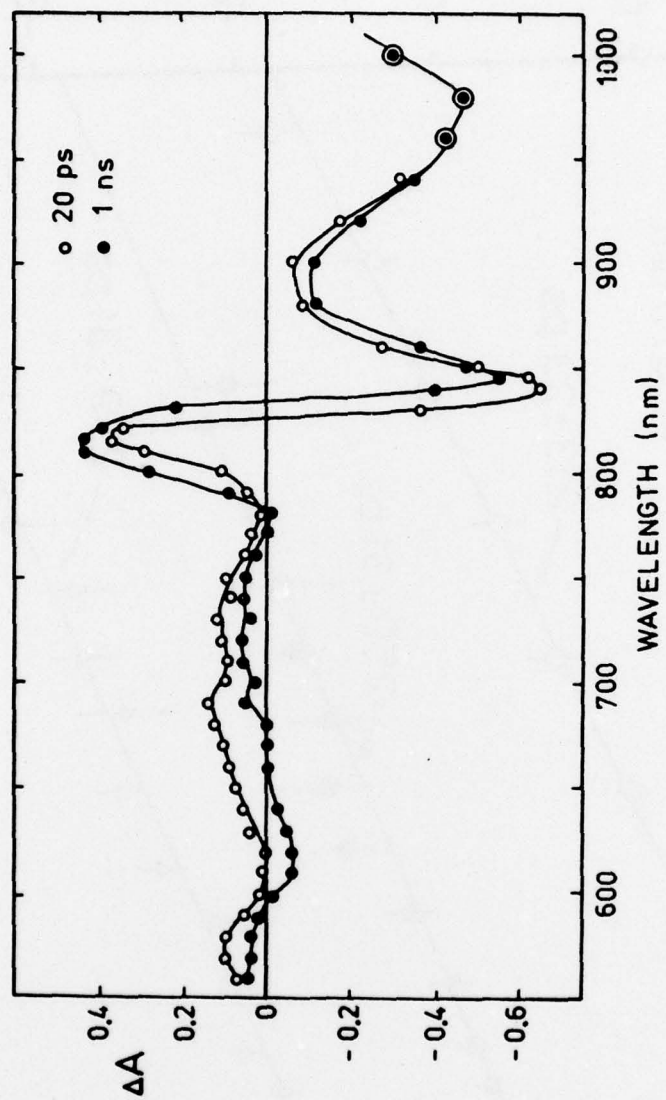


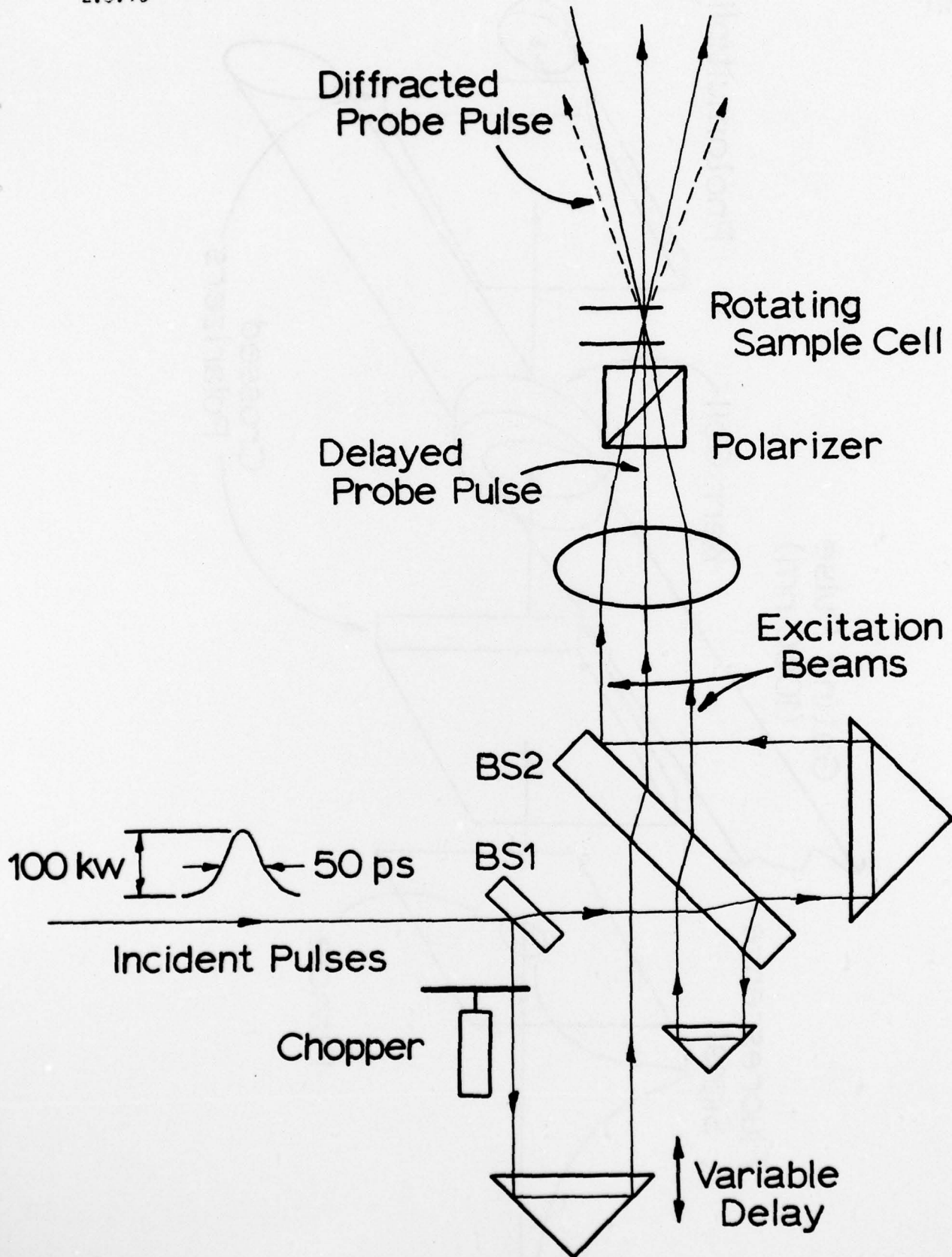


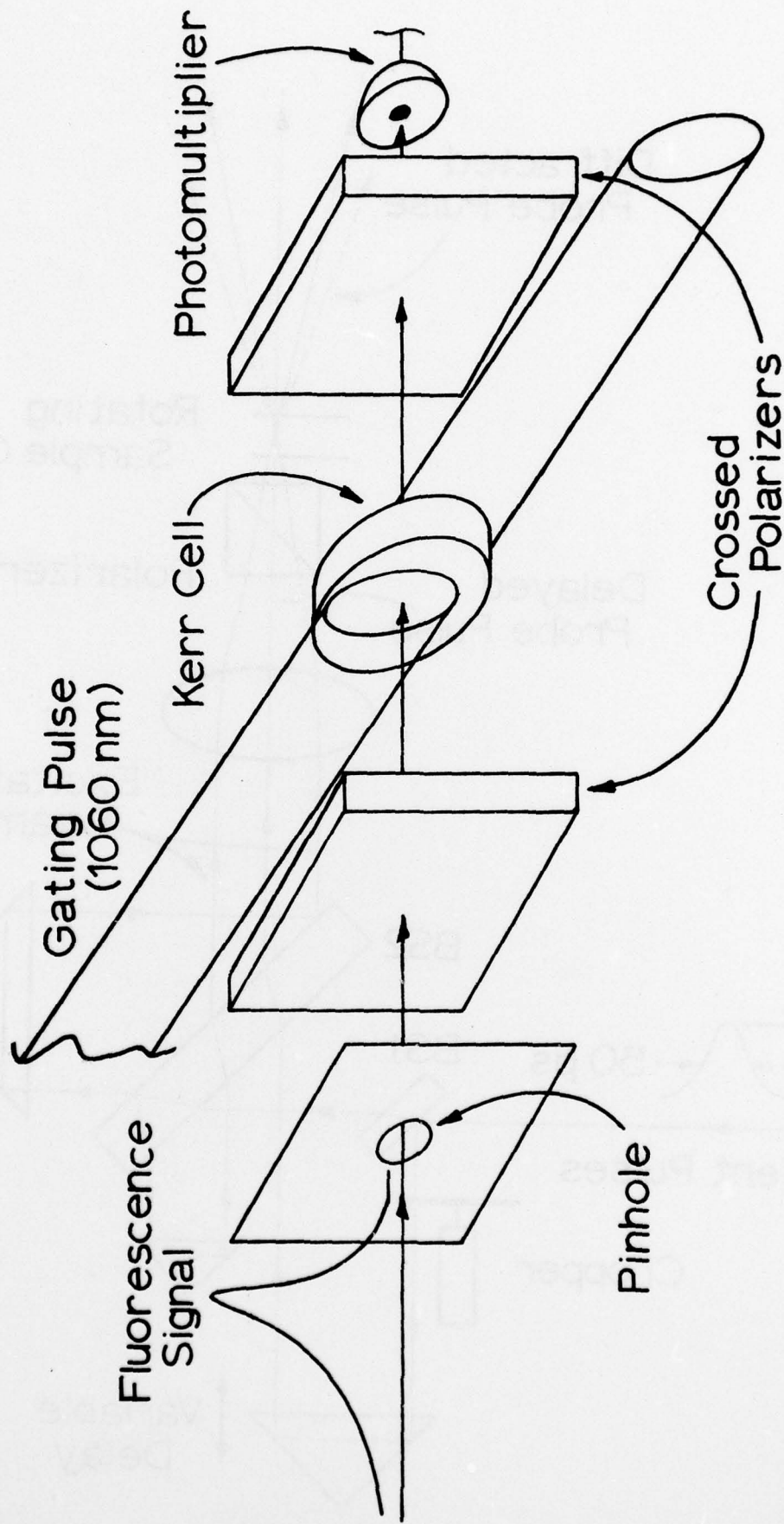


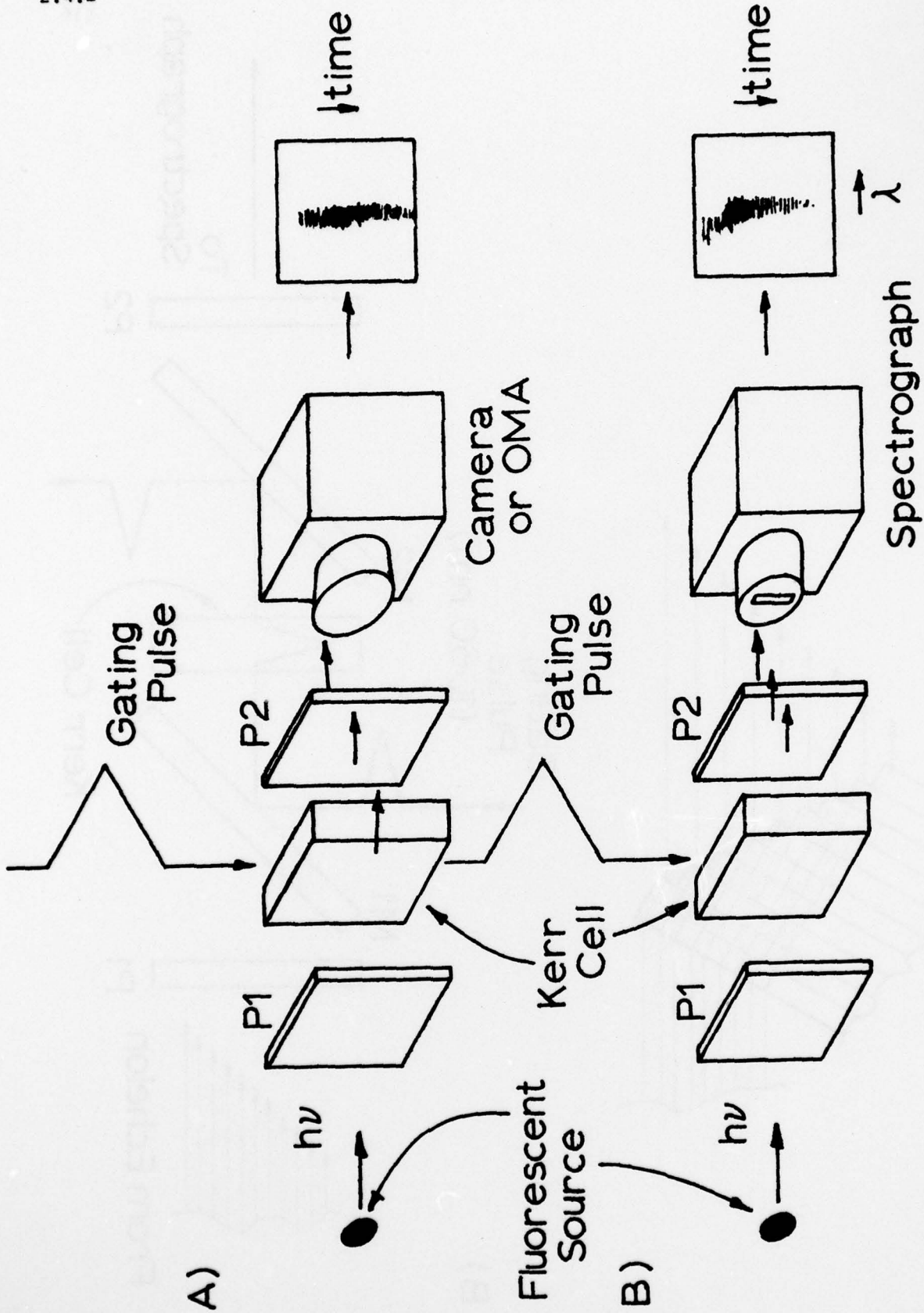


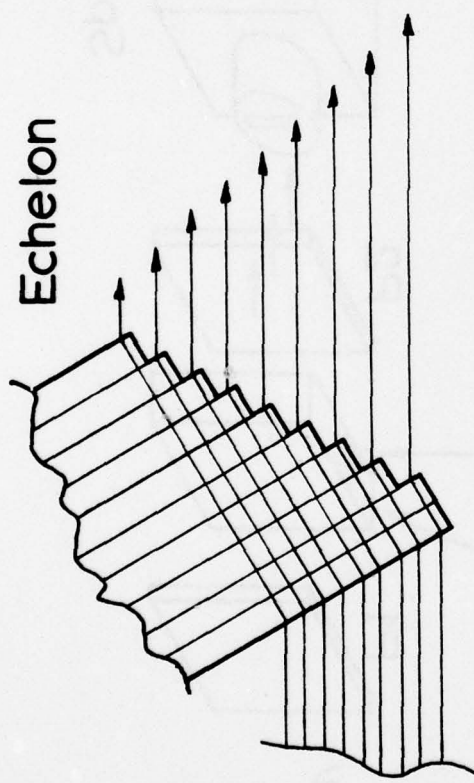




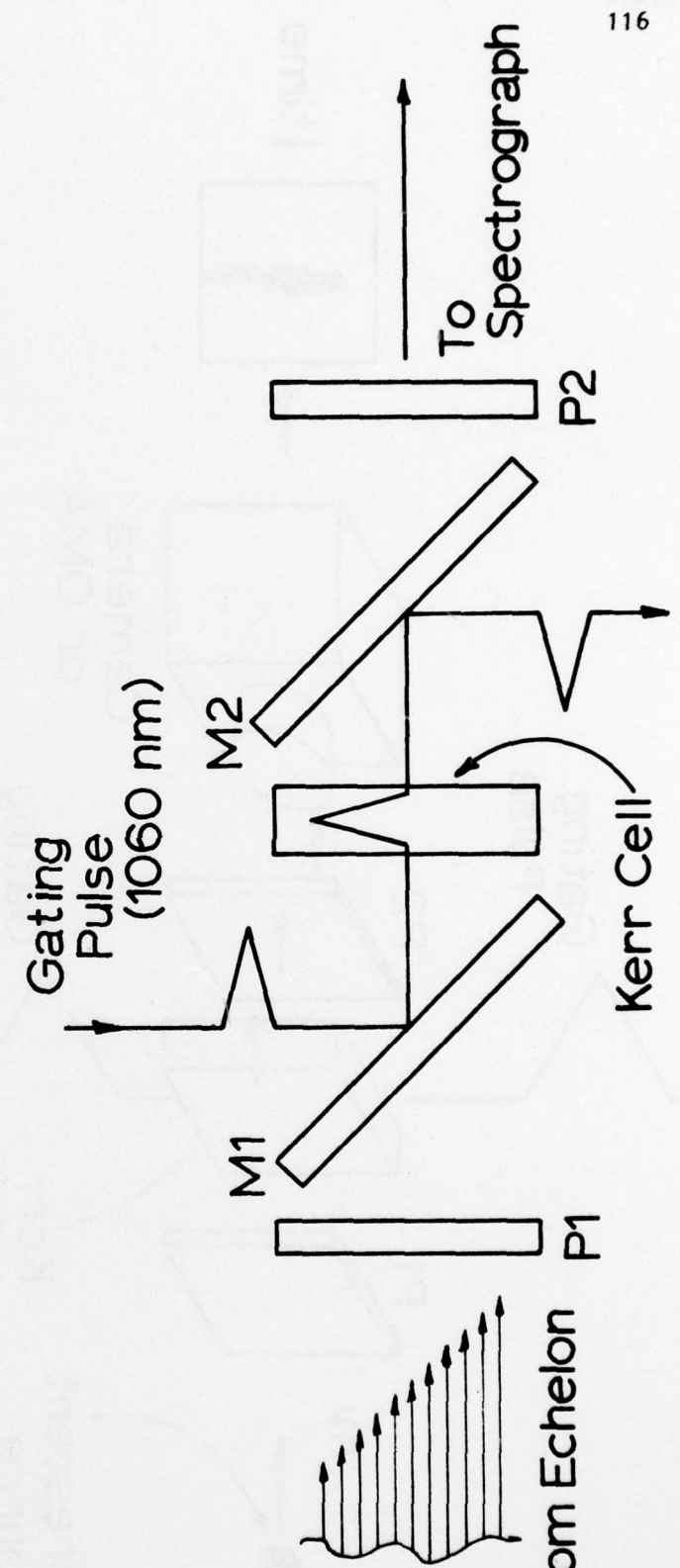




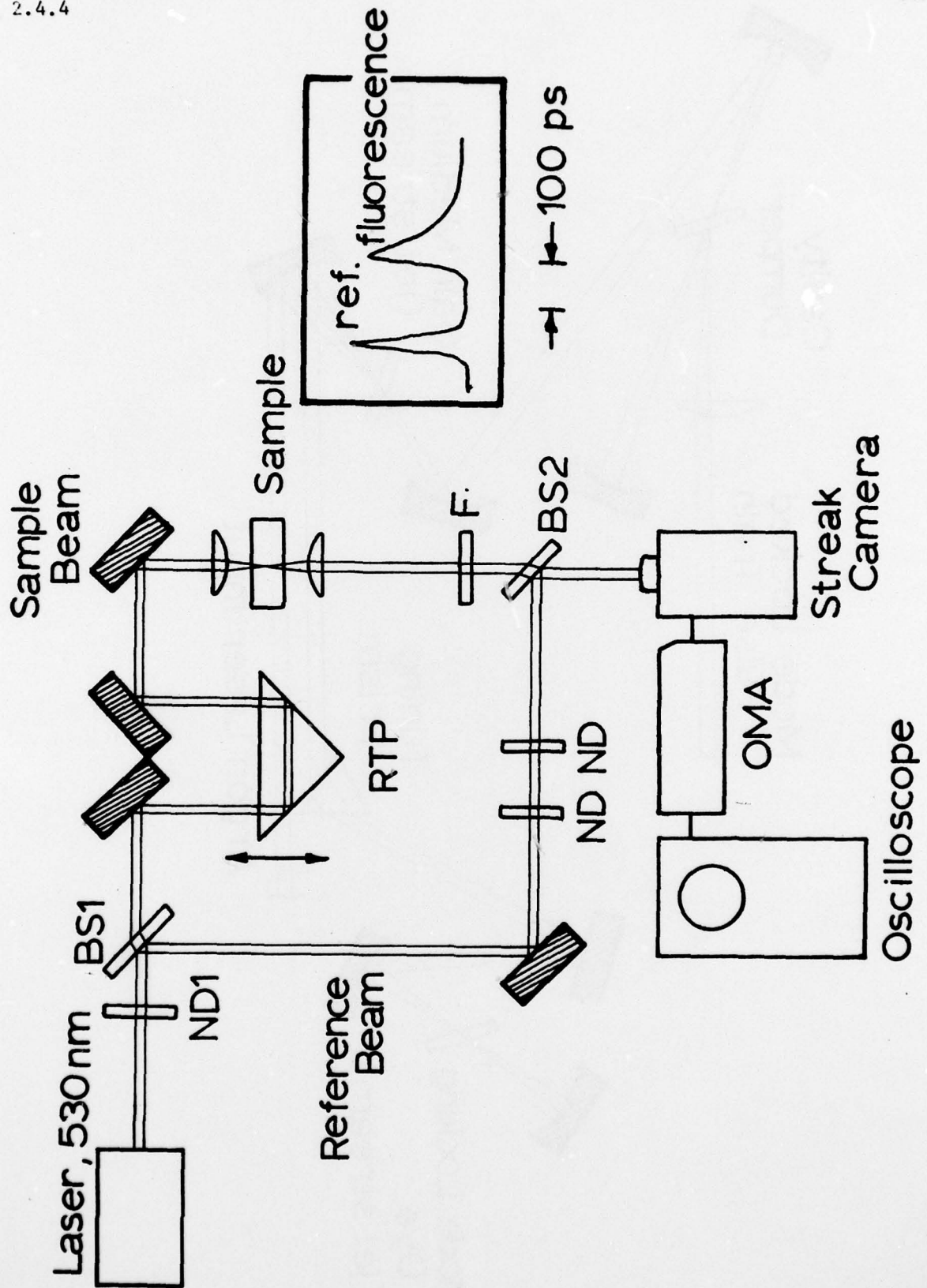


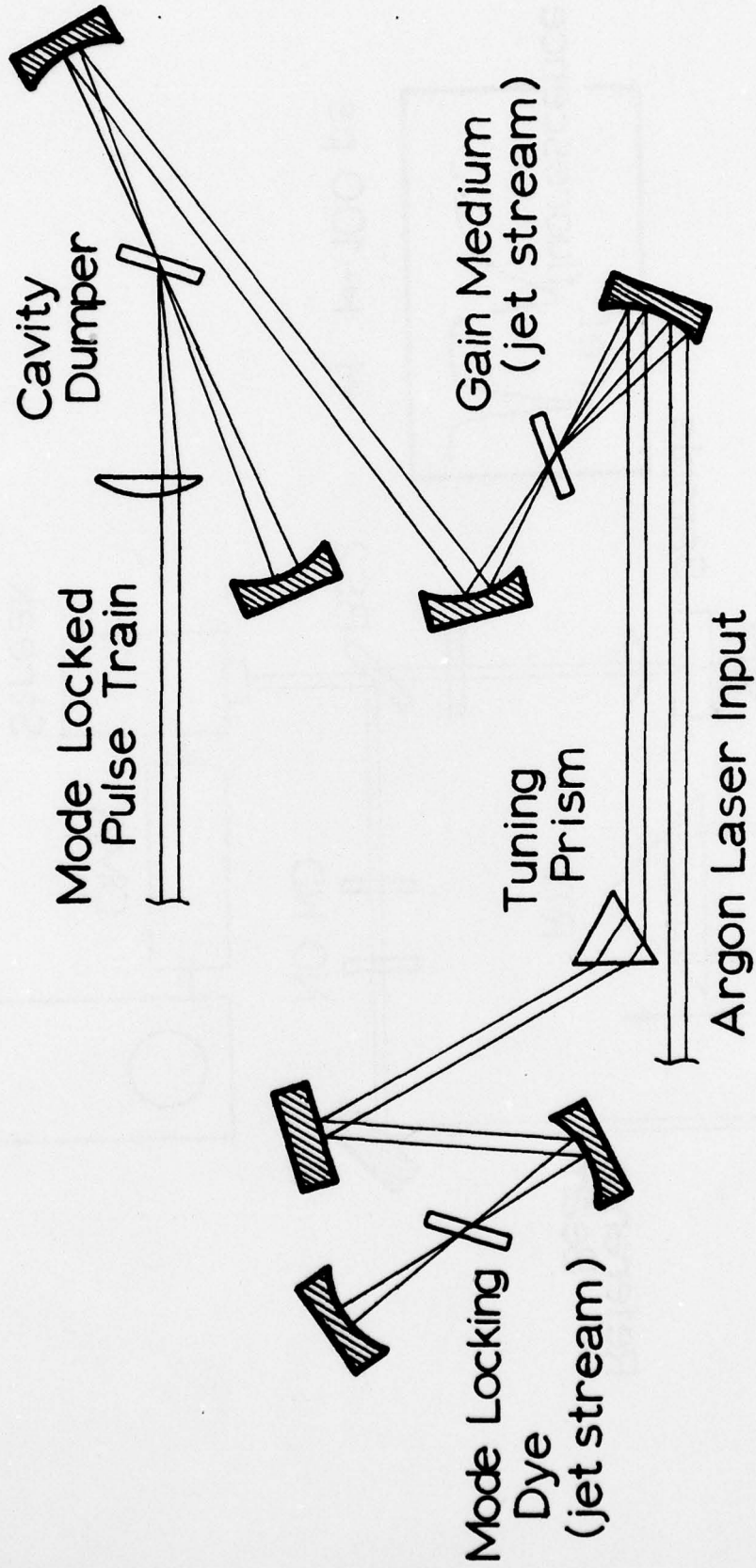


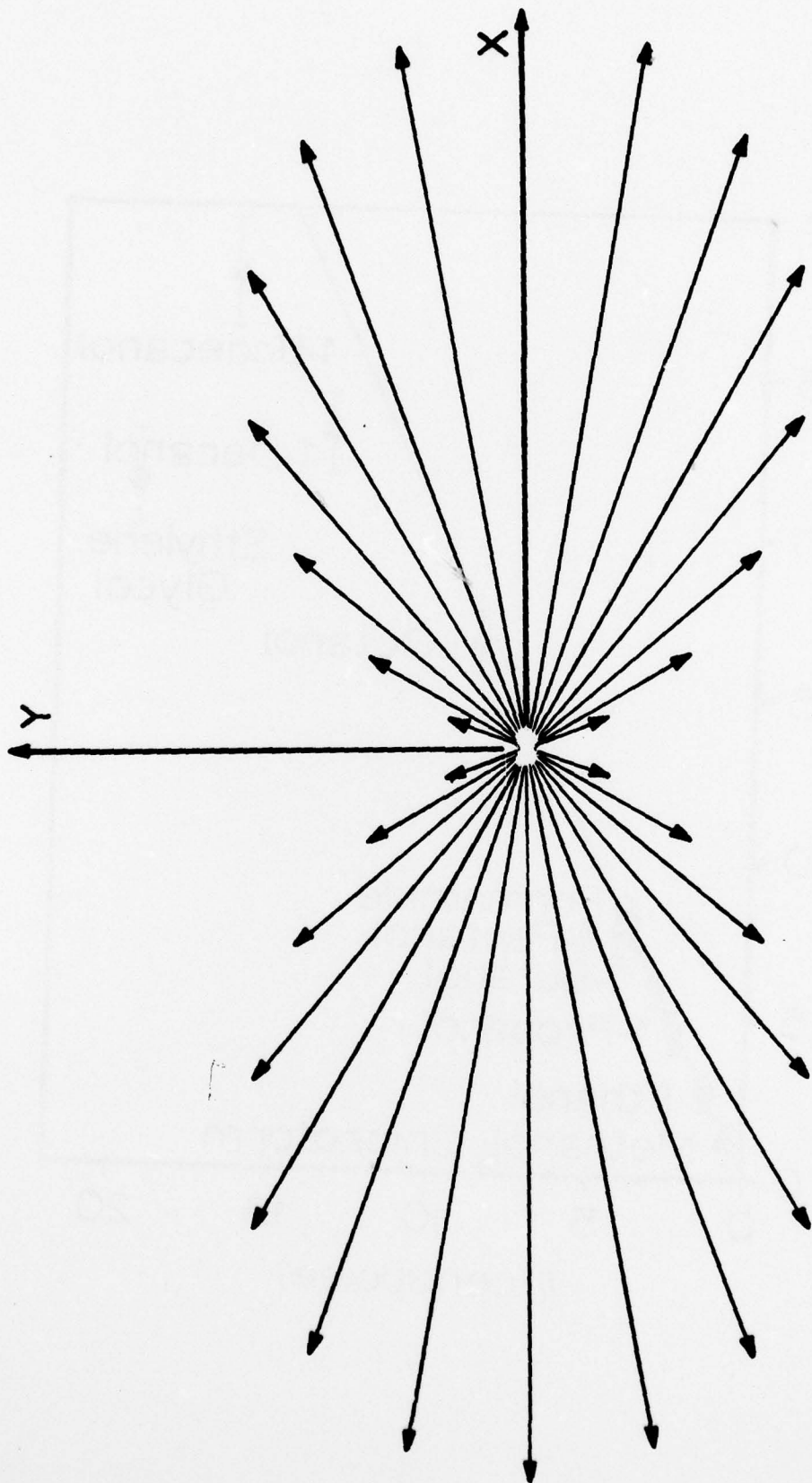
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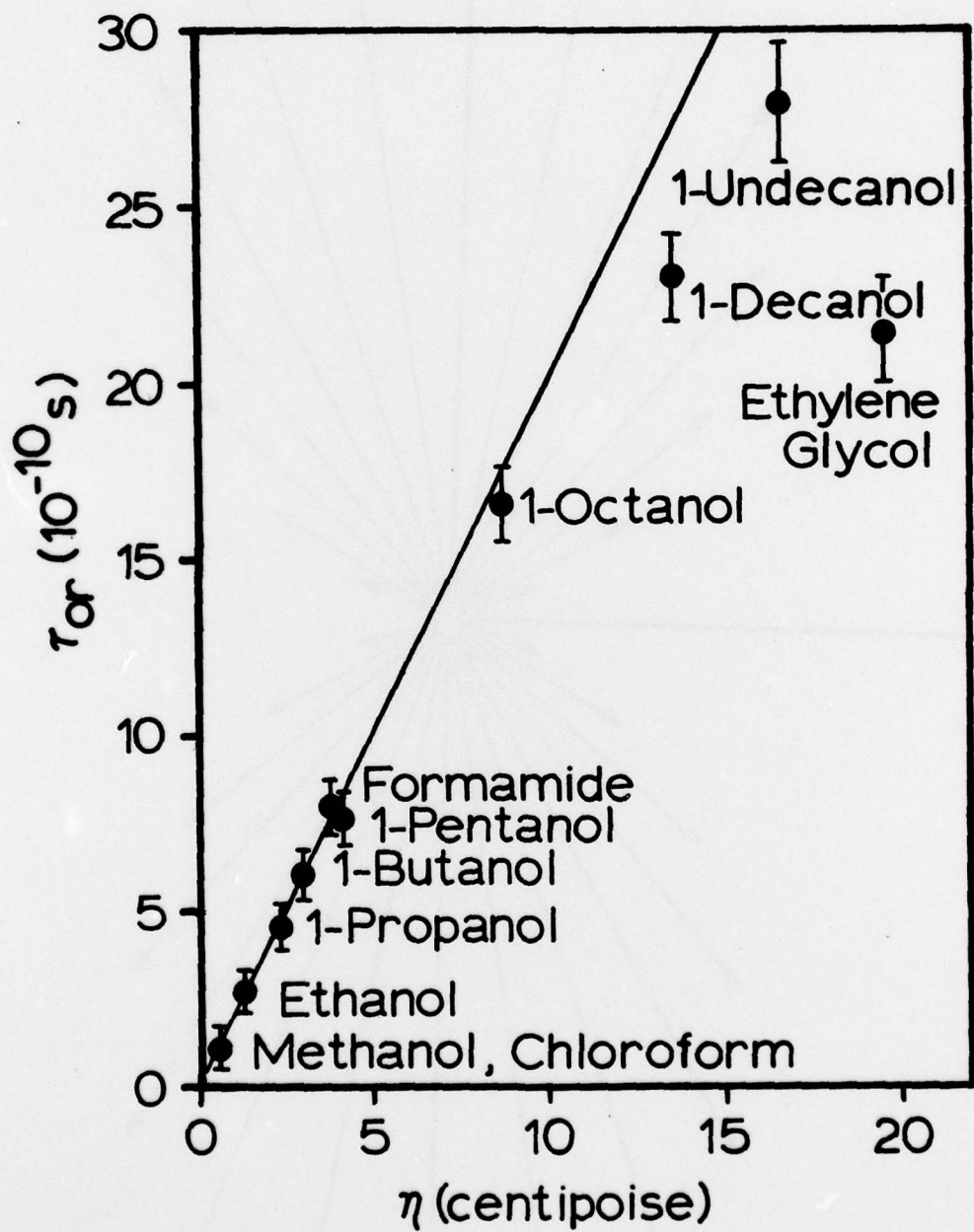


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