Lesson 8
Case Studies
You Will Learn Instrumentation for:

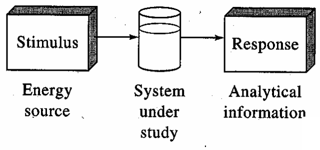
- A. **Laser photochemistry and photoelectrochemistry**
- B. **Scanning Probe Microscopy**
- C. **PID control in chemical engineering**

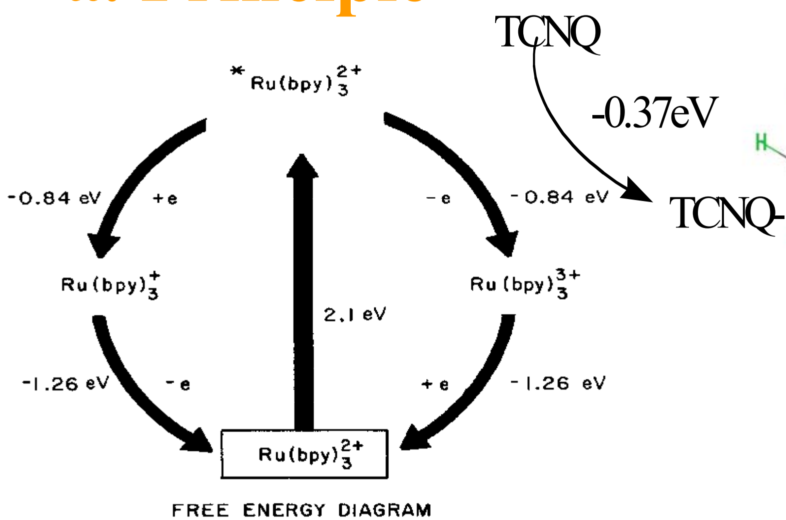
- **As well as data treatment and presentation**

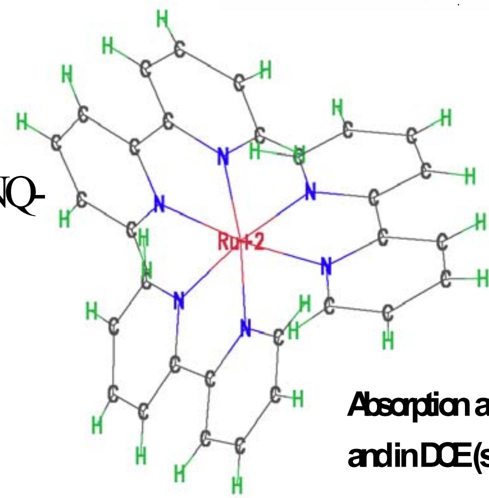
A. Laser photochemistry and photoelectrochemistry

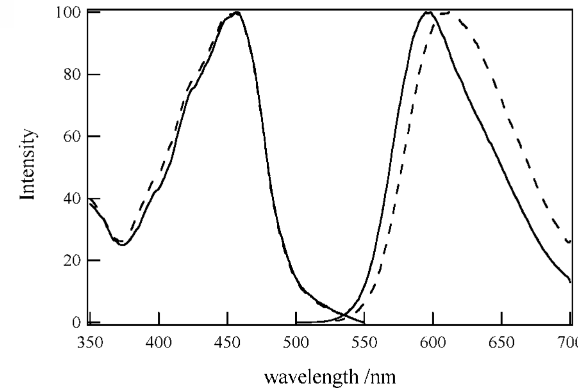
(1) Laser photochemistry

a. Principle









Absorption and fluorescence spectra of $Ru(bpy)_3^{2+}$ in water (dashed line) and in DCE (solid line)

$$S_w \xrightarrow{h\nu} S_w^*$$ Photoexcitation (1)

$$S_w^* \xrightarrow{k_{dec}} S_w$$ Decay of the excited state (2)

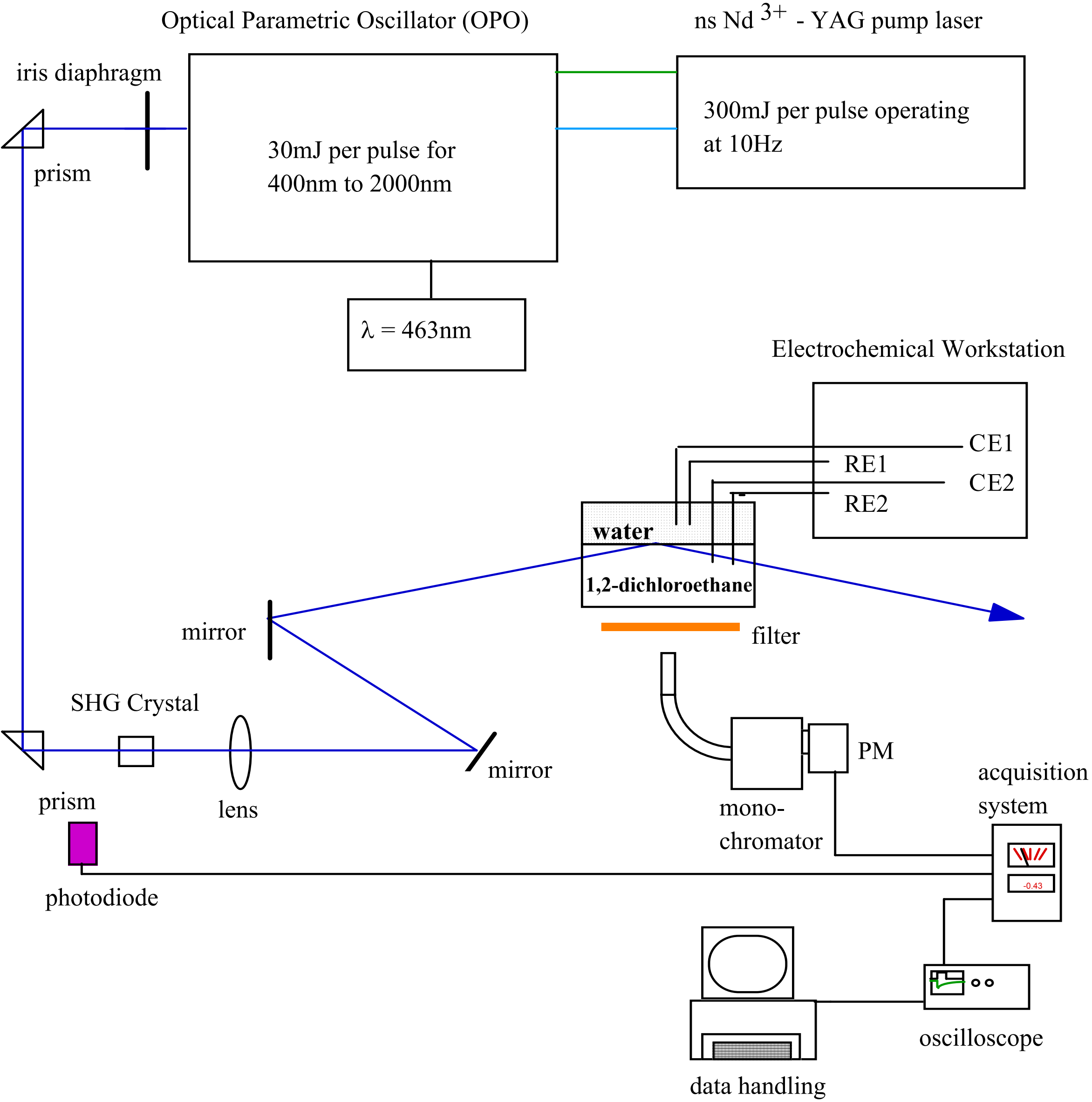
$$S_w^* + Q_o \xrightarrow{k_{et}} \left[S^- - Q^+\right]_{int}$$ Electron transfer (ET) (3)

$$\frac{1}{\tau_{app}} = \frac{1}{\tau_0} + k_q c_q$$ Stern-Volmer Equation to measure ET rate

(1) Laser photochemistry

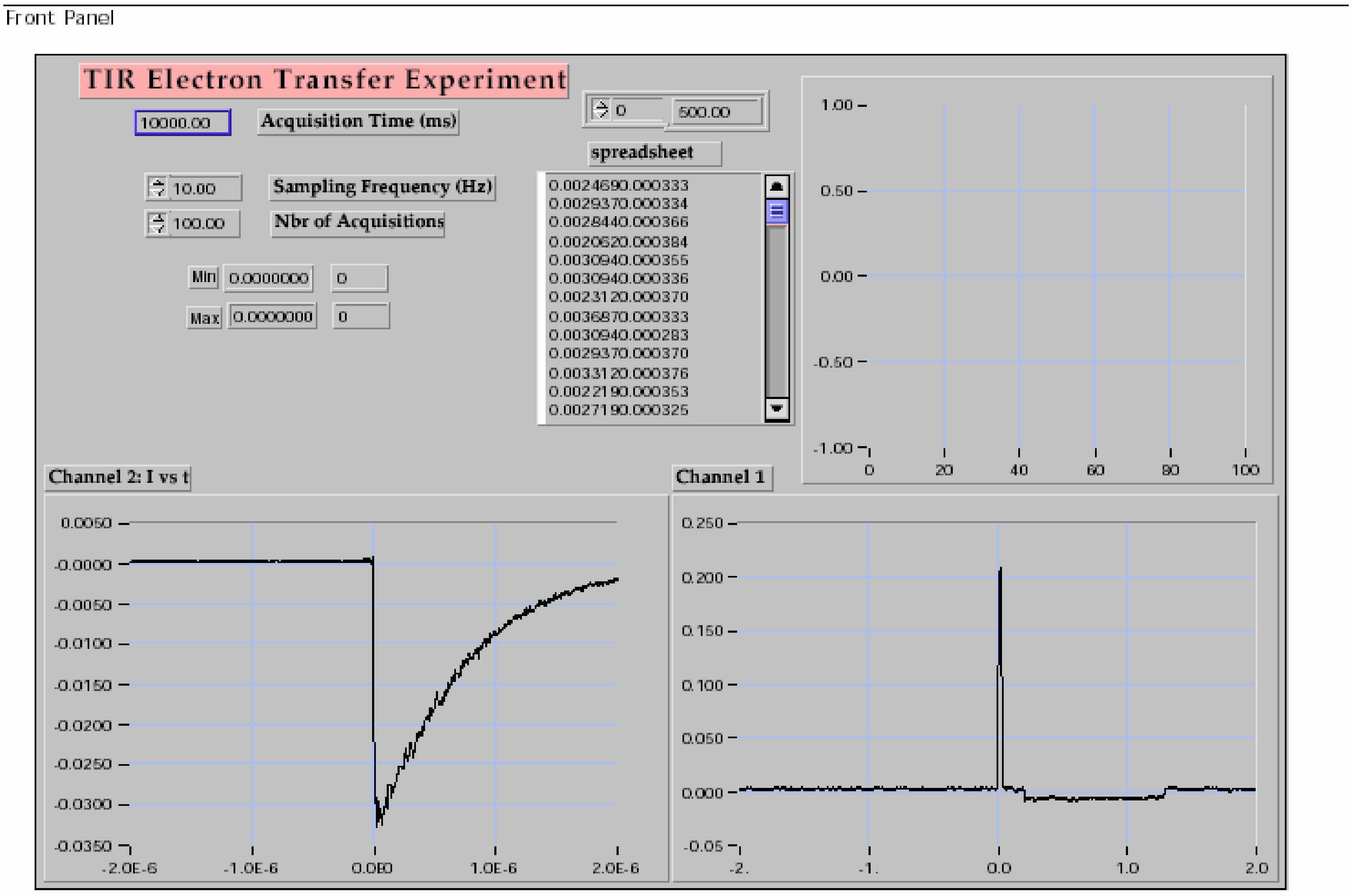
b. Instrumentation

Z. F. Ding, R. G. Wellington, P. F. Brevet, H. H. Girault, "Spectroelectrochemical Studies of Ru(bpy)3(2+) at the Water/1,2-Dichloroethane Interface", *J. Phys. Chem.* 100 (1996) 10658-10663.



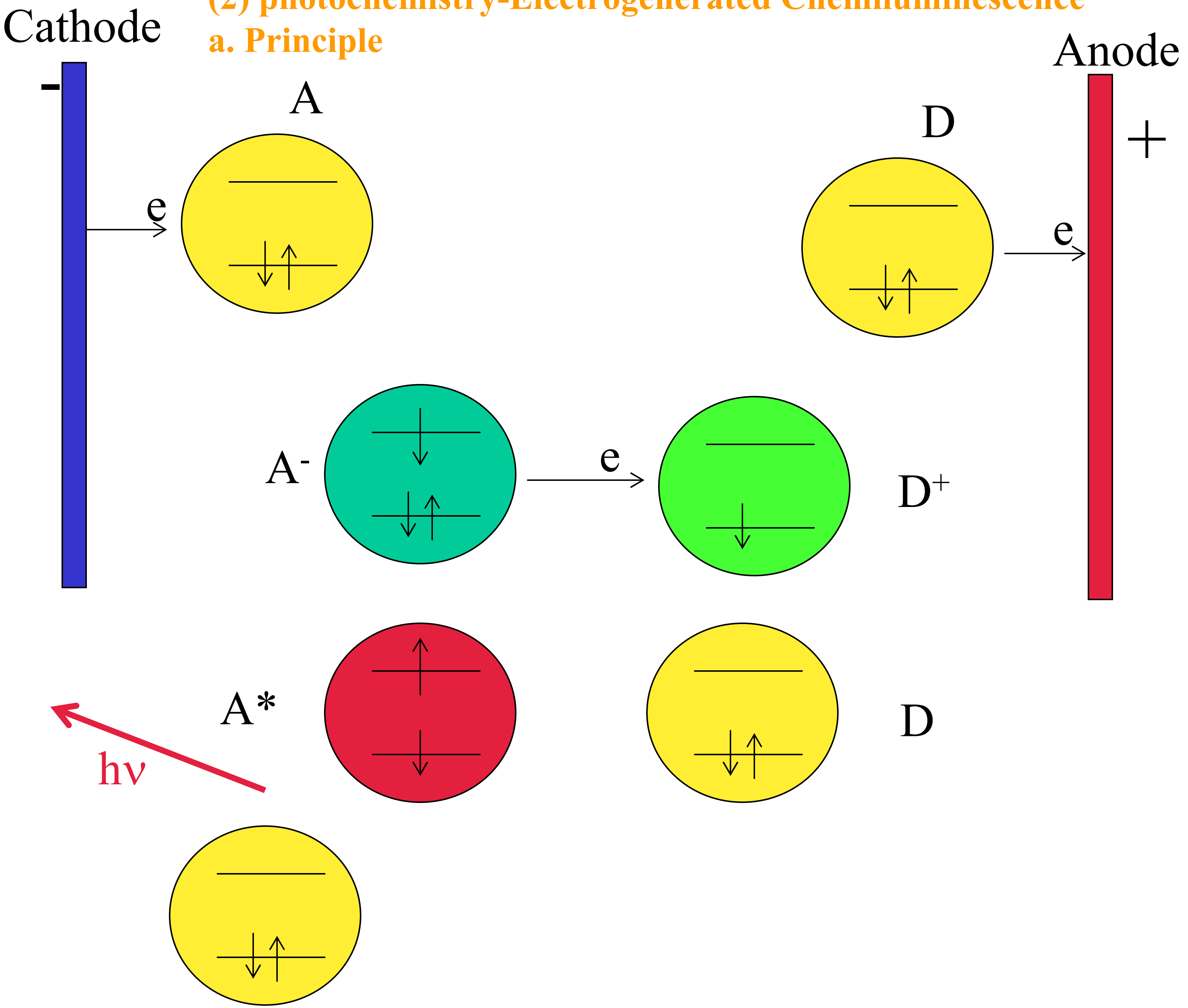
(1) Laser photochemistry
b. LabVIEW Data Acquisition

GPIB Oscilloscope driver

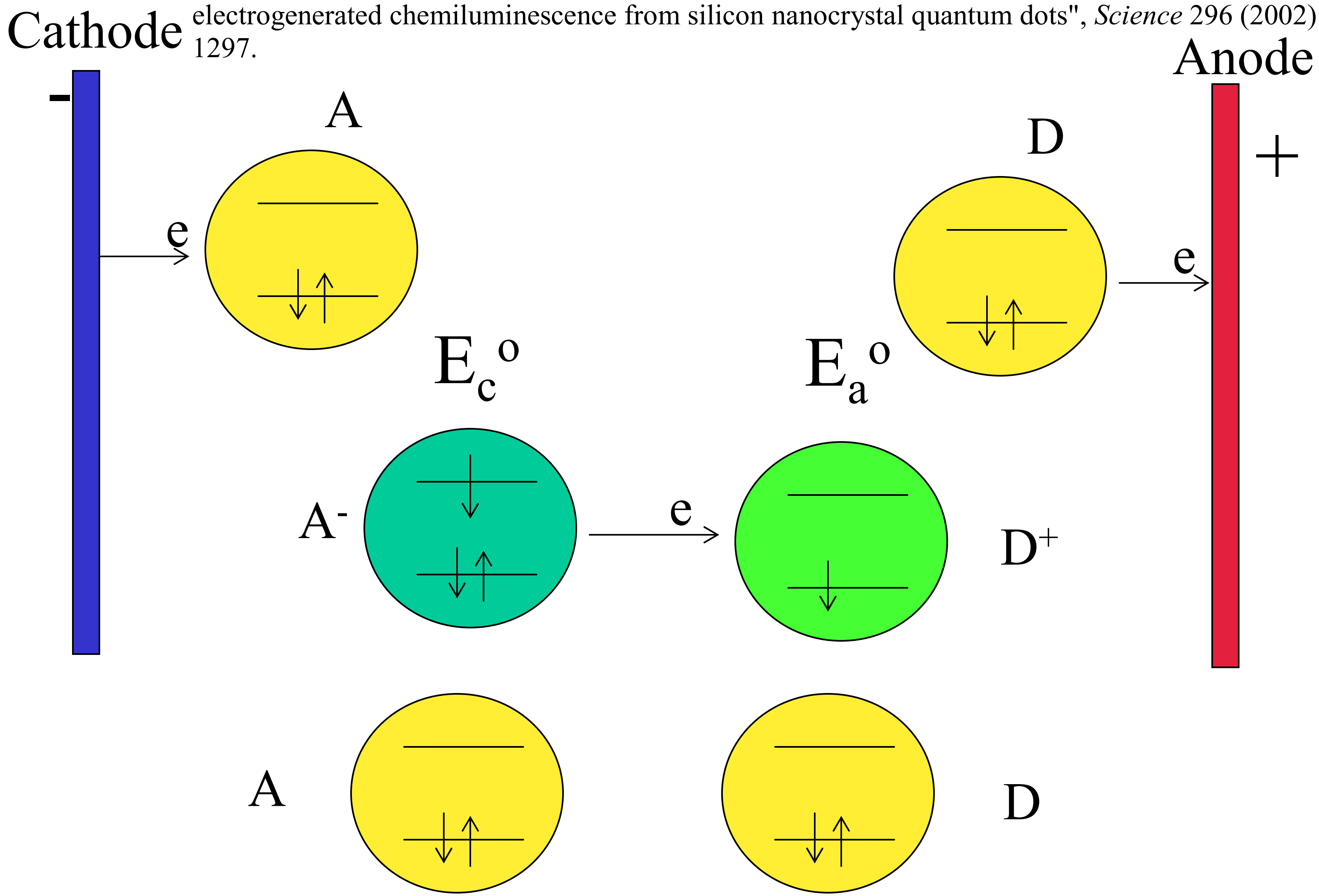


(2) photochemistry-Electrogenerated Chemiluminescence

a. Principle

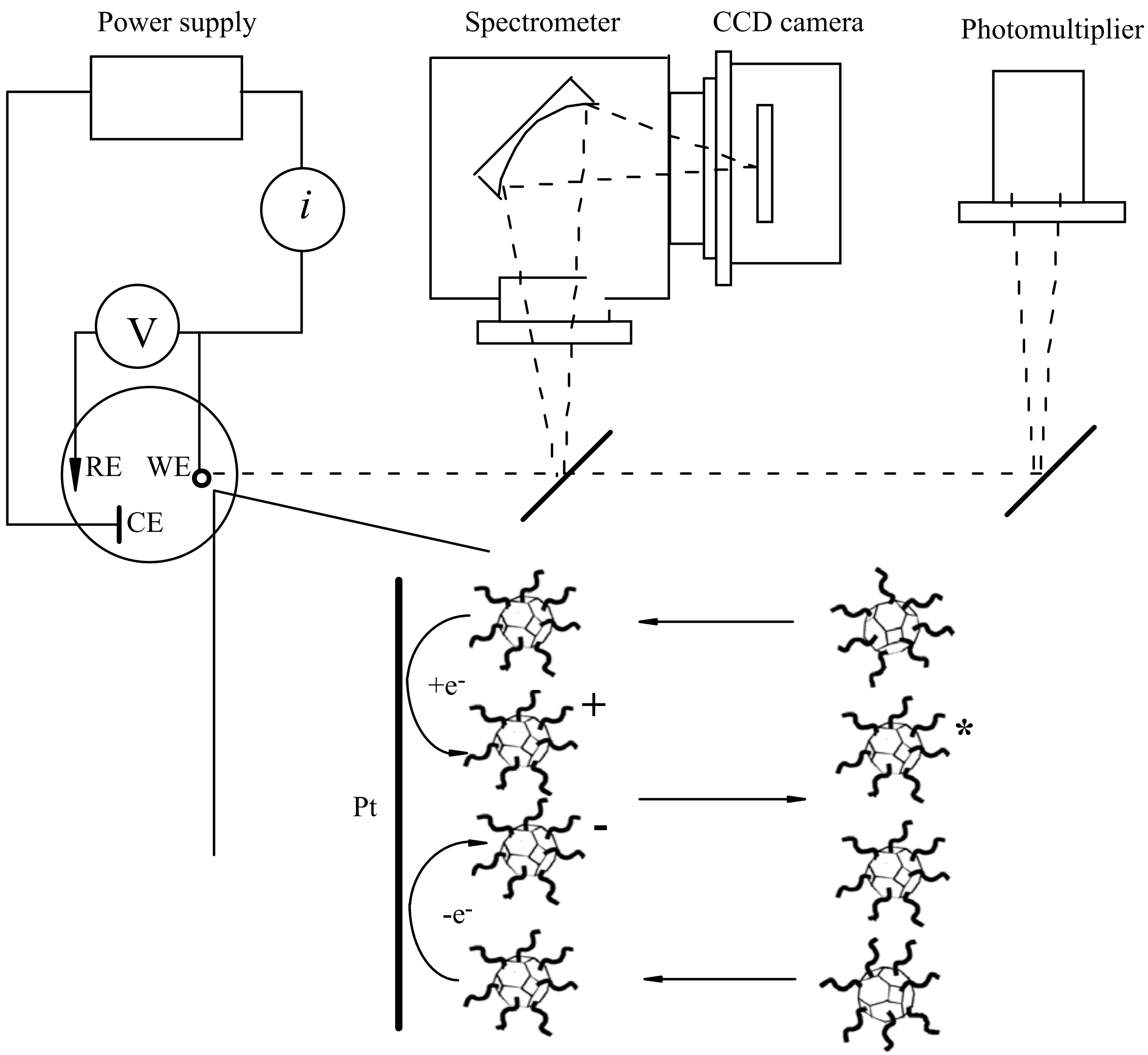


Z. Ding, B. M. Quinn, S. K. Haram, L. E. Pell, B. A. Korgel, A. J. Bard, "Electrochemistry and electrogenerated chemiluminescence from silicon nanocrystal quantum dots", *Science* 296 (2002) 1293-1297.



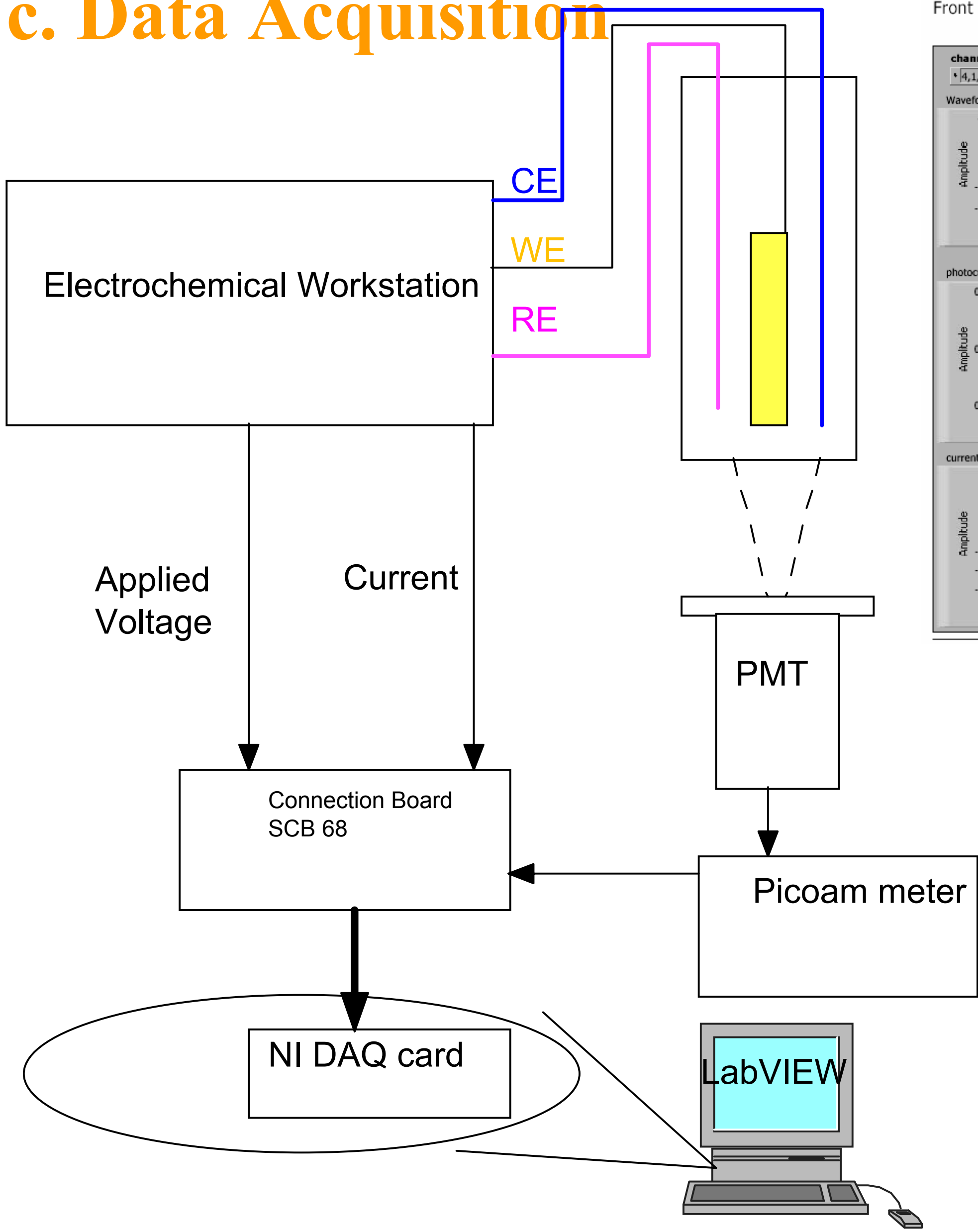
Criterion for excited state formation → $\mathbf{E_a^o - E_c^o - 0.1 > E_S}$

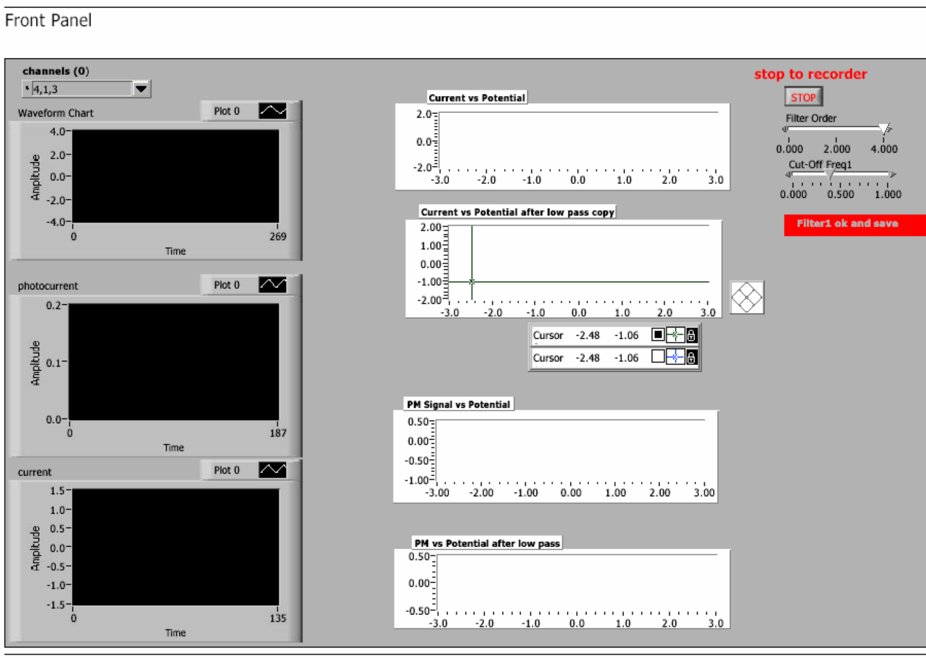
(2) photochemistry-Electrogenerated Chemiluminescence
b. Instrumentation



(2) photochemistry-Electrogenerated Chemiluminescence

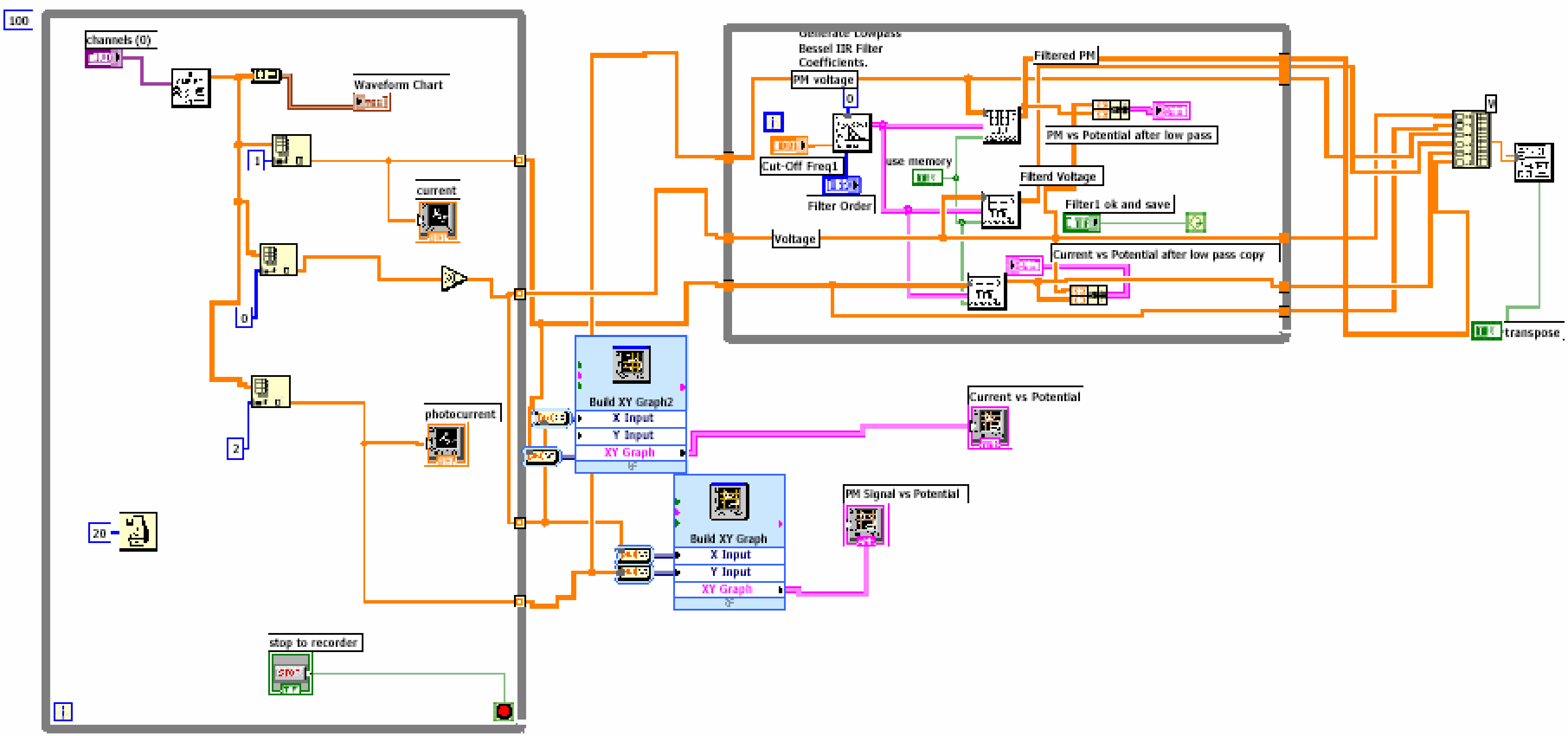
c. Data Acquisition





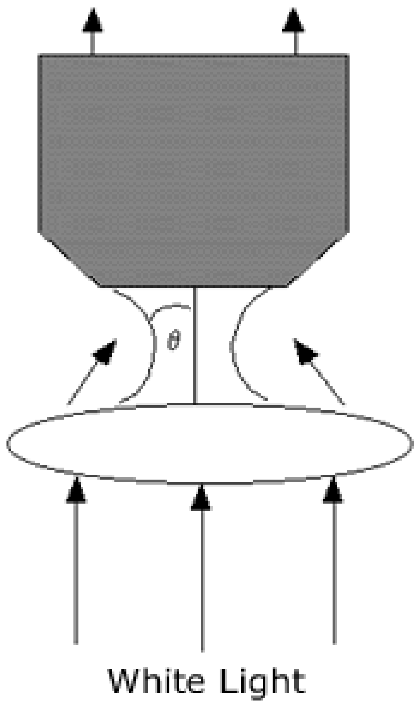
ECL_PMT610A.vi

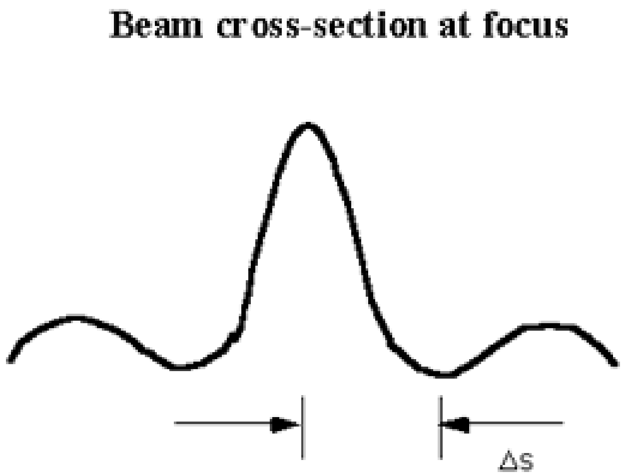
Block Diagram



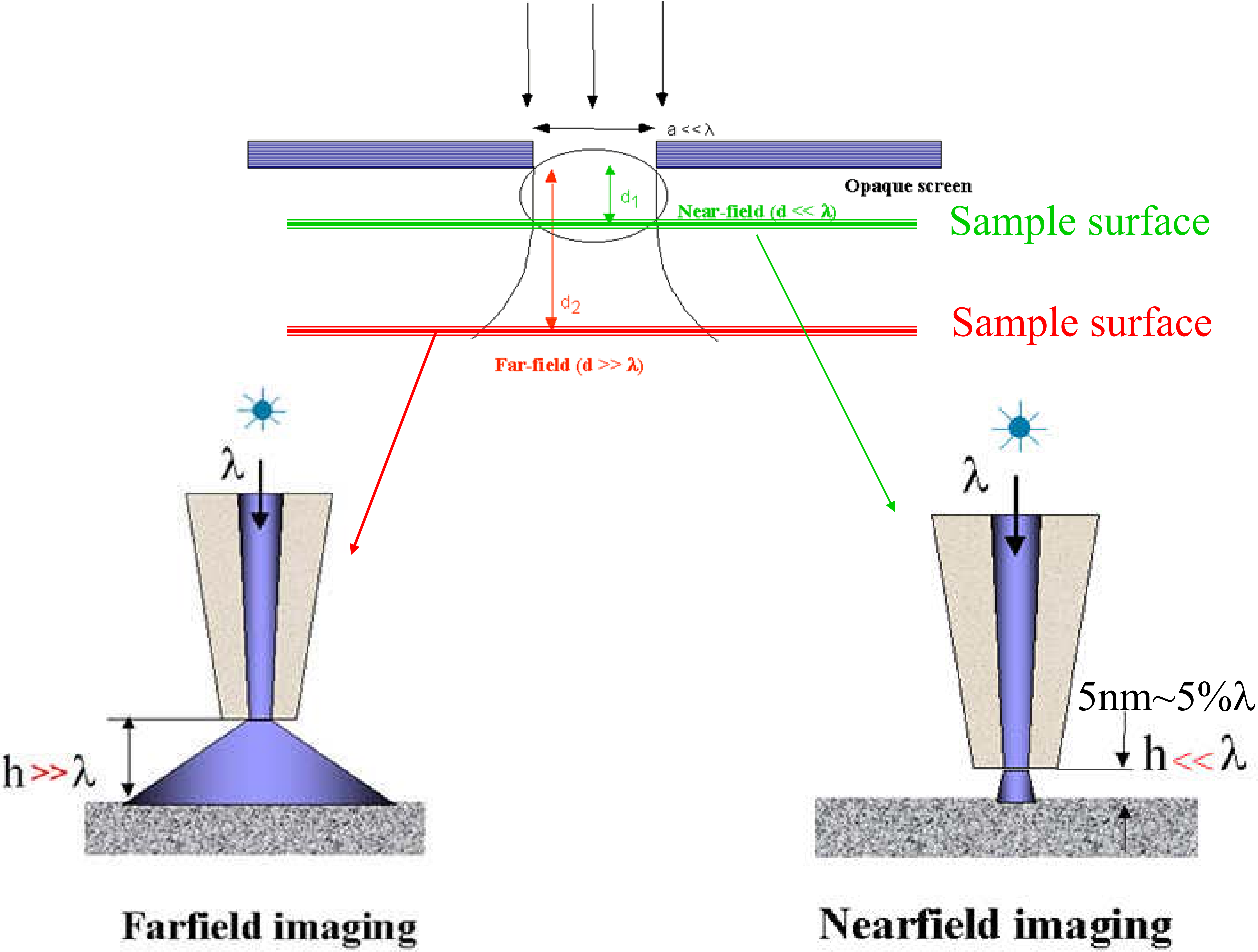
B. Scanning Probe Microscopy
Near-field Scanning Optical Microscopy (NSOM or SNOM)
a. principle

The diffraction limit in conventional microscopy
(Abbe diffraction limit)

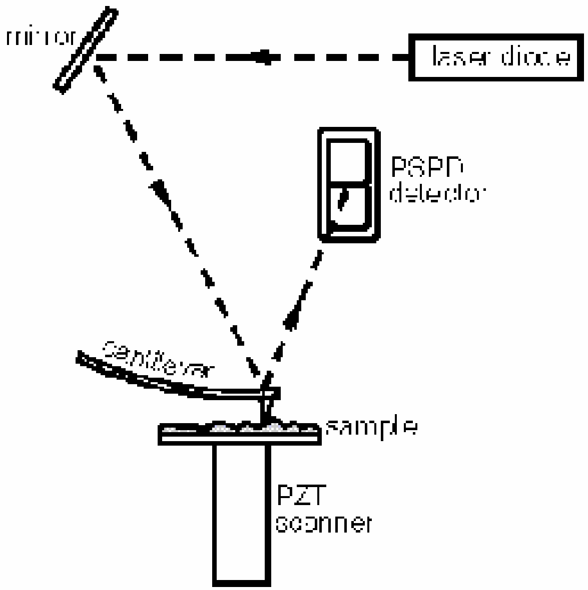


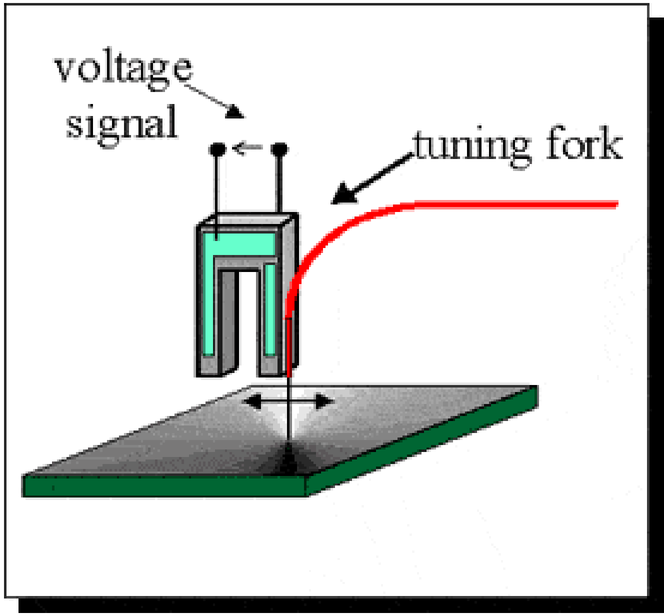


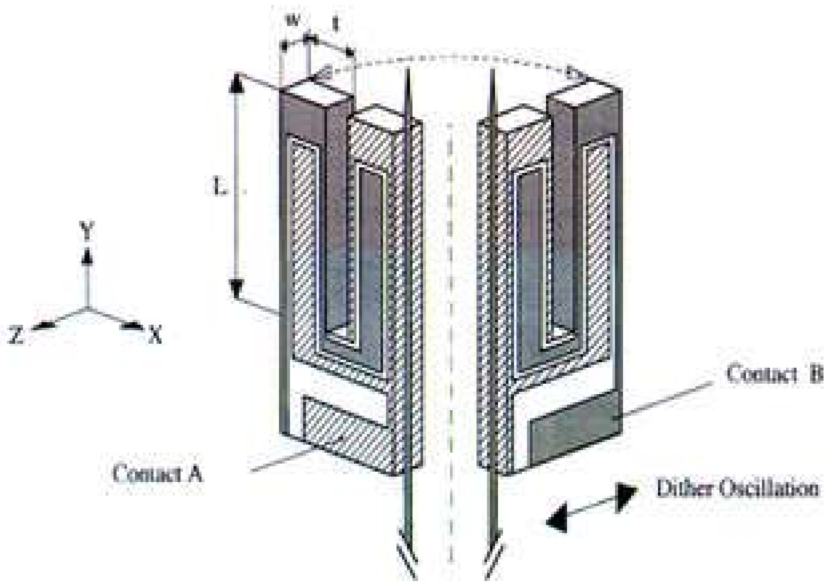
$$\Delta S = \frac{0.61\lambda}{NA(\text{numerical aperture})} = \frac{0.61\lambda}{n\sin\theta} \approx \lambda/2$$

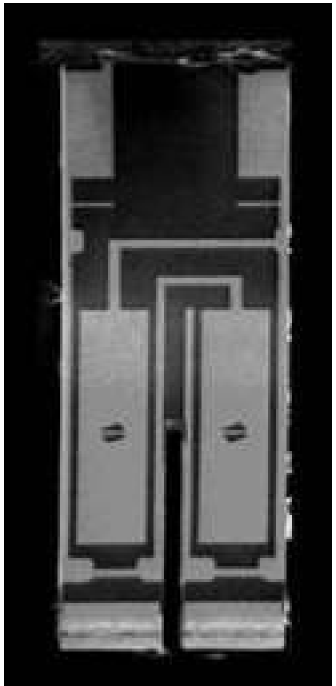

a << λ
Opaque screen
d_1
Near-field (d << λ)
Sample surface
d_2
Sample surface
Far-field (d >> λ)
λ
h >> λ
λ
5nm~5%λ
h << λ
Farfield imaging
Nearfield imaging

Positioning the probe

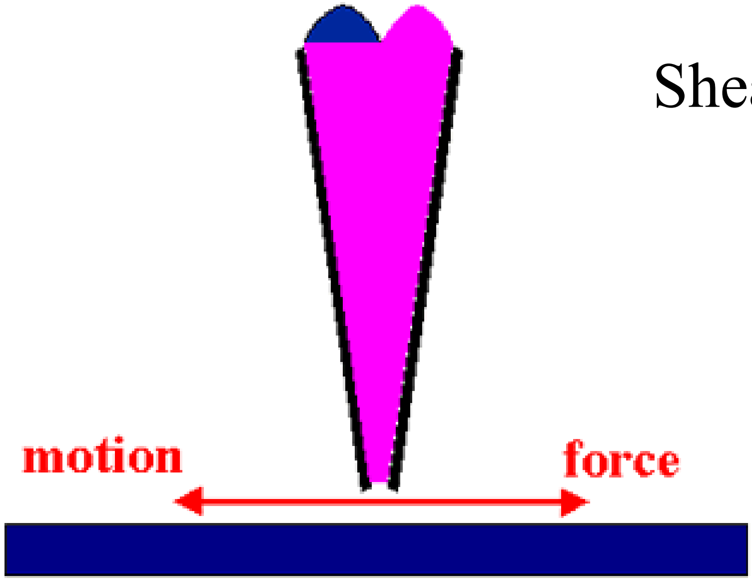


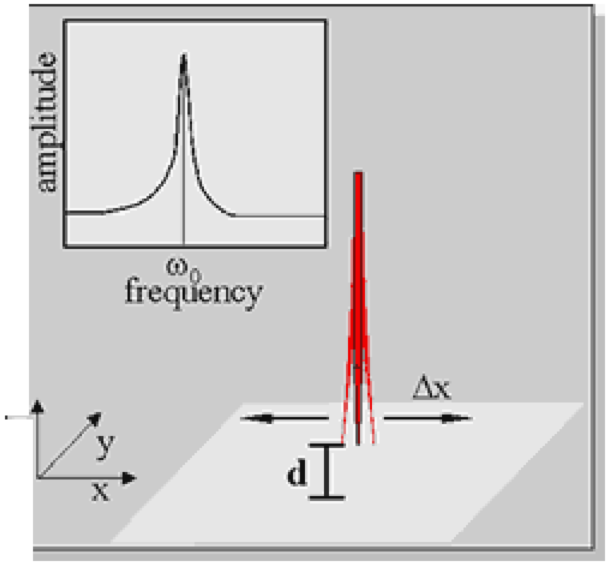


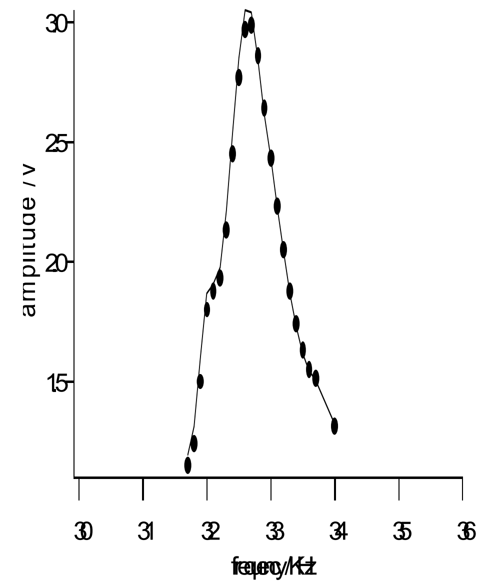




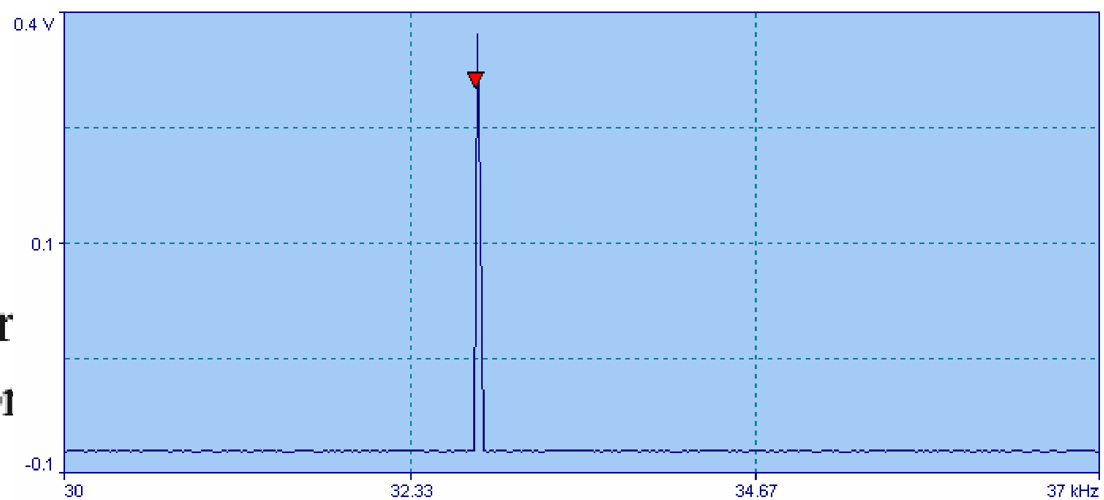
Shear force detection





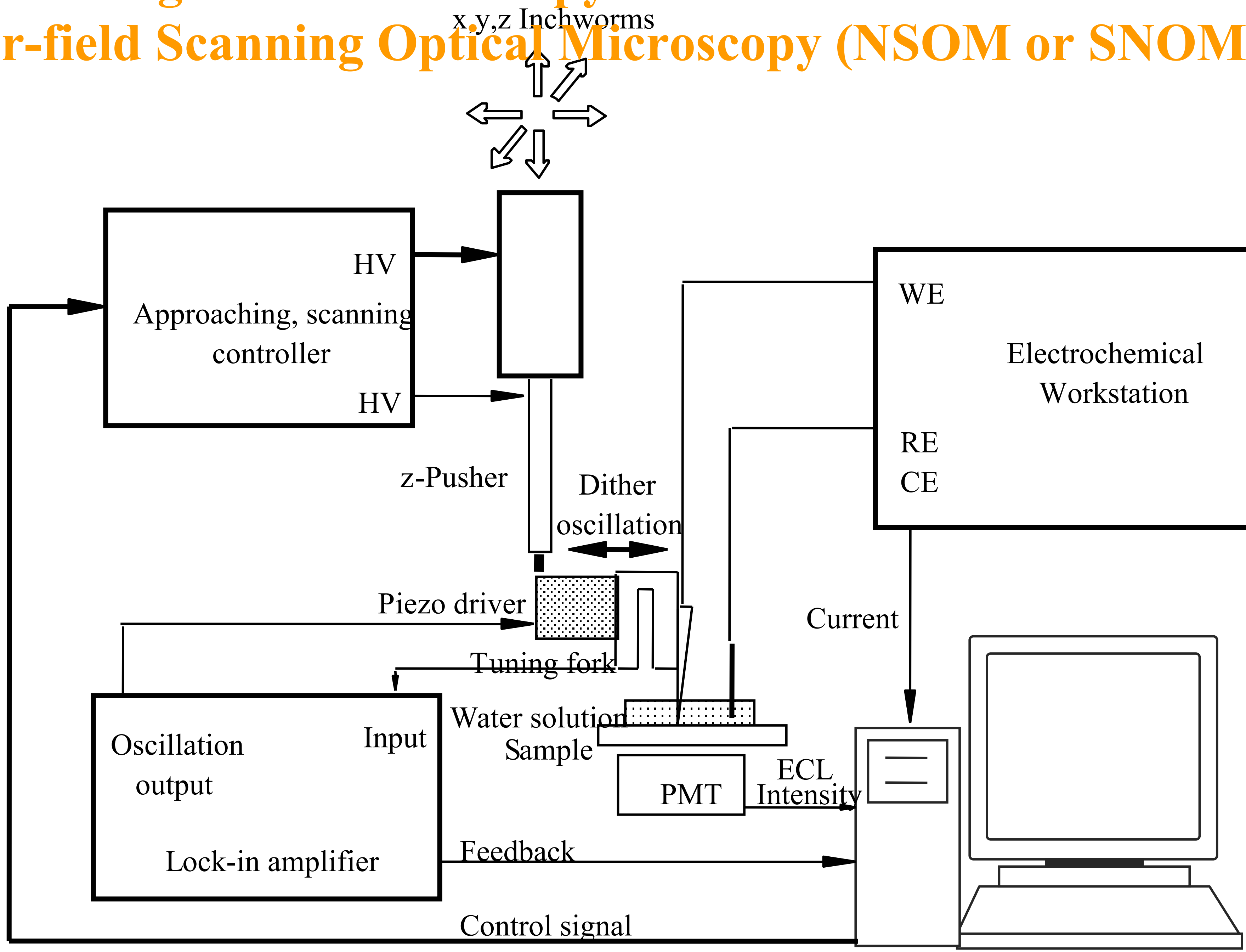


- Lateral vibration of tip at its resonance frequency ω_0
- Measurement of oscillation amplitude Δx or phase φ



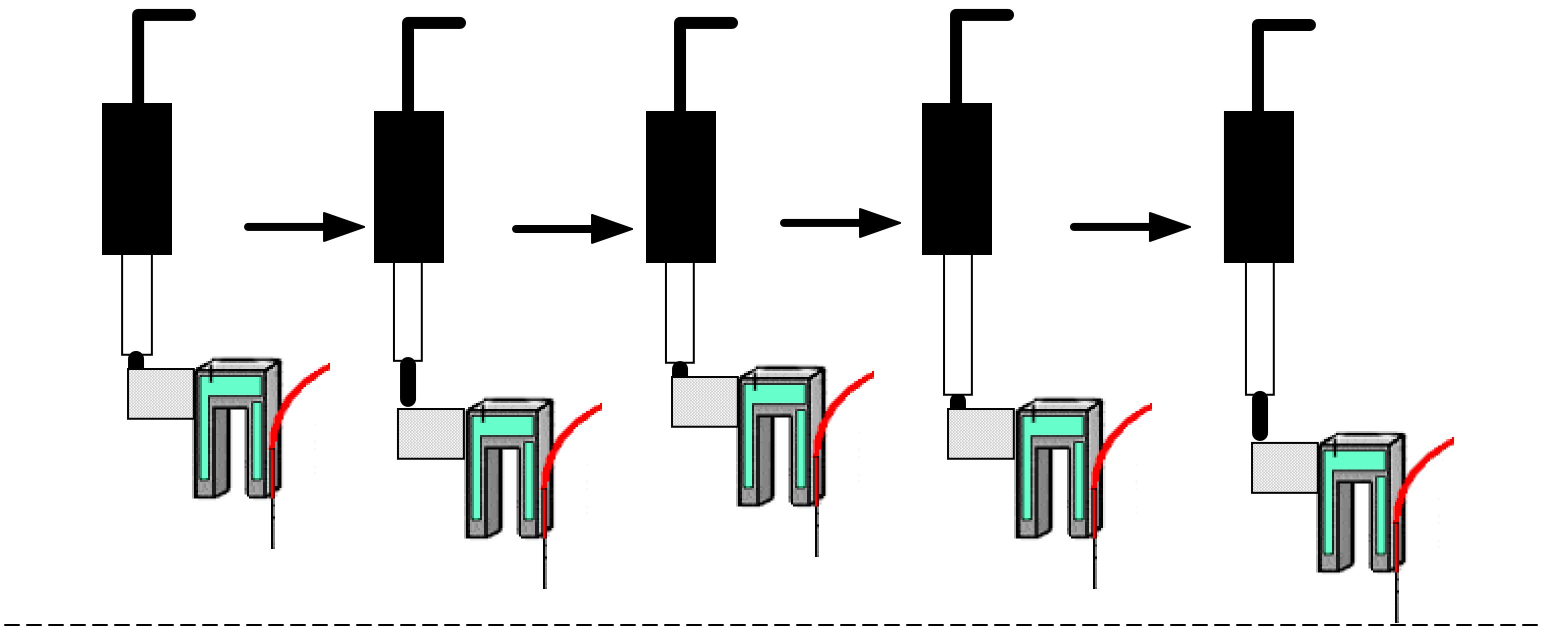
- Oscillation amplitude and phase are changed by shear forces and are a measure for the tip-sample distance d

B. Scanning Probe Microscopy
Near-field Scanning Optical Microscopy (NSOM or SNOM)



positioning of the tip to the substrate

P-F-6.4μm P-W-6.4μm I-F-6.4μm P-F-6.4μm



Y. Zu, Z. Ding, J. Zhou, Y. Lee, A. J. Bard, "Scanning Optical Microscopy with an Electrogenerated Chemiluminescent Light Source at a Nanometer Tip", *Anal. Chem.* 73 (2001) 2153-2156

B. Scanning Probe Microscopy
Near-field Scanning Optical Microscopy (NSOM or SNOM)
b. Instrumentation

Shear-force device: tuning fork driven by a lock-in amplifier

Feedback: lock-in amplifier

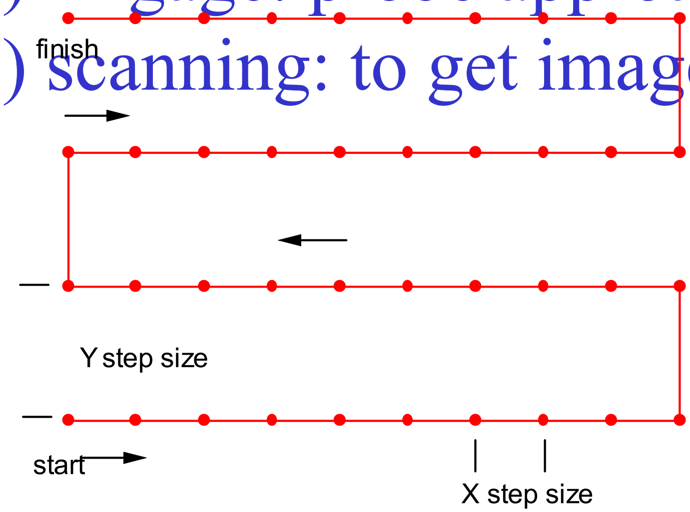
micro-positioner: 1.inchworm motor stage+controller

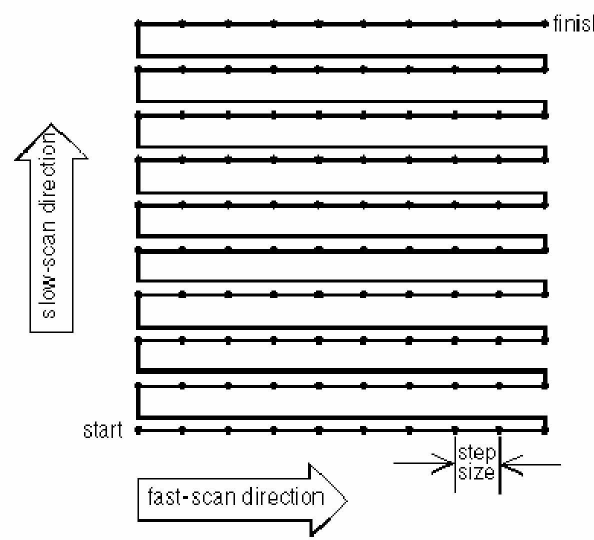
2. Piezo pusher+controller(using DAQ out)

Two processes

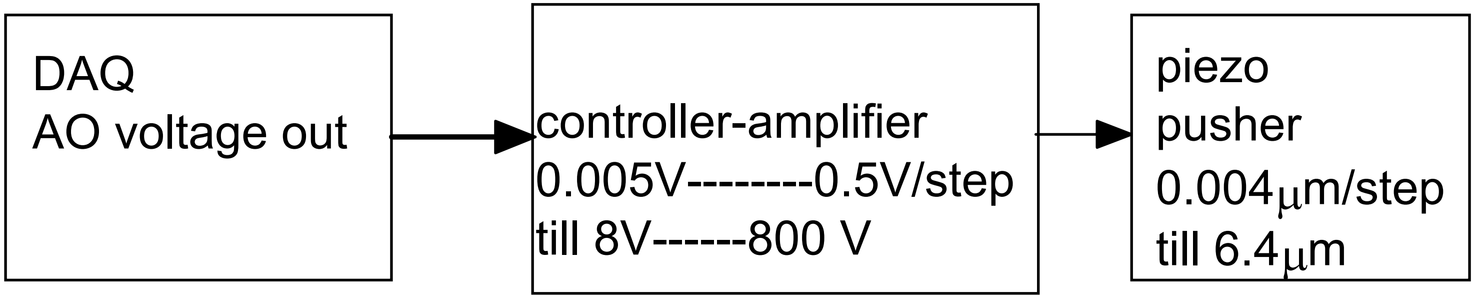
(1) Engage: probe approaches ... ear-field

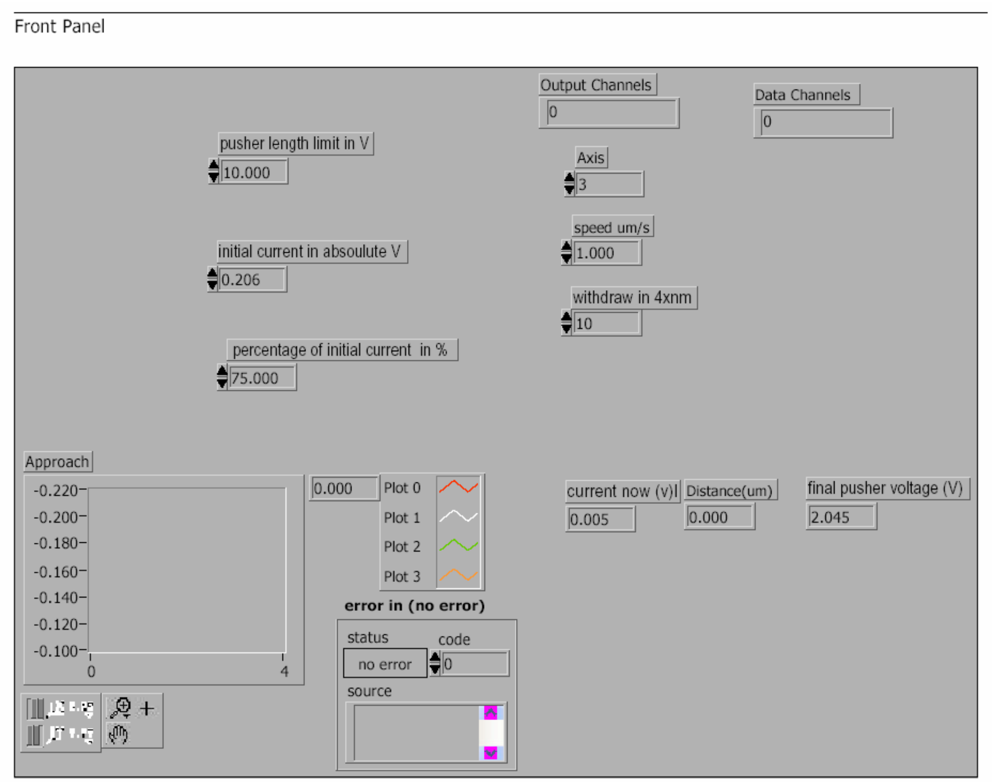
(2) scanning: to get images

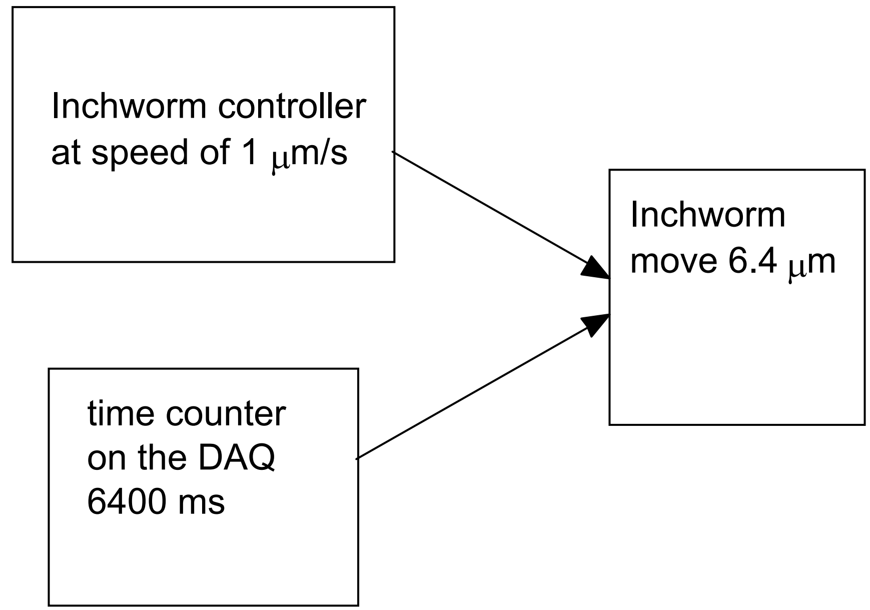




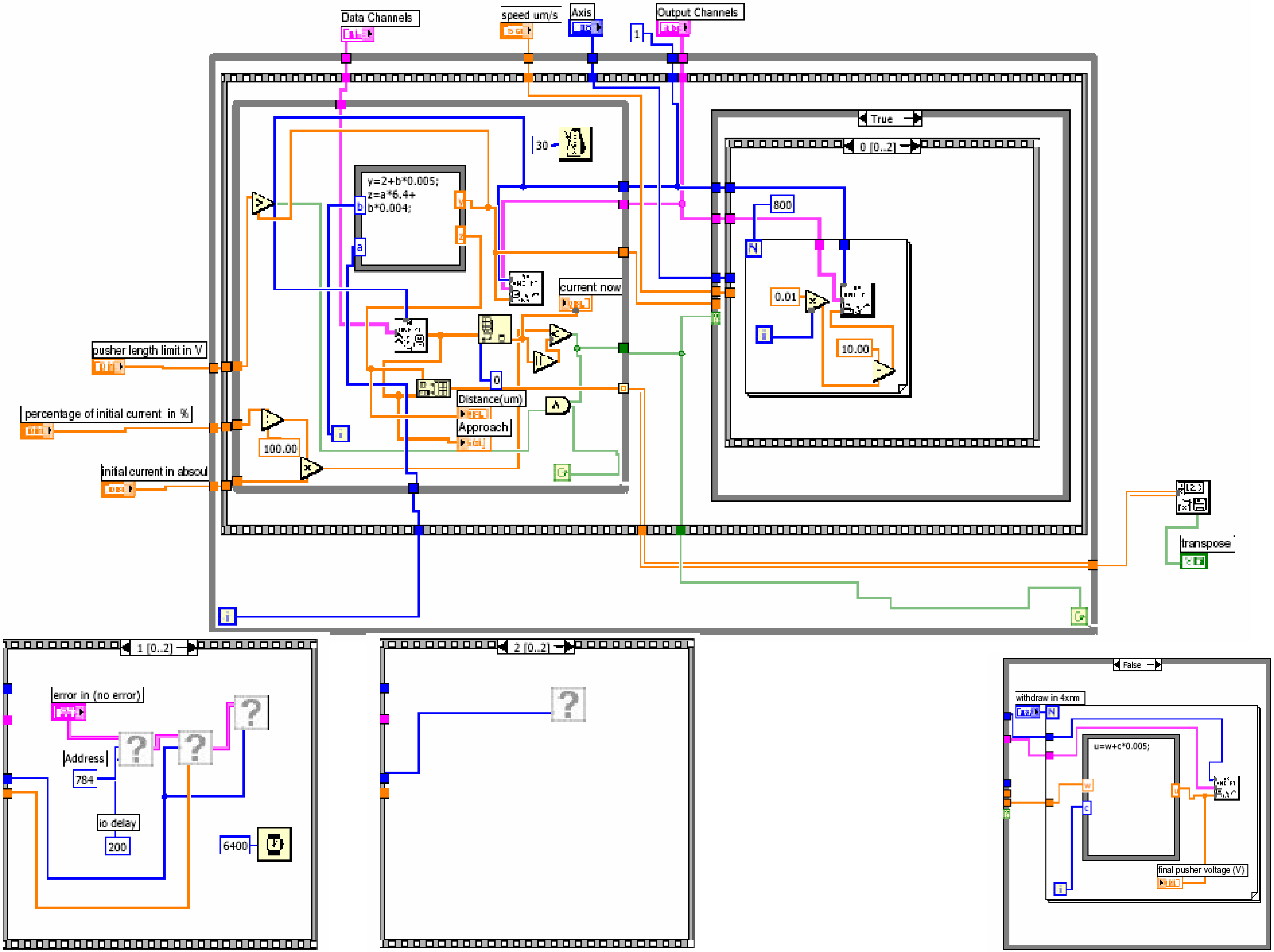
B. Scanning Probe Microscopy
Near-field Scanning Optical Microscopy (NSOM or SNOM)
b. Programming in LabVIEW



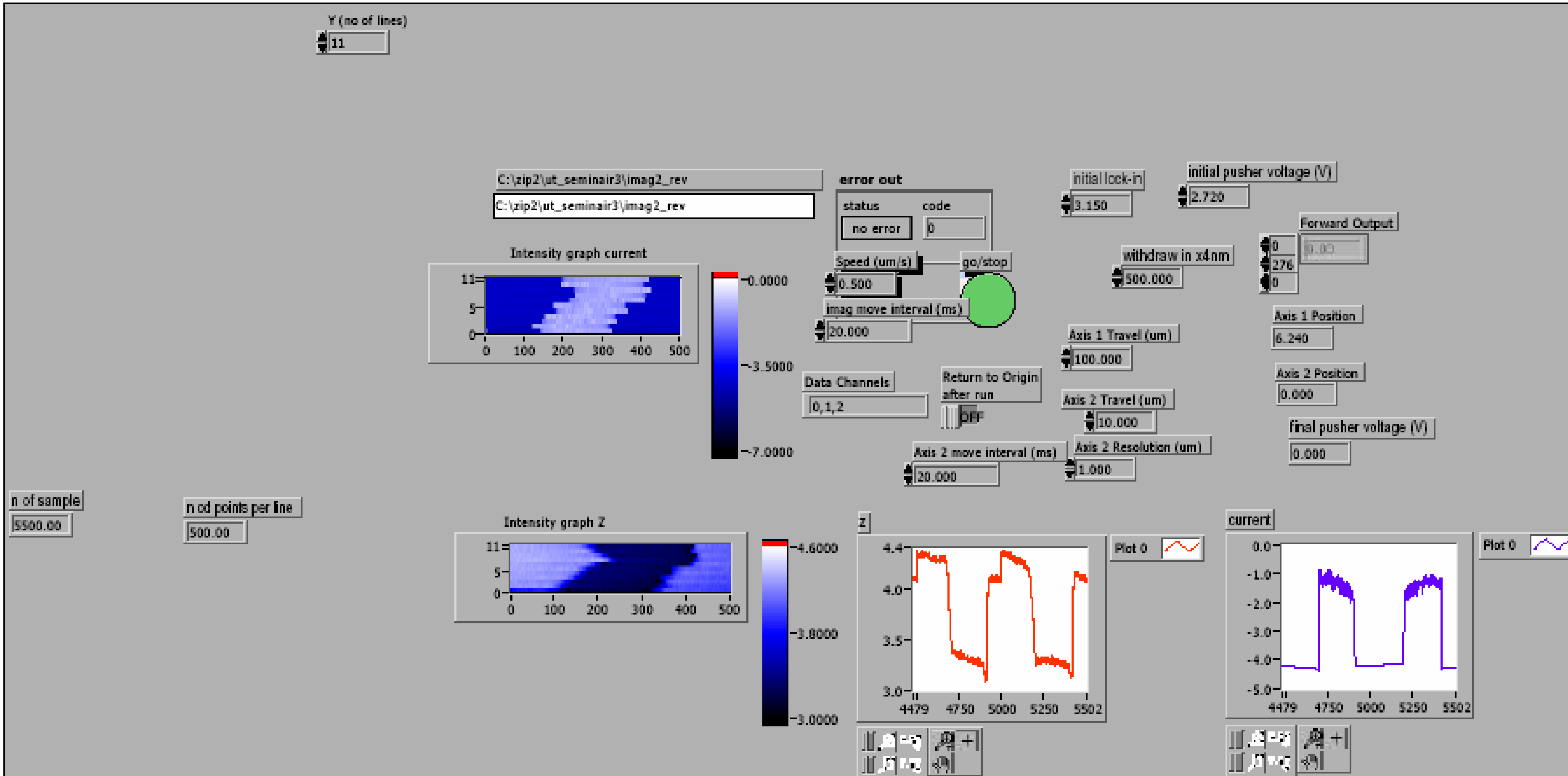


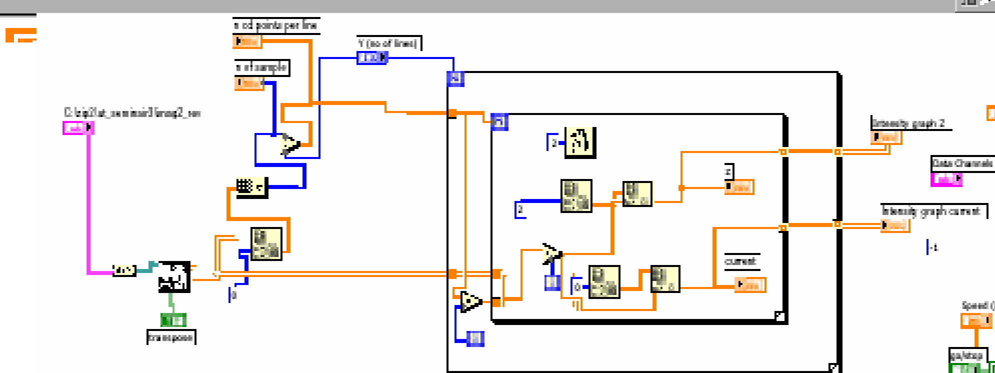


Finally withdraw 40 nm


Data Channels
speed um/s
Axis
Output Channels
1
True
0 [0..2]
30
y=2+b*0.005;
z=a*6.4+
b*0.004;
800
current now
0.01
10.00
pusher length limit in V
percentage of initial current in %
100.00
initial current in absoul
0
Distance(um)
Approach
transpose
1 [0..2]
error in (no error)
Address
784
io delay
200
6400
2 [0..2]
False
withdraw in 4xnm
u=w+c*0.005;
final pusher voltage (V)

Let's play imag_demo.vi





C. PID control in chemical engineering

In the PID (Proportional-Integral-Derivative) controller, the setpoint is compared to the process variable to obtain the error

$$e = SP - PV.$$

You can then calculate the controller action theoretically as

$$u(t) = K_c\left(e + \frac{1}{T_i}\int_0^t e\,dt + T_d\frac{de}{dt}\right),$$

where K_c is controller gain. If the error and the controller output have the same range, that is –100% to 100%, controller gain is the reciprocal of *proportional band*. T_i is the integral time in minutes (also called *reset time*), and T_d is the derivative time in minutes (also called *rate*). The proportional action is

$$u_p(t) = K_c e,$$

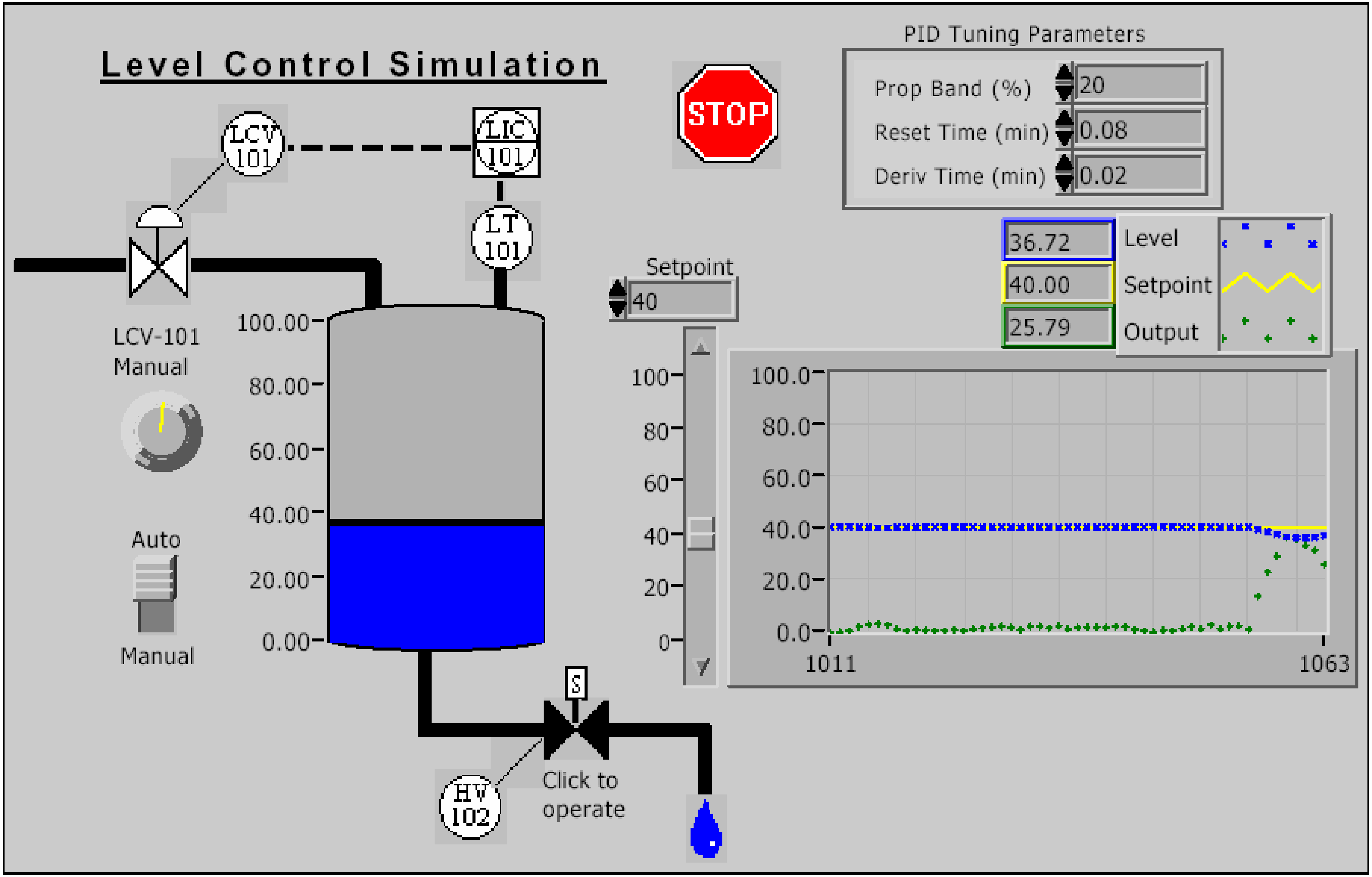
the integral action is

$$u_I(t) = \frac{K_c}{T_i}\int_0^t e\,dt,$$

and the derivative action is

$$u_D(t) = K_c T_d\frac{de}{dt}.$$

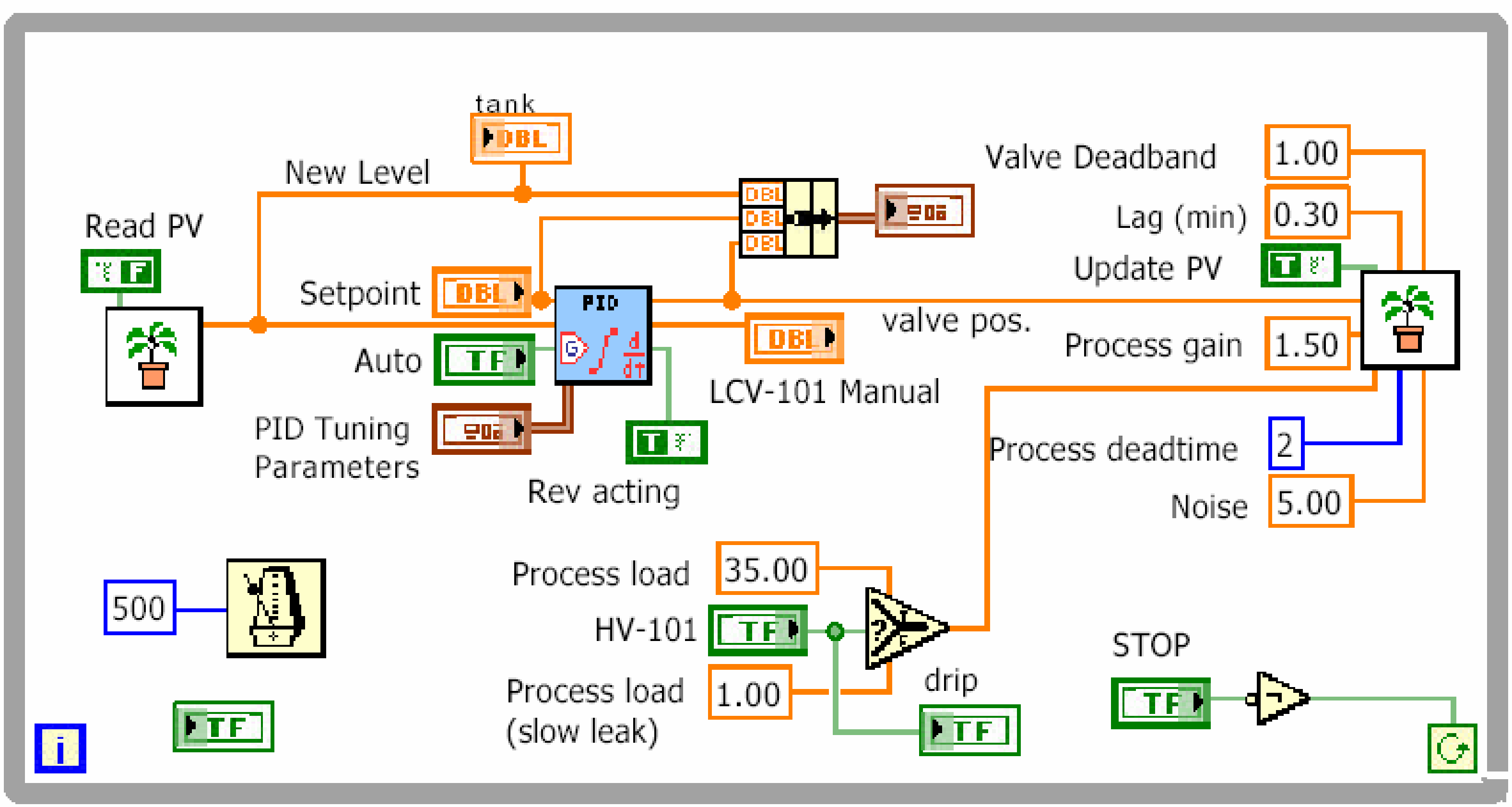
Front Panel



Level Control Simulation
LCV 101
LIC 101
LT 101
STOP
PID Tuning Parameters
Prop Band (%)
20
Reset Time (min)
0.08
Deriv Time (min)
0.02
LCV-101 Manual
Auto
Manual
Setpoint
40
36.72
Level
40.00
Setpoint
25.79
Output
100.00
80.00
60.00
40.00
20.00
0.00
100
80
60
40
20
0
100.0
80.0
60.0
40.0
20.0
0.0
1011
1063
S
HV 102
Click to operate

The Plant Simulator subVI, which simulates this process, reads and delays the previous valve position and scales it according to the process gain. The gain represents how fast the tank fills versus the position of the valve. The process load value depends on the state of HV-101, the drain valve. When you open the valve, the tank level drops.

Block Diagram



PID application to Scanning Probe Microscopy

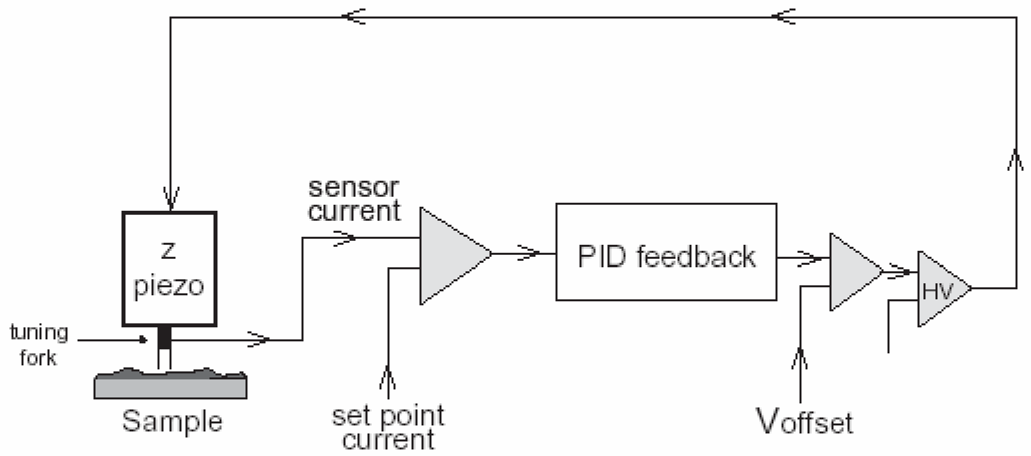


Figure 4-1. Feedback loop.

- Proportional gain responds quickly to small features but is not optimized to respond to large features.
- Integral gain controls the response time of the piezo to large, slow sensor changes. If set too high, integral gain can result in oscillation or noise in the image. This oscillation will be apparent on the oscilloscope signals.
- Derivative gain tends to reduce oscillation but may amplify high-frequency noise.

References

1. Z. F. Ding, R. G. Wellington, P. F. Brevet, H. H. Girault, "Spectroelectrochemical Studies of Ru(bpy)3(2+) at the Water/1,2-Dichloroethane Interface", *J. Phys. Chem.* 100 (1996) 10658-10663.

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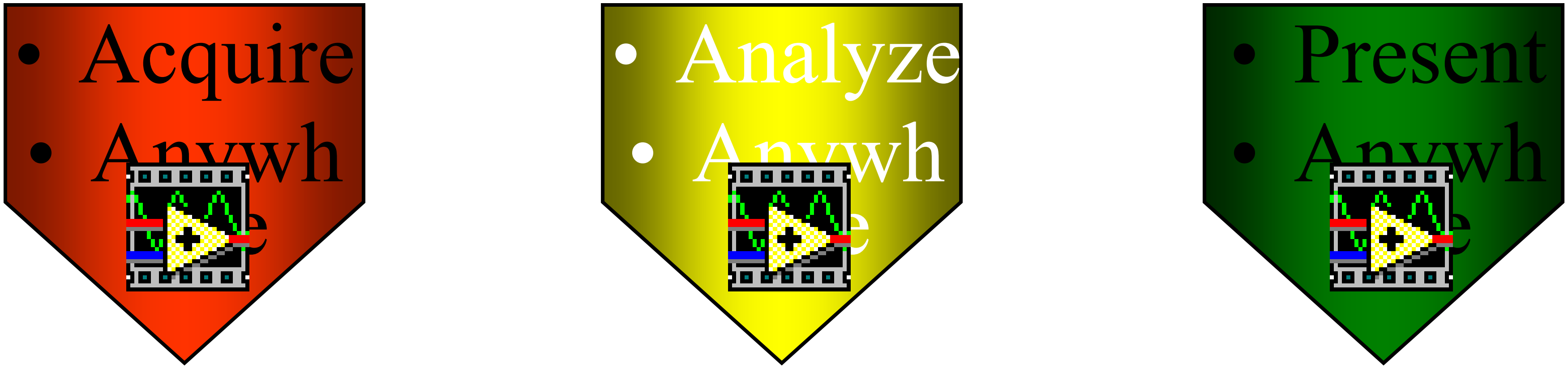
Summary



In-situ reaction monitoring, electrochemistry, spectroelectrochemistry can easily be done.