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Dynamics of photoexcited states in polyaniline

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The Ohio State University, 1993
DYNAMICS OF PHOTOEXCITED STATES IN POLYANILINE

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy
in the Graduate School of The Ohio State University

By
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1993

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To My Parents
ACKNOWLEDGEMENTS

I express sincere appreciation to my advisor Professor Arthur Epstein for his guidance and support throughout the research. Gratitude is expressed to Professor Terry Gustafson, who kindly allowed me to work in his lab and enlightened me through many discussions.

For the years spent in the optics labs, I feel fortunate to have had good colleagues who are also nice friends: Dr. John Ginder, Dr. Richard McCall, Kim Coplin, Jim Blatchford, Scott Jessen, Liang-bih Lin, Randy Kohlman, Dr. Gregg Roe, Dr. Jingmin Leng, and Larry Pelz. I thank those in the Chemistry Dept.; Ronda, Jeff, Roger, Lisa, Kayla, James, Jiin-Jou, Daniel, and William; for their friendship and assistance. Discussions with Jaewan Kim were very helpful.

Another large thanks go to the group members who shared my school life, Dr. Shashi Jasty, Steve Long, Ping Zhou, Gang Du, Ziemowit Oblakowski, Dr. Keith Cromack, Dr. Mik Józefowicz, Dr. Zhaohui Wang, Dr. Hamid Javadi, Steve Treat, Dr. Fulin Zuo, Dr. Jiang Yue, Will Brinkerhoff, Jinsoo Joo, Dr. Narayan, Dr. Andrew Burns, Jackie Parris, Fleda Crawford, and others.

For their devoted technical support, my appreciation goes to Bob L. Kindler, Tom Kelch, and Mark Johnson. I appreciate Professor A. MacDiarmid and his group members including Drs. Y. Sun and Jim Masters for their kind provision of samples and many valuable discussions.
Other thanks go to Yongjin Song and all other Koreans in the OSU community for their friendship and support. I will never forget the warmth shared with the Korean students and their family members in Mathematics Dept., especially the Songs.

I deeply appreciate the encouragement and support from my family members and friends in Korea for the long years. Finally thanks go to ETRI, for allowing me to study abroad.
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- Photoluminescence
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CHAPTER I

INTRODUCTION

The well-established energy band theory in solid state physics successfully explained the wide variations of the DC conductivity of materials, from insulators to metals. But when polyacetylene was synthesized, the spins in pristine sample were not properly explained, since this one-dimensional system with one $\pi$ electron per lattice site should become a semiconductor with fully filled valence band and empty conduction band following Peierls theorem. Furthermore, when doped with donor or acceptor, the DC conductivity of polyacetylene dramatically increased from semiconductor range to metallic range.

In an attempt to explain these observations, localized excitations, based upon the soft one-dimensional backbone structure, were introduced and classified to be solitons, polarons, and bipolarons. These electronic defects may or may not have net charge and/or spin but always introduce intragap absorption peaks. While the detailed conduction mechanism of the conducting polymers is still controversial, these new concepts have played the central role in the development of the understanding in the still growing new findings of peculiar physical properties of the conducting polymers, like nonlinear optical response, charge storage, and electroluminescence, to
name a few.

Polyaniline is very interesting polymer which has three different oxidation states. Though only one of which meets the simplest definition of conjugated polymer, to understand the various physical properties of polyaniline, the concepts developed for the conjugated polymers are very important.

In chapter II, the physical properties of polyacetylene and polythiophene are introduced to explain the concept of electronic defects. Especially the optical properties are emphasized. Near-steady-state and ultrafast photoinduced absorption measurement results are discussed. Chapter III summarizes the previous results on polyaniline. An attempt is made to explain the time dynamics and pump intensity dependence of the near-steady-state and long-time photoinduced absorption results for various oxidation levels.

Chapter IV explains the experimental details of picosecond photoinduced absorption. The measurement of photoluminescence decay time is summarized. Chapter V shows the results of the picosecond photoinduced absorption and the photoluminescence decay time measurements. The interpretation of the physical meaning of the data follows. Conclusion and a suggestion of future work are in chapter VI.
CHAPTER II

BACKGROUND: CONDUCTING POLYMERS

A conjugated polymer is a polymer with a \( \pi \)-electron system, one that the backbone atoms are usually connected by alternating single and double bonding in chemical structure notation convention. Polymers were generally believed to be insulators. So it was a surprise when the DC conductivity of polyacetylene, the simplest form of the conjugated polymer, reached that of metals upon doping. Soon after that, it was discovered that the conductivity of many polymers with \( \pi \) electrons can be manipulated by doping method. These conducting polymers show many other interesting physical properties beyond the one-dimensional DC conductivity. And spins were detected in pristine polyacetylene.

The increase of conductivity and the odd magnetic properties of conducting polymers could not be understood in the framework of rigid band theory. Since polymers are essentially one dimensional systems, from the Peierls' theorem, the existence of the intragap defect states in conducting polymers are predicted to explain the phenomena.[1, 2, 3, 4] Since then, many attempts have been made to determine experimentally and classify the intragap defect states, for example solitons, polarons, and bipolarons of various charge. They can be distinguished by three characteristics,
their spin, charge, and electronic structure.

There are two conventional ways of creating the intragap defects, chemical doping and optical pumping. As for the optically created defects, the spin can be directly observed by light-induced electron spin resonance (LESR). Presence of the charge is detected by measuring the photoinduced infrared (IR) absorption. The added charge breaks the symmetry to change Raman mode into IR active mode. The creation of the electronic states in the energy gap changes the photoinduced ultraviolet/visible (UV/VIS) range absorption.

There can be more than one intragap defect state under given conditions. To match the charge and electronic states, the behavior comparison of the photoinduced absorption at IR range and UV/VIS range is used. Generally, the sample temperature, the pump beam intensity, or pump beam time modulation frequency is varied. To verify the spin status of the electronic states, spin-dependent photomodulation (SDPM) technique is newly developed.[5, 6]

Research into photoinduced absorption of two conducting polymers are summarized below. The most extensively examined trans-polyacetylene has a degenerate ground state. Polythiophene is a non-degenerate ground state (NDGS) conjugated polymer.

2.1 Polyacetylene

In 1974, Shirakawa and co-workers succeeded to prepare a mechanically strong, free-standing film form of polyacetylene.[7] In 1977, MacDiarmid, Heeger, Shirakawa and their co-workers showed that the DC conductivity of polyacetylene can be enhanced by 13 orders of magnitude upon doping with various materials which are either electron-
accepting (p-doping) or electron-donating (n-doping).[7] Thus began the new science
of conducting polymers.

In polyacetylene, three of the four carbon valence electrons are in \( sp^2 \) hybridized
orbitals, making \( \sigma \) bonds with two neighboring carbons and one hydrogen atom. The
fourth electrons remain in a \( p_z \) orbitals perpendicular to the plane containing \( sp^2 \)
orbitals and make \( \pi \) bonds. If all the carbon to carbon bond lengths are equal, by
applying the tight binding method, one dimensional metallic behavior is expected
since the \( \pi \) bonded electrons in (CH)\(_x\) would form a half filled band. But such a one
dimensional half filled system is unstable with respect to the dimerization distortion,
the Peierls instability.[8]

Polyacetylene has two major isomer states, \textit{cis}-polyacetylene, c-(CH)\(_x\), and \textit{trans}polyacetylene, t-(CH)\(_x\), as shown in figure 1. All the backbone atoms in this conju­
gated polymer are connected by \( \sigma \) bonds. In addition, each of the carbon atoms has
an electron in its \( \pi \) orbital. The lone \( \pi \) electrons tend to be paired with a neighbor,
since it is energetically favored following the Peierls' theorem. As a result, the back­
bone atoms of a conjugated polymer are connected by alternating single (longer) and
double (shorter) bonds.

Conjugated polymers can have two different configurations by exchanging sin­
gle and double bonds. By convention, the two are called as A-phase and B-phase,
respectively. In most conjugated polymers, the geometries of the two phases are
distinguishable, having different condensation energies. Between the two possible
phases, naturally, the phase with lower condensation energy is favored. These are
called non-degenerate ground state (NDGS) conjugated polymers. A typical example
is \textit{cis}-polyacetylene as shown in figure 1 (b). But \textit{trans}-polyacetylene has a property
such that the A- and B-phases are identical under the mirror symmetry. Hence it
Figure 1: The various isomer structures of polyacetylene. (a) \( t-(CH)_x \), (b) \( c-(CH)_x \), and (c) two possible configurations of \( t-(CH)_x \). From [9].
has a degenerate ground states. Until the pernigraniline base form of polyaniline was recently investigated[10, 11], it was considered that only $t$-(CH)$_2$ has this ground state degeneracy.

Between the two isomer states, $t$-(CH)$_2$ is thermodynamically more stable than $c$-(CH)$_2$. When polyacetylene is heated to around 150°C, nearly all the $c$-(CH)$_2$ portion created upon synthesis transforms to $t$-(CH)$_2$.

Various methods to synthesize polyacetylene can be classified into two major branches. Shirakawa was the first to make a free standing film. The Shirakawa method and other methods which modified Shirakawa's work start with acetylene monomers.[7, 12] On the other hand, after making a precursor polymer from different kinds of monomers, the precursor form can be transformed into polyacetylene.[9, 13] This precursor method is usually called the Durham method. It is claimed that the newly developed precursor method gives more homogeneous and dense morphology than the Shirakawa method.[9, 14]

Conjugated polymers, including polyacetylene, can be reversibly doped to be negatively or positively charged. The doping process is different from that of conventional three-dimensional semiconductors. Since the polymers have quasi-linear structure, the dopant atoms can sit between the chains and accept or donate charges to the chain backbone, forming dopant-induced defect states such as solitons, polaron, or bipolarons.[9]

The DC conductivity of polyacetylene increases dramatically upon doping. At room temperature, the DC conductivity of pristine $c$-(CH)$_2$ and $t$-(CH)$_2$ are $\sim 10^{-10}$ $\Omega^{-1}/$cm and $\sim 10^{-5}$ $\Omega^{-1}/$cm respectively[15], but the conductivity can be raised to $\sim 10^3$ $\Omega^{-1}/$cm or more in trans-polyacetylene by proper doping.[7, 12]
Early measurements of electron spin resonance (ESR) revealed interesting properties of polyacetylene. Undoped trans-polyacetylene showed a singlet spectrum, indicating one unpaired electron per $\sim 3 \times 10^3$ carbon atoms.[9] It was suggested, from the analysis of ESR spectra of pristine and AsF$_6$ or NH$_3$ doped trans-polyacetylene, that a neutral mobile defect in the $\pi$ electron system of the polymer was responsible for the signal. To explain the defect, the concept of a highly mobile domain wall which separates the two possible double and single bond alternation configurations (A-phase and B-phase) was introduced.[16]

### 2.1.1 SSH Model

Su, Schrieffer, and Heeger (SSH) proposed a Hamiltonian, which describes trans-polyacetylene, $t$-(CH)$_2$, concentrating on the $\pi$ bond electrons under the tight-binding approximation and assuming that the motion of each site including $\sigma$ bonded electrons to be adiabatic.[1, 2]

Let $u_n$ be the displacement of $n$-th backbone carbon-hydrogen unit along the chain direction from their equal distance position. The Hamiltonian used is

$$H_{SSH} = H_\pi + H_{\pi-ph} + H_{ph},$$

where

$$H_\pi = -t_o \sum_{n,s} (c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}),$$

$$H_{\pi-ph} = \alpha \sum_{n,s} (u_{n+1} - u_n)(c_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s}),$$

and

$$H_{ph} = \frac{M}{2} \sum_n \dot{u}_n^2 + \frac{K}{2} \sum_n (u_{n+1} - u_n)^2,$$
here $t_o$ is the transfer integral and $c^+_n s (c_{n,s})$ is the creation (annihilation) operator of spin $s$ electron at $n$-th site. $\alpha$ is an electron-phonon constant and $M$ and $K$ are the mass of a (CH) unit and the spring constant between the units, respectively.

The first term $H_w$ shows the electron hopping along the chain and $H_{\pi-ph}$ describes the electron-phonon interaction in a linear approximation. $H_{ph}$ is the sum of the (CH) group kinetic energy and the lattice potential energy.[1, 2, 9] The Coulomb interaction is not shown explicitly. This SSH Hamiltonian describes only intrachain phenomena.

Because spontaneous Peierls distortion is expected, $u_n$ can be set to uniform dimerization, $u_n = (-1)^n u$. With this, the SSH Hamiltonian can be simplified as

$$H_{SSH}(u) = -\sum_{n,s} \left\{ t_o + (-1)^n 2\alpha u \right\} (c^+_n s c_{n,s} + c^+_n s c_{n+1,s}) + 2NKu^2$$

(2.5)

with closed periodic boundary condition of $N$ sites.

When $u = 0$, by diagonalizing the Hamiltonian with the Bloch operators

$$c_{k,s} = \frac{1}{\sqrt{N}} \sum_{n,s} e^{-ikna} c_{n,s},$$

(2.6)

The energy bands in a reduced zone scheme with zone boundaries at $\pm \pi/2\alpha$ are obtained as

$$\varepsilon_{k-} = -2t_o \cos(ka)$$

(2.7)

$$\varepsilon_{k+} = +2t_o \cos(ka)$$

(2.8)

with no energy gap. The distance between the nearest carbon atoms is $\sim 1.4$ Å. Since the angle between two adjacent $\sigma$ bonds is $120^\circ$, $a \approx \sqrt{3}/2 \times 1.4$ Å $\approx 1.22$ Å is the distance between sites along the chain.[2] Figure 2 (a) shows the energy band and the density of states with no dimerization. The band will be exactly half filled to give metallic behavior, because there is one $\pi$ electron per (CH) unit. But pristine polyacetylene shows very poor conductivity.
Figure 2: The energy band of trans-polyacetylene (a) under the assumption of no dimerization and (b) when the Peierls transition is included. From [2].
For $u \neq 0$, by employing the valence band ($-$) and conduction band ($+$) operators
\begin{align}
    c_{k,s}^- &= \frac{1}{\sqrt{N}} \sum_{n,a} e^{-i k a} c_{n,a}, \\
    c_{k,s}^+ &= \frac{1}{\sqrt{N}} \sum_{n,a} e^{-i k a} (-1)^n c_{n,a}
\end{align}
(2.9) (2.10)
to the Hamiltonian,
\begin{align}
    H_{SSH}(u) &= \sum_{k,s} \{\epsilon_{k,+} c_{k,s,+}^\dagger c_{k,s}^- + \epsilon_{k,-} c_{k,s,-}^\dagger c_{k,s,+} + \Delta_k (c_{k,s,+}^\dagger c_{k,s,-} + c_{k,s,-}^\dagger c_{k,s,+})\} \\
    &\quad + 2NKu^2
\end{align}
(2.11)
is obtained where
\begin{align}
    \Delta_k = 4\alpha u \sin(ka)
\end{align}
(2.12)
is the energy gap parameter. Now, from the canonical transformation diagonalizing method, the Hamiltonian can be rewritten as
\begin{align}
    H_{SSH}(u) &= \sum_{k,s} (E_{k,+} n_{k,s,+} + E_{k,-} n_{k,s,-}) + 2NKu^2
\end{align}
(2.13)
with the quasi-particle energy
\begin{align}
    E_{k,\pm} &= \pm \sqrt{\epsilon_{k,\pm}^2 + \Delta_k^2}.
\end{align}
(2.14)
This gives energy gap $2\Delta_{kp}$. The energy bands are shown in figure 2 (b).[2]

At the ground state, $n_{k,+} = 0$ and $n_{k,-} = 1$. By replacing the sum to integral, the energy becomes
\begin{align}
    E_0(u) &= 2 \sum_k E_{k,-} + 2NKu^2 \\
    &= \frac{4N\ell_o}{\pi} \int_0^{\frac{\pi}{2}} \sqrt{1 - (1 - z^2) \sin^2(x)} \, dx + 2NKu^2 \\
    &\approx \frac{4N\ell_o}{\pi} - \frac{2N\ell_o}{\pi} \left\{ \ln(\frac{4}{\ell_o} - \frac{1}{2}) \right\} z^2 + \frac{NK\ell_o^2 z^2}{2\alpha^2} + \ldots
\end{align}
(2.15)
for small $z = 2\alpha u/t_\alpha$. $E_\alpha(u)$ is an even function of $u$. [2]

As was shown in figure 1, there are two degenerate ground states in $t$-(CH)$_z$. When the values of the effective spring constant $K = 21$ eV/Å and the π bandwidth $W_\pi = 4t_\alpha = 10$ eV are chosen and $\alpha$ is adjusted to make the energy gap $E_g = 8\alpha u = 1.4$ eV, $E_\alpha(u)$ becomes minimum at $u = \pm u_0 = \pm 0.04$ Å. Then the condensation energy $E_c$ per site is[2]

$$-\frac{E_c}{N} = \frac{1}{N}\{E_\alpha(u_0) - E_\alpha(0)\} = -0.015eV.$$  \hspace{1cm} (2.16)

The negativity means that the dimerization is energetically favored. This justifies the chemical bond notation where dimerization is implied by the alternation of single and double bonds. In other words, the existence of the two different phases in $t$-(CH)$_z$ is justified.

### 2.1.2 Solitons in Trans-Polyacetylene

It is convenient to introduce the staggered displacement field[2, 9]

$$\psi_n = (-1)^n u_n.$$  \hspace{1cm} (2.17)

The sign of $\psi_n$ can be chosen such that $\psi_n$ is positive in the A-phase and negative in the B-phase. The soliton $S$ (antisoliton $\bar{S}$) is a minimum energy state of a phonon field configuration in a long chain with the A-phase at one end and the B-phase at the other end. In other words, a soliton is a boundary between the two phases. It is named as soliton since its shape does not change in translation. But unlike conventional concept of soliton, a pair of solitons (actually a soliton and an antisoliton) may vanish when collided with each other.[9] Because of this topological property, solitons can be created only in soliton-antisoliton pairs in an infinitely long system.
From numerical calculations it can be shown that\[1\]

\[\psi_n \simeq u_0 \tanh\left(\frac{(n - n_o)a}{\xi}\right)\]  \hspace{1cm} (2.18)

for a soliton centered at \(n_o\)-th site. The soliton formation energy \(E_s\) is \(0.61\Delta_{kp}\) or \(E_s = \frac{2}{\varepsilon} \Delta_{kp} \simeq 0.63\Delta_{kp}\) in the continuum limit.\[17\]

To make an electron state accompanied to a soliton, the valence and conduction bands are each depleted by one-half of a state. A soliton state can accommodate 0, 1, or 2 electrons. When there is only one electron, the soliton is electrically neutral and has spin 1/2. The neutral soliton is denoted as \(S^0\). The negative and positive solitons, \(S^-\) and \(S^+\), have spin 0. This unusual relation is summarized in the figure 3.\[9\]

### 2.1.3 Other Excited States

In non-degenerate ground state (NDGS) conjugated polymers, since one phase is energetically favoured over the other phase, isolated topological solitons cannot exist. The possible electronic defects are polarons, bipolarons, and polaron-excitons in this case. These nontopological excitations can be interpreted as a confined pair of solitons with various charges. They have two electronic levels compared to single level in solitons. Polaron, \(P^\pm\), is a combination of a charged soliton and a neutral soliton, to have net charge of \(\pm|e|\) and spin 1/2. Even degenerate ground state polymers can have polarons upon injection of a net charge.\[18\] Bipolaron, \(BP^{2\pm}\), is a bound state of two charged solitons of same kind, or two polarons of same charge. A bipolaron has two units of electron charge and no spin. When two differently charged solitons or polarons are forming a bound state, it is called a polaron-exciton. The net charge of a polaron-exciton is zero.

Figure 4 compares polaron, bipolaron, and polaron-exciton. It is suggested that
Figure 3: The charge-spin relation of soliton. From [9].
two polarons attract each other to form a bipolaron when the Coulomb effects are neglected. Bipolarons repel each other and there is no interaction between polarons and bipolarons.[19] From figure 4, it can be predicted that, while polarons will create three new intragap absorptions, there will be two intragap absorptions generated by bipolarons.[9, 20]

### 2.1.4 Near-Steady-State Photoinduced Absorption

The near-steady-state photoinduced absorption (NSSPIA) measurements of cis- and trans-polyacetylene were first made by Orenstein and Baker.[21] When they optically pumped trans-polyacetylene at 2.2 eV, contrary to the prediction of the SSH model[1, 2] that the newly created electronic states should be at the middle of the energy gap, the photoinduced absorption peaks were found at 0.5 and 1.35 eV.[21] These are called the low energy (LE) peak and the high energy (HE) peak, respectively. At the same time, three dominant photoinduced infrared active vibration (IRAV) peaks were observed at 500, 1270, and 1360 cm$^{-1}$.[22, 23, 24, 25, 26] The full spectrum trans-polyacetylene NSSPIA result[27] is shown in figure 5.

When trans-polyacetylene was chemically n-doped or p-doped, independent of the dopant, 900, 1270, and 1360 cm$^{-1}$ IRAV peaks appeared with a very broad peak around the LE peak energy.[9, 28, 29, 30, 31, 32, 33] From this, it is evident that the LE peak and IRAV modes are from the charged solitons, $S^\pm$, as predicted by the SSH model.[1, 2, 9] Cis-polyacetylene showed only one photoinduced absorption (PIA) peak at 1.55 eV and the LE and the IRAV peaks are very small compared to those of the trans-polyacetylene.[21, 22]

Orenstein and Baker[21] suggested that the HE peak in trans-polyacetylene is
Figure 4: The structures of polaron, bipolaron, and polaron-exciton.
Figure 5: NSSPIA of trans-polyacetylene. From [27].
from a neutral state, while the LE peak is from a state with net charge. Vardeny et al.[22] supported the idea by showing the relation of the LE and the 1270 and 1360 cm\(^{-1}\) IRAV peaks from the comparison of the chopping frequency and temperature dependencies of the LE and IRAV peaks.

The origin of the 500 and 900 cm\(^{-1}\) peaks are interpreted as the pinned uniform translation mode of charged solitons. The presence of the counter ions in chemically doped case makes larger shift than photoinduced defects, where there is no such pinning potentials, except possibly the interchain interaction of oppositely charged solitons.[9, 22, 34] While the photoinduced LE peak is at \(\sim 0.45\) eV, the intragap absorption peak due to chemical doping is at \(\sim 0.75\) eV, near to the half of energy gap as predicted by the SSH model.[1, 2, 9] This shows the importance of electron-electron Coulomb interaction in photoinduced electronic defects, which is appreciably neutralized by the counter ions in chemical doping.[9]

### 2.1.5 Spin-Dependent Photomodulation

Though at first it was believed that neutral solitons cannot be photogenerated due to the inversion symmetry (parity) and charge conjugation symmetry in the SSH Hamiltonian[35], later Kivelson and Wu[36] argued that even a weak interaction that breaks the charge conjugation symmetry can allow the photogeneration of neutral triplet soliton pairs[37], out of oppositely charged soliton pairs. Bishop et al.[38] suggested that the breather, which is created when an electron-hole pair converts to a charged soliton pair, is responsible for the HE peak. By LESR measurement, Levey et al.[39] showed the presence of spin 1/2 photoinduced defect, strongly implying the presence of neutral solitons in optically pumped trans-polyacetylene.
Figure 6: SDPM of trans-polyacetylene. From [6].
The origin of the HE peak was verified by spin-dependent photomodulation (SDPM) method.[5, 6] In SDPM, the variation of the probe beam absorption under the electron spin resonance is measured. If the electronic defects caused by the optical pumping has spin and the decay time of the electronic defects depends on the spin status, the population of the defects can be changed by changing the spin status. There are two different ways of measurement. When the probe beam energy is fixed and the magnetic field is swept, it is called H-SDPM. P-SDPM is when the probe beam wavelength is changed, while the magnetic field intensity is fixed.[5, 6]

A brief description of the technique follows. The sample is in a microwave cavity between magnets, with wavelength 488 nm (2.54 eV) pump beam on. The 2.99 GHz microwave is time modulated at 500 Hz. Under the presence of magnetic field, when the microwave is off, the spin configurations keep the thermal equilibrium. When the microwave is applied and it resonates between the spin energy levels created by the applied magnetic field, the spin population over the energy levels no longer maintains the thermal equilibrium.[5, 6]

The inset of figure 6 shows the H-SDPM result of the HE peak. The probe beam was fixed at the HE peak, while the applied magnetic field intensity was varied. The sample was held at 4 K. The detected absorption change implies the presence of spins which are strongly related to the HE peak. The absorption becomes minimum at 1067 Gauss and there is only one peak. This fixes the spin to 1/2, excluding all the possibilities like triplet (spin 1) or breather (spin 0).[5, 6]

The main diagram of figure 6 shows the result of P-SDPM, where the probe beam photon energy is changed, while the pump beam and magnetic field is held constant at which the HE peak gave H-SDPM peak. The normalized modulation amplitude of the probe beam intensity is measured while the microwave is time modulated.
This verifies that the HE peak has spin 1/2, or originates from neutral solitons. At the same time, the weak increase of the LE peak, which is correlated to the HE P-SDPM peak, is interpreted as an evidence of the transition from neutral to charged solitons.[6, 5]

2.1.6 Picosecond Photoinduced Absorption

As will be explained in the next chapter, near-steady-state photoinduced absorption (NSSPIA) can detect mainly those defects whose decay time is in the range of the modulation period employed in the measurement, which is from a few \( \mu \)sec to a few msec. Since it was predicted that the electron-hole pair created upon the absorption of pump photon decays into soliton-antisoliton pairs within 100 fsec[40], to understand the temporal behavior of the electronic defects, it is necessary to monitor the defects with better time resolution. This can be done by using the picosecond photoinduced absorption (PSPIA) method. The details of the PSPIA method will be in chapter IV.

The trans-polyacetylene dichroism of PSPIA with pump and probe both at 2.0 eV was studied by Vardeny et al.[41]. When the probe polarization is parallel to the pump beam polarization, the photoinduced bleaching (PIB) is larger than the orthogonal case until the delay time between the pump and probe pulses reaches 1 nsec. This shows the electronic structure and the electronic defects in trans-polyacetylene are mainly one-dimensional.

Shank et al.[42, 43] measured the photoinduced absorption (PIA) of polyacetylene with sub-psec time resolution. They pumped at 2.0 eV, while probing 1.2 – 1.9 eV range with a white-light continuum generated by passing intense 2.0 eV pulse through
1 cm water. The result shows a PIA peak inside the band gap at 1.45 eV for trans-polyacetylene and 1.55 eV for cis-polyacetylene, rising within a few hundred fsec and last for more than 200 psec. These spectra peaks matched to the NSSPIA high energy (HE) peaks of Orenstein and Baker.[21]

Rothberg et al.[44, 45, 46] measured the PSPIA of trans-polyacetylene in probe range of 2.5 to 5.5 μm (0.23 to 0.5 eV) with pump at 2.1 eV. The spectrum in zero pump-probe delay time matches to the NSSPIA low energy (LE) peak, which is from the photoinduced charged solitons. The time dynamics of 2.8 μm (0.45 eV) probe at two different temperatures are shown in figure 7. Interestingly, the PSPIA rises twice. This implies two different origins of charged solitons. The first peak with zero delay time is interpreted as the intrachain photoinduced charged solitons, following Su and Schrieffer.[9, 40] The second peak or the second population increase of charged solitons comes from the conversion of either polarons or neutral solitons into charged solitons.[9, 44, 46, 47] The polarons can be created by interchain absorption and are assumed to be responsible for the psec range fast photoconductivity.[9, 18, 48]

Based on the observation of the 0.45 eV low energy (LE) peak PSPIA dynamics and its pump intensity, temperature, and polarization dependence, Rothberg et al.[46] developed a schematic diagram of the electronic defects in trans-polyacetylene, preferring the path

\[ P^\pm + S^0 \rightarrow S^\pm \]  \hspace{1cm} (2.19)

to the path[47, 49],

\[ P^\pm + P^\pm \rightarrow S^\pm + S^\pm \]  \hspace{1cm} (2.20)

The two point of views are shown in figure 8.

Extensive photoinduced absorption measurements of oriented polyacetylene from
the psec to the µsec range is reported by Yoshizawa et al.\cite{49, 50, 51, 52} From the polarization dependence, they conclude the 1.4 eV PIA peak in the nsec range at 10 K comes from polarons in contrast to the $S^0$ origin proposed by Vardeny et al.\cite{5, 6}. It is possible that both paths of equations 2.19 and 2.20 are responsible for the creation of the charged solitons which appear in the PSSPIA measurements.

### 2.1.7 Third Harmonic Generation

Though conducting polymers started to get attention for their unusual DC conductivity, it was soon noted that they have strong potential in Nonlinear Optics applications. In this subsection, after a brief introduction to the basic theory of harmonic generation, the nonlinear optical properties of polyacetylene are surveyed.

#### Basic Theory

From the Maxwell equations and the charge conservation law, the famous wave equation is derived to be\cite{53, 54}

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E} - \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 \vec{P}}{\partial t^2},$$  \hspace{1cm} (2.21)

where $\vec{E}$ is the electric field and $\vec{P}$ is the electric polarization density.

$\vec{P}$ is, in general, a nonlinear function of $\vec{E}$. $\vec{P}$ can be expanded with respect to $\vec{E}$ under the assumption of weak electric field,\cite{53}

$$\vec{P}(\vec{k}, \omega) = \vec{P}^{(1)}(\vec{k}, \omega) + \vec{P}^{(2)}(\vec{k}, \omega) + \vec{P}^{(3)}(\vec{k}, \omega) + \ldots$$  \hspace{1cm} (2.22)

with

$$\vec{P}^{(1)}(\vec{k}, \omega) = \chi^{(1)}(\vec{k}, \omega) \cdot \vec{E}(\vec{k}, \omega)$$  \hspace{1cm} (2.23)
Figure 7: Trans-polyacetylene PSPIA spectra at (a) 25 K and (b) 300 K. From [44]
Figure 8: Two schematic diagrams showing possible electronic defects evolution in trans-polyacetylene. Upper one is from [46] and lower one is from [49].
\[ \vec{P}^{(2)}(\vec{k}, \omega) = \chi^{(2)}(\vec{k} = \vec{k}_i + \vec{k}_j, \omega = \omega_i + \omega_j) : \vec{E}(\vec{k}_i, \omega_i) \vec{E}(\vec{k}_j, \omega_j) \quad (2.24) \]
\[ \vec{P}^{(3)}(\vec{k}, \omega) = \chi^{(3)}(\vec{k} = \vec{k}_i + \vec{k}_j + \vec{k}_l, \omega = \omega_i + \omega_j + \omega_l) : \vec{E}(\vec{k}_i, \omega_i) \vec{E}(\vec{k}_j, \omega_j) \vec{E}(\vec{k}_l, \omega_l). \quad (2.25) \]

\( \chi^{(2)} \) in equation 2.24 and \( \chi^{(3)} \) in equation 2.25 are the second and third order nonlinear susceptibilities. The terms of equation 2.22 in even powers of electric field are not vanishing only in noncentrosymmetric media—those lacking a natural center of inversion symmetry.\[^{[55]}\] As a result, the second order nonlinear susceptibilities of many materials, including polyacetylene and polyaniline, are practically zero.

Since the third order nonlinear susceptibility \( \chi^{(3)} \) is a fourth-rank tensor in three-dimension, it can have up to 81 independent nonvanishing components. The number of nonvanishing and independent components depends on the symmetry of the medium. For example, monoclinic crystals have 41 independent nonzero elements, while isotropic media allow 21 nonvanishing components which have only three independent values.\[^{[54]}\]

As for the conjugated polymers, it has long been known that the main contribution to the third order susceptibility comes from the delocalization of the \( \pi \)-band electrons along the chain axis.\[^{[56, 57, 58]}\] Hence when the chain direction is set to be \( \pi \)-axis, usually \( \chi^{(3)}_{zzzz} \) is of interest. It was calculated that the \( \chi^{(3)}_{zzzz} \) of one-dimensional conjugated polymers is inversely proportional to the sixth power of the energy gap \( E_g.\[^{[57, 58, 59]}\] According to this result, very large value of \( \chi^{(3)}_{zzzz} \) is expected from narrow bandgap conjugated polymers, though at the same time the lower bound of transparent wavelength is limited.
Polyacetylene

As mentioned earlier, solitons can exist in \( t-(CH)_x \) because of the ground state degeneracy, while \( c-(CH)_x \) can have only polarons and bipolarons. From the photoinduced absorption experiments, it is known that large changes in the optical constants of \( t-(CH)_x \) occur for the resonant pumping.[9]

In the nonresonant case, that is, when the photon energy is less than the energy gap, \( \chi^{(3)}_{zzzz} \) of \( t-(CH)_x \) is measured to be 15~20 times larger than that of \( c-(CH)_x \). The difference cannot be fully explained by the bandgap dependence, which gives less than 3 times difference. The energy gaps of \( t-(CH)_x \) and \( c-(CH)_x \) are 1.7~1.9 eV and \( \sim 2.0 \) eV, respectively.

To describe this big difference, Sinclair et al.[56, 60] used the concept of instantons. According to the SSH model, which treats the lattice in the classical approximation, no absorption is possible inside the energy gap.[61] To explain the tail of the absorption coefficient inside the energy gap, the concept of instantons, or the virtual soliton-antisoliton pairs in the ground state distribution coming from the quantum fluctuations in the lattice coordinates, was introduced.[62, 63] The fluctuations are described by using the staggered order parameter

\[
\psi_p(x) = u_o\{1 - \tanh(2x_o/\xi)[\tanh(x - x_o/\xi) - \tanh(x + x_o/\xi)]\},
\]

(2.26)

where \( u_o \) is the magnitude of the displacement of the (CH) unit at which the total energy of the \( t-(CH)_x \) becomes minimum and \( \xi \) is the coherence length.

From this, the total Hamiltonian can be written as

\[
H_o(s) = E_p(s) + \frac{M}{2} \left( \frac{ds}{dt} \right)^2
\]

(2.27)

with a new coordinate \( s = s(x) \) and an effective potential \( E_p(s) \).[56, 63] After solving
the Schrödinger equation with the above Hamiltonian, Yu et al.[63] found the ground state energy to be $E_g = 0.06$ eV and first excited state energy 0.35 eV.

If the pumping photon energy $\hbar \omega_p$ exceeds the energy gap, the SSH solitons are created within the order of $\sim 10^{-13}$ sec.[9] Sinclair et al. argued that[56, 63], if $\hbar \omega_p$ is between the energy gap $2\Delta$ and the soliton-antisoliton pair creation energy $(4/\pi)\Delta$, the system is resonant between the ground and the first excited potential at a point $s$, and evolves toward a well separated charged soliton pair each with a state at midgap.

Since the ground state of $c-(\text{CH})_x$ is not degenerate, the $E_p(s)$ of $c-(\text{CH})_x$ will be larger than that of $t-(\text{CH})_x$ and become proportional to $s$ at large $s$. So the nonlinear response of $c-(\text{CH})_x$ is suppressed compared to the response of $t-(\text{CH})_x$. Sinclair et al.[56, 60] concentrated on the ground and the first excited states in the $s$-configuration space. They estimated the size of the third harmonic generation $\chi^{(3)} \sim (1 - 5) \times 10^{-10}$ esu which is of the same order as their measurement.[56]

Another theoretical approach was made by Wu.[64] For the description of essentially nonequilibrium systems such as the system of electrons in a strong external field, a graph technique analogous to the usual Feynman technique in field theory for calculating Green's functions was developed by Keldysh.[65] Based on the Keldysh nonequilibrium Green's function method, Wu derived the third-order nonlinear optical susceptibility of polyacetylene without using any adjustable parameter.[64]

There have been many experiments to measure $\chi^{(3)}$ of $(\text{CII})_x$, especially $t-(\text{CH})_x$. Sinclair et al.[56, 60] measured $\chi^{(3)}_{zzzz}(-3\omega; \omega, \omega, \omega) = (4 \pm 2) \times 10^{-10}$ esu at 1064 nm (1.17 eV). The samples were prepared by the Shirakawa method. From the Durham polyacetylene samples, Krausz et al.[66] measured $\chi^{(3)}_{zzzz}(-3\omega; \omega, \omega, \omega) = (9 \pm 4) \times 10^{-9}$ esu at 1064 nm (1.17 eV) and $\chi^{(3)}_{zzzz}(-3\omega; \omega, \omega, \omega) = (1.7 \pm 0.7) \times 10^{-8}$ esu at 1907
Figure 9: The $\chi^{(3)}$ spectrum of $t$-(CH)$_2$. The open and closed squares are measured results and the solid and dashed curves are calculated ones. From [67].
nm (0.65 eV).

The results of Fann et al.[67] (open square) and Kajzar et al.[68, 59] (closed square) coming from Shirakawa polyacetylene films are shown in figure 9, compared to the calculations of Wu[64] (solid line) and Soos and Ramasesha[69] (dashed line). The data of Fann et al. shows two resonances at 0.6 eV and 0.89 eV, which seem to be a three-photon resonance and two-photon resonance, respectively.[67]

Halvorson et al.[70] recently measured $\chi^{(3)}$ of polyacetylene in wider probe range, from 0.55 to 1.25 eV. Again they found $\chi^{(3)}$ of $t$-(CH)$_x$ is $\sim 15 - 20$ times larger than that of $c$-(CH)$_x$. They concluded that, for a degenerate ground state system, there will be an enhancement of $\chi^{(3)}$ by two orders of magnitude compared to the rigid band contribution, due to the S–S pair intermediate state contribution.

### 2.2 Polythiophene

Conjugated polymers can have two ground state configurations, as explained in the previous section, due to the two possible ways of $\pi$-electron pairing. Practically all the known conjugated polymers except trans-polyacetylene and pernigraniline base form of polyaniline are non-degenerate ground state (NDGS) polymers.

As a typical NDGS conjugate polymer, the properties of polythiophene are summarized in this section. Polythiophene is a heterocyclic polymer, consisting of five-membered rings with four carbon atoms and a sulfur atom in each ring. Since the sulfur atom does not have any $\pi$-electron, the carbon backbone is important in polythiophene, as shown in figure 10. Because of their solubility and processability, many of the derivatives of polythiophene are synthesized and studied. Among them are poly(3-alkythienylenes) (P3AT’s), as in figure 10 (c). Depending on the alkyl chain
(-C\textsubscript{n}H\textsubscript{2n+1}) length, the names of rather frequently studied ones are polythiophene (PT) (n = 0), poly(3-methylthiophene) (P3MT) (n = 1), poly(3-butylthiophene) (P3BT) (n = 4), poly(3-hexylthiophene) (P3HT) (n = 6), poly(3-octylthiophene) (P3OT) (n = 8), and poly(3-decylthiophene) (P3DT) (n = 10).

### 2.2.1 Chemical Doping

Chung et al.[71] measured the absorption change of electrochemically polymerized polythiophene (PT) in LiClO\textsubscript{4} solution. The absorption was measured while changing the doping level of PT by changing the applied voltage with respect to a Li electrode in the electrochemical cell. Figure 11 shows the voltage-induced or chemical-doping-induced absorption change. Starting from the undoped state at 2.5 V, two absorption peaks are apparent until 4.05 V, where the number of injected holes is about 20% of the number of sulfur atoms in polythiophene. The two intragap absorption peaks imply the existence of two empty electronic levels symmetric with respect to the middle of energy gap. They are interpreted to be from a hole bipolaron, BP\textsuperscript{++}.[9, 20, 71]

### 2.2.2 Near-Steady-State Photoinduced Absorption

The near-steady-state photoinduced absorption (NSSPIA) measurement of polythiophene (PT) shows two electronic photoinduced absorption peaks and strong IR peaks, as shown in figure 12.[72, 73] The NSSPIA IR peaks correspond to the chemical doping induced IR peaks, indicating the two are from the same species.[72] All the peaks in figure 12 showed same dependence upon the variation of the pump intensity, temperature, and chopping frequency, implying that all of them are from a common
Figure 10: Polythiophene structure; (a) the chemical structure (b) two possible configurations (c) poly(3-alkylthienylenes) (P3AT’s). From [9].
Figure 11: The in situ absorption curves of polythiophene during electrochemical doping with (ClO$_4$)$^-$. From [71].
Figure 12: NSSPIA of polythiophene at 20 K. Pumped at 2.7 eV with intensity 10 mW/cm². Lower inset shows the allowed transitions for BP++. From [73].
origin. The signal grew proportional to the square root of the pump intensity, until saturation. There was $\sim 40^\circ$ phase lag in the whole range of PIA peaks compared to the 140 Hz chopped pump beam, indicating their decay time is $\sim 5$ ms. The peak intensity decreased monotonically by an order of magnitude when the temperature increased from 20 K to 300 K.[73]

Though a light-induced electron spin resonance (LESR) signal was measured in PT, the spin density was low and there were only two PIA peaks beyond IR region.[72, 73] In other words, the charged excitations detected in the NSSPIA measurement are dominantly bipolarons, not polarons.[73]

From the amplitude mode analysis[25] of the photoinduced absorption of IR active vibration (IRAV) modes and resonant Raman scattering (RRS), it was concluded that the bipolarons in PT are strongly pinned. Their kinetic mass was estimated to be in the same range with that of solitons in *trans*-polyacetylene or about one free electron mass.[74]

If there were no Coulomb interaction, because the energy levels attached to the excitation are symmetric with respect to the energy gap center, $\omega_1 + \omega_3 = E_g$ will hold from the lower inset of figure 12. If the Coulomb interaction is included,

$$\omega_1 + \omega_3 = E_g - 2U_B$$

is correct, where $2U_B$ is the Coulomb energy difference between the initial hole bipolaron state and the final state with one electron at each level. Since $E_g = 2.2$ eV and $\omega_1 + \omega_3 = 1.7$ eV, $U_B/E_g \approx 0.12$ is obtained. Because repulsive Coulomb interaction should occur when a bipolaron is created from two charged excitations, this implies that the Coulomb interaction between the like charges is not large, consistent with the dominance of bipolaron over polaron.[73]
2.2.3 Photoluminescence

Like many other NDGS conjugated polymers, polythiophene (PT) shows photoluminescence (PL).\cite{75, 76, 77, 78, 79} In figure 13, the PL spectrum at 20 K shows equally spaced multiple peaks at 1.95, 1.77, 1.59 and 1.41 eV with a vibronic structure of 0.18 eV, which is close to the strong resonant Raman scattering (RRS) peak at 1460 cm\(^{-1}\) (0.183 eV).\cite{74} This RRS peak is attributed to the carbon-carbon stretching mode in the PT backbone.\cite{75}

The PL profile of PT was theoretically calculated.\cite{78} In the model, bipolaron and polaron-exciton cannot be distinguished since the Coulomb interaction is not included.\cite{78} The calculated profile fits well to the measured one, if the size of the polaron-exciton is chosen much larger than that of the bipolaron estimated from the experiment.\cite{71} This suggests the importance of the Coulomb interaction.\cite{78}

When the excitation energy was scanned at 20 K while the PL intensity was monitored, the PL intensity was abruptly enhanced at 1.95 eV of excitation energy and remained constant when the excitation energy was increased further.\cite{75} At the same time, the excitation profile of NSSPIA at 20 K shows a narrow peak at 1.95 eV.\cite{75}

Optically detected magnetic resonance (ODMR) or PL-detected magnetic resonance was performed on PT, by measuring the PL intensity modulation due to the modulation of applied magnetic field, under the presence of a pumping laser and an X-band microwave field.\cite{75} When the magnetic field intensity was scanned, only one peak was detected, showing that a spin of 1/2 is involved in the decay procedure. At the magnetic resonance condition, the PL intensity decreased. This means the unthermalization of the spins enhances spin-dependent nonradiative recombination.
From these pieces of evidence, it was concluded that the 1.95 eV peak is from an intrachain exciton bound to defects with spin 1/2.[75]

Electrochemically polymerized PT films were stretched to 1 – 2 times their original lengths.[80] Optical anisotropy was detected both in the absorption coefficient and PL magnitudes. From the data, under the assumption that the polymer is made up of very long rodlike chains and stretching makes them rotate independently of each other, the intrinsic absorption coefficients along a chain, $\alpha_\parallel$, and perpendicular to it, $\alpha_\perp$, were calculated. Their ratio was estimated to be larger than 14.[80] The PL excitation profiles in the range of 2 – 3 eV were measured at a PL emission of 1.9 eV with the four possible combinations of polarization directions of pumping light and PL emission. The PL emission perpendicular to the stretch direction was weakest and independent of the polarization direction of the pumping light. When the parallel portion of the PL emission was monitored, the intensity depended on the pump beam polarization direction. With parallel pumping, the parallel PL emission was about 3 times stronger than the orthogonal PL emission. Orthogonal pumping gave about 2 times stronger emission. When the film was not stretched, the parallel PL emission intensity was independent of the pump beam polarization. From this, it was concluded that PL occurs from an intrachain exciton which migrates before radiative recombination.[80]

### 2.2.4 Picosecond Photoinduced Absorption

Kobayashi et al.[77] prepared a P3MT film by the electrochemical polymerization method and pumped at 1.97 eV (600 nm) and probed by a white light in the range of 1.3 – 2.2 eV. The time resolution of the measuring system was $\sim$ 100 fsec.[77] A self-trapped exciton was created with 70 ± 50 fsec rising time and decayed with
Figure 13: Photoluminescence of polythiophene. From [75].
$800 \pm 100 \text{ fsec decay time, both at } 10 \text{ K and } 290 \text{ K.}[77, 81] \text{ At time delays of } -0.1 \text{ and } 0 \text{ psec, a strong minimum at } 1.8 \text{ eV and a weaker minimum at } 1.62 \text{ eV were shown in the photoinduced absorption spectrum, suggesting that the C=C backbone vibration mode at } 0.18 \text{ eV shown in resonant Raman scattering (RRS) plays an important role in the self-trapping of the free exciton created upon optical pumping. At a delay time of } 0 \text{ psec, a sharp photoinduced bleaching (PIB) peak appears at } 1.97 \text{ eV, indicating unthermalized free excitons.}[77, 81]$

The trapping of exciton in P3MT occurs mainly through the carbon backbone, with little contribution from the methyl group. The energy delivered to the carbon-carbon backbone stretching through the electron-photon interaction is dissipated to other phonons within a few cycles of oscillation to achieve a lowest excited singlet self-trapped exciton.[77] While the formation time of soliton pairs in trans-polyacetylene is determined by the dissociation of domain walls, in the NDGS system the energy redistribution from the strongly coupled phonon to the other phonon modes determines the formation time of the self-trapped excitons.[77]

In photoinduced absorption of P3MT at 0 psec delay time, a featureless absorption spectrum was observed in $1.35 - 1.9 \text{ eV. This was interpreted as the transition of free excitons to higher excited states. After } 0.2 - 0.5 \text{ psec, a peak in the range of } 1.8 - 1.95 \text{ eV was shown, reflecting the transition to excitons of higher energies or to the conduction band.}[77, 81] \text{ A time constant } 0.8 \pm 0.1 \text{ psec of bleaching recovery and the broad absorption decay were measured, implying the relaxation of the self-trapped exciton to the ground state or to other long-lived species, possibly triplet excitons, polarons, and/or bipolarons.}[77, 81]$

The PL decay was measured to be faster than the time resolution of the instrument giving lower limit of 9 psec[82] or 2 psec accompanied by a slow decay
component which behaves differently from the PSPIA results.[83] Since there were no other prominent features seen within tens of psec except the self-trapped exciton which rises and decays within 1 psec[77, 81], it was suggested that the initial self-trapped exciton is responsible for the PL of PT, not the polarons or bipolarons which may be formed in the longer time scale.[77, 81, 82]
CHAPTER III

POLYANILINE

Most conducting polymers are conjugated polymers which have a two-fold degenerate or a non-degenerate ground states. Their DC conductivities are dramatically increased from the insulator or semiconductor region to the metallic region when extra electrons or holes are introduced by a doping process. Polyaniline is found to exhibit such a large increase in DC conductivity upon doping. But polyaniline has distinctive properties when compared to the conventional conducting polymers.

First, its backbone is composed of two different atoms, carbon and nitrogen. Second, it can have three well defined oxidation states whose DC conductivities are very low (i.e., they are insulators). Third, the oxidation state whose DC conductivity increases upon doping is not a Peierls system and in the doping process not electrons or holes but protons are added to the system. Fourth, the fully oxidized state is the first degenerate ground state Peierls system other than trans-polyacetylene. Fifth, not only bond-alternation but also the ring-torsion plays an important role in the description of the localized electronic defects. In this chapter, general properties of polyaniline are summarized with an emphasis on the optical results and their analysis.

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3.1 Possible Oxidation States and their Structures

Polyaniline has one interesting variation which is not known for any other conducting polymers, the oxidation state. Polyaniline is made up of alternating nitrogen atoms and benzene rings. The nitrogen site may (amine, \(-\text{N}(\text{H})-\)) or may not (imine, \(-\text{N} = \)) accommodate one hydrogen atom. Amine sites become imine sites through the oxidation procedure. Polyaniline can be reduced by adding hydrogen atoms to imine sites. As a result, the most general description of polyaniline becomes \([-(\text{C}_6\text{H}_4)\text{-N-}(\text{C}_6\text{H}_4)=\text{N-}]_y\{-(\text{C}_6\text{H}_4)\text{-N(}\text{H})-(\text{C}_6\text{H}_4)\text{-N(}\text{H})-\}_1-y\}_n\), with \(0 < y \leq 1\). Here \(-(\text{C}_6\text{H}_4)\) and \(=(\text{C}_6\text{H}_4)=\) denote a benzenoid unit and a quinoid unit, respectively.

The polyaniline bases can have only three discrete oxidation states at the molecular level\[84\]; the fully oxidized \((y = 1)\) pernigraniline base (PNB), the fully reduced \((y = 0)\) leucoemeraldine base (LEB), and half oxidized \((y = 0.5)\) emeraldine base (EB). The chemical structures of these states are in figure 14. When the absorption spectra were monitored while the oxidation state was changed from LEB to EB and from EB to PNB in N-methyl pyrrolidinone (NMP) solution, two and three different isosbestic points were observed, respectively. This means that all the three oxidation states are distinctive states. EB is not a mere physical mixture of LEB and PNB.\[84, 85\] Upon exposure to air, polyaniline of any oxidation level slowly changes its oxidation status to become slightly over oxidized EB state.\[86\]

From figure 14, it is clear that only PNB has two possible configurations based on the bond length alteration or \(\pi\) electron pairing. The presence of amine \((-\text{N}(\text{H})-)\) group in the backbone of LEB and EB prevents them from having an alternative chemical bonding backbone structure, because of the surplus of single bonds to double
Figure 14: The various oxidation states of polyaniline; (a) leucoemeraldine base, (b) emeraldine base, and (c) pernigraniline base. From [87].
bonds.

Polyaniline is a partially crystallized material. The crystal structures of EB, its chemically doped form emeraldine salt (ES), the fully reduced LEB, and the derivatives of them have been investigated by the x-ray diffraction method. The ratio between amorphous and crystal structures depends on the history of the material, including synthesis methods, chemical doping, and solvents.[88, 89, 90, 91, 92, 93] At the same time, when the film or fiber form of emeraldine base is stretched under heat, the crystallinity increases.[92, 94, 95, 96]

### 3.2 Optics of Films

The most commonly used sample form in optics is a film, with wide variety of thickness. Sometimes a film is made up of pure sample material. In some cases the sample is diluted by some material like KBr, which should be transparent in the concerned spectral range and chemically inactive in contact with the sample, to enhance the mechanical properties or thermal dissipation efficiency of the film.

#### 3.2.1 Linear Optical Constants

The linear susceptibility $\chi^{(1)}(\vec{k}, \omega)$ is related to the linear dielectric constant $\varepsilon(\vec{k}, \omega)$ by

$$\varepsilon(\vec{k}, \omega) = 1 + 4\pi \chi^{(1)}(\vec{k}, \omega).$$

In the electric dipole approximation, $\chi^{(1)}(\vec{r}, t)$ is independent of $\vec{r}$, and hence both $\chi^{(1)}(\vec{k}, \omega)$ and $\varepsilon(\vec{k}, \omega)$ are independent of $\vec{k}$. [53]

By assuming weak light intensity, the nonlinear terms can be ignored in equa-
tion 2.22. If a plane wave solution

\[ E(\vec{r}, t) = \tilde{E}_o \exp\{i(\vec{K} \cdot \vec{r} - \omega t)\} \]  

(3.2)

and equations 2.23 and 3.1 are substituted in the wave equation 2.21, the dispersion relation

\[ K^2 = \frac{\omega^2}{c^2} \varepsilon(\omega) \]  

(3.3)

is obtained. From the phase velocity relation

\[ v = \frac{c}{N} = \frac{\omega}{K} \]  

(3.4)

the refractive index \( N \) is related to the wave number \( K \) by

\[ N = \frac{c}{\omega} K. \]  

(3.5)

Generally, because of absorption and scattering, the light intensity is reduced while the light propagates through a medium. To describe this effect, the wave number \( K \) is treated as a complex quantity. Then from equations 3.3 and 3.5, the refractive index \( N \) and the dielectric constant \( \varepsilon \) both have imaginary parts:

\[ N(\omega) = n(\omega) + ik(\omega) \]  

(3.6)

\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega). \]  

(3.7)

Here \( n \) is the real part of refractive index and \( k \) is the extinction coefficient. From equations 3.3, 3.7, and 3.7, the relation between the real and imaginary parts of \( N \) and \( \varepsilon \) becomes

\[ \varepsilon_1(\omega) = n^2(\omega) - k^2(\omega) \]  

(3.8)

\[ \varepsilon_2(\omega) = 2n(\omega)k(\omega). \]  

(3.9)
The optical conductivity $\sigma(\omega)$ and the imaginary part of dielectric constant $\varepsilon_2(\omega)$ are related by

$$\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega).$$ (3.10)

The absorption coefficient $\alpha(\omega)$ is defined as

$$\alpha = \frac{1}{I} \frac{dI}{dr},$$ (3.11)

with light intensity $I = I(r)$, and is related to the imaginary part of refractive index $k(\omega)$ by

$$\alpha = \frac{2\omega}{c} k.$$ (3.12)

At the boundary between vacuum and a medium with the complex refractive index $N = n + ik$, the reflectance $R$ can be expressed as[8, 13]

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}.$$ (3.13)

All coefficients described above are intrinsic to the medium.

### 3.2.2 Thin Film

When a light beam is normally applied to a thin film with thickness $d$, the transmissivity $T$ is defined as the ratio of resultant light intensity transmitted through the film to the incident light intensity. The reflectivity $R$ is the ratio of the total reflected light intensity to the incident light intensity. Generally, for a thin film, multiple internal reflections and interference between the multiple beams can be considered to give:[13]

$$T = T(1 - R)^2(1 + k^2/n^2)/D$$ (3.14)

$$R = R[1 + T^2 - 2T^2 \cos(2\omega nd/c)]/D$$ (3.15)
where the transmittance $T$ is the ratio by which the light intensity is reduced when the light travels distance $d$ in the material and

$$D = 1 + R^2T^2 - 2RT \cos(2\omega nd/c + 2\delta) \quad (3.16)$$

$$\delta = \arctan[2k/(n^2 + k^2 - 1)] , \quad (3.17)$$

with light velocity $c$.[13] Here $\delta$ is the phase difference between incident and reflected electric fields.[8] The real and imaginary part of the refractive index are obtained by the relations[13]

$$n = \frac{1 - R}{1 + R - 2\sqrt{R} \cos \delta} \quad (3.18)$$

$$k = \frac{2\sqrt{R} \sin \delta}{1 + R - 2\sqrt{R} \cos \delta} . \quad (3.19)$$

If both of the transmissivity and the reflectivity of a film are measured simultaneously at a given frequency, other optical constants of the material at the frequency are obtained by solving the above equations.

From equation 3.11,

$$I(r) = I(0) \exp(-\alpha r) . \quad (3.20)$$

From this, the transmittance $T$ can be related to $\alpha$ by

$$T \equiv \frac{I(d)}{I(0)} = \exp(-\alpha d) . \quad (3.21)$$

A rigorous calculation using the above equations is essential to get accurate optical coefficients, especially when interference fringes are detected. On the other hand, if the reflection is small and the optical coefficient is large enough, the measured value transmissivity $T$ and the calculated value transmittance $\tilde{T}$ do not show much difference. As a result, it is customary to use straightforward concepts $T$ and $R$
instead of much more complicated $T$ and $R$ in the analysis of photoinduced absorption (PIA). The usage of $T$ instead of $T$ facilitates physical interpretation.

The optical density or absorbance $A$ is defined to be

$$A = - \log_{10} T \simeq - \log_{10} T = \frac{\alpha d}{\ln 10} \simeq 0.4343 \alpha d. \quad (3.22)$$

Most commercialized UV/VIS spectroscopies measure the optical density $A$ of films or solutions.

The PIA experiment monitors the change of the absorption coefficient of a material caused by optical pumping. Usually the result is presented in the form of the normalized transmittance change, $-\Delta T/T$. From above relations,

$$- \frac{\Delta T}{T} = - \frac{\Delta I(d)}{I(d)} = 1 - \exp\{-\alpha d\} \simeq (\Delta \alpha) d = (\ln 10) \Delta A \simeq 2.303 \Delta A. \quad (3.23)$$

Above equation is valid as far as $|\Delta T| \ll T$. When $\alpha$ increases, or photoinduced absorption (PIA) occurs, $-\Delta T/T$ gives a positive value. At the same time, $-\Delta T/T$ becomes negative when photoinduced bleaching (PIB) occurs.

### 3.3 Absorption Spectra of Polyaniline Family

In a normal UV/VIS/IR absorption spectroscopy, the sample is probed with a weak light beam and the optical density or transmittance is measured as a function of the probe photon energy. From this, information about the electron and phonon structure of the material can be obtained. The probe beam should be weak enough not to cause any appreciable secondary effects.
3.3.1 Electronic Absorption

The three oxidation states of polyaniline base have very different UV/VIS absorption spectra, as shown in figure 15. The fully reduced state, leucoemeraldine base (LEB), has a wide energy gap and shows an absorption peak at \( \sim 3.6 \) eV, which is due to the \( \pi - \pi^* \) transition of the phenyl rings. The very weak peak at \( \sim 2 \) eV seems to reflect the existence of small portion of quinoid rings due to imperfect reduction. Since the peak is at \( \sim 2 \) eV rather than \( \sim 2.3 \) eV, it is believed that the oxidized portions form emeraldine base (EB), not pernigraniline base (PNB).

The \( \sim 2.0 \) eV peak of EB was interpreted as an exciton peak, caused by a molecular exciton whose electron is localized on a quinoid ring and hole is localized on the two benzenoid nearest neighbors.[98, 99] Sometimes this absorption peak is directly referred to as the energy gap. In solution, the \( \sim 2.0 \) eV peak shifts to lower energy when the dielectric constant of the solvent increases.[100] The \( \sim 3.8 \) eV peak comes from the \( \pi - \pi^* \) band gap.[99] The peak is shifted to higher energy and the full width half maximum (FWHM) is larger than in the LEB case. It seems that the \( \sim 4.3 \) eV peak shown in PNB is hidden in the slope of the \( \sim 3.8 \) eV peak in EB, to make the peak shift toward higher energy and broader than the \( \sim 3.6 \) eV peak in LEB.

PNB has three dominant absorption peaks. The \( \sim 2.3 \) eV peak again comes from the quinoid rings. Since the alternative existence of quinoid rings and benzenoid rings constitutes the two-fold degenerate ground state as in trans-polyacetylene, this peak is referred to as a Peierls energy gap. The \( \sim 3.8 \) and \( \sim 4.3 \) eV peaks are from \( \pi - \pi^* \) transitions.[101] In all three oxidation states, the \( \pi - \pi^* \) transition peak at \( \sim 3.8 \) eV shifted to higher energy and weakened as the temperature went up from \( \sim 20^\circ \)C to
Figure 15: UV/VIS range optical absorption of polyaniline bases. From [97].
3.3.2 Infrared Absorption

While the UV/VIS spectra give information on electronic structure, the infrared (IR) spectra play an important role in verifying chemical structure. Figure 16 shows the IR spectra of polyaniline bases. The prominent peaks are at 816, 1284, 1497, and 1613 cm$^{-1}$ in LEB, 831, 1166, 1304, 1498, and 1592 cm$^{-1}$ in EB, and 848, 1106, 1164, 1215, 1318, 1485, and 1585 cm$^{-1}$ in PNB.[97, 99]

As is obvious from the figure 16, the peak at $\sim 1600$ cm$^{-1}$ is related to the presence of quinoid rings. Comparison of the two absorption peaks at $\sim 1500$ cm$^{-1}$ and $\sim 1600$ cm$^{-1}$ makes a convenient measure to determine the level of oxidation, like the $\sim 2$ eV absorption peak in the UV/VIS spectra.[99]

3.4 Chemical Doping

Pristine conducting polymers show DC conductivities characteristic to insulators or semiconductors. Only upon doping, does the high DC conductivity appear. As described earlier, doping is a process in which electric charge is added to or subtracted from the system. The apparent effect is the dramatic change of DC conductivity.

When an acceptor is used, the polymer loses a net amount of electrons or gains holes (p-doping). Likewise, a donor will add electrons to the conducting polymer (n-doping). The newly introduced charges change the physical properties of the polymer. Generally, chemical doping of a polymer is a reversible procedure. Electron-donating or electron-accepting chemicals are mixed to the polymer to achieve doping. The
Figure 16: IR spectra of polyaniline bases. From [97].
dopants are stable in their position since they are connected to the backbone of the polymer by Coulomb forces, following the charge transfer. When a proper neutralizer is added, due to the one-dimensional property of polymers, the added donors or acceptors can be removed. In some cases, the dopant can be permanently added to be part of the polymer when the polymer is synthesized. Such a self-doped polymer has been reported recently.[103, 104]

### 3.4.1 Emeraldine Base

Polyaniline is the first conducting polymer to be doped to a metallic state without oxidation or reduction.[105, 106, 107] This doping process is a protonation process such that H\(^+\) ions, or protons, are added to the system. The number of electrons in the polymer remains the same throughout the doping procedure. This addition of positive charge induces an electronic and possibly a structural rearrangement of the system. Though any acid can give up protons, it is convenient to use a volatile acid so that the excess acid can be removed when the sample is dried. Hydrochloride, HCl, is suitable for the purpose.[108] Commonly, 1 M HCl solution or HCl vapor is used to convert emeraldine base (EB) to emeraldine salt (ES).

Figure 17 shows the absorption curves of EB and ES. The difference between the two is the doping-induced absorption (DIA). In the DIA curve, both of EB absorption peaks at \(~ 2.3\) and \(~ 3.8\) eV are strongly suppressed and new absorption peaks are found at 0.9, 1.5, and 3.0 eV. The crossover between doping-induced absorption and doping-induced bleaching occurs at 1.72, 2.90, and 3.20 eV.

Nitrogen atoms in polyaniline make either amine sites (\(-N(H)-\)) or imine sites (\(-N\equiv\)), depending on the oxidation level. The DC conductivity of leucoemeraldine
Figure 17: Optical density (absorbance) curves of EB and ES. The solid line is the doping-induced absorption (DIA).
base (LEB), which contains no imine sites, does not change upon protonation and remains at \( \sim 10^{-10} \text{S/cm} \). But that of EB increases from \( \sim 10^{-10} \text{S/cm} \) to \( \sim 5 \text{S/cm} \) upon HCl doping. This shows protonation occurs at imine sites.[106, 108] The total number of electrons in the polymer does not change during the doping process.[107, 108, 109]

An imine site in polyaniline lies between a benzenoid ring and a quinoid ring. The nitrogen atom has three \( \sigma \) orbitals from \( sp^2 \) hybridization. Two of them form \( \sigma \) bonds with two neighboring carbon atoms. Two out of five nitrogen outer shell electrons are used for this. The remaining one \( \sigma \) orbital does not form a bond and contains two electrons from nitrogen. At the same time, the fifth nitrogen electron makes a \( \pi \) bond with the carbon atom at the quinoid ring.

A possible configuration of the protonated form of emeraldine base (EB), emeraldine salt (ES), was first suggested by Chiang et al.[108]. When EB is doped with HCl, or H\(^+\) and Cl\(^-\) ions, the proton or H\(^+\) goes to the filled \( \sigma \) orbital of an imine site nitrogen atom, which is not previously used for a bond, and forms a \( \sigma \) bond with the nitrogen. It should be noted that overall electron configuration does not change by this protonation or doping process. The counter-ion, Cl\(^-\), remains close to neutralize the charge. Still, in every four ring unit, there are three benzenoid rings and one quinoid ring, as shown in figure 18 (b). It was suggested that all four rings can become a quinoid ring, one at a time, resulting in a resonance state.[108]

The magnetic susceptibility of the emeraldine form as a function of protonation and temperature was reported by Ginder et al.[110] Based upon the existence of a Pauli-like susceptibility, the polaron-lattice model was proposed. When both of the neighboring imine sites are protonated, the quinoid ring becomes a benzenoid ring. This creates two lone pair \( \pi \) electrons, one at each nitrogen atom, as shown
Figure 18: Formation of a polaron lattice. (a) Emeraldine base. (b) Protons make \( \sigma \) bond at imine sites. (c) A bipolaron form. (d) Polarons are separated to form a lattice. From [111].
in figure 18 (c). This is regarded as a bipolaron state. To explain the existence of a Pauli-like susceptibility and high DC conductivity, one more step is needed: the bipolaron splits into polarons. Because half of all the nitrogen can be doped, to realize the polaron status, every other nitrogen will have spin, as in figure 18 (d).[110] Furthermore, phase segregation is suggested between metallic and nonmetallic phases, based upon observation of a proportionality between the Pauli susceptibility and the protonation level, as seen in figure 19.[110] This polaron lattice model is supported by a comparison of calculated band structures for the bipolaron and polaron lattices to the optical absorption curve of emeraldine salt.[111]

Recent ESR measurements of EB and PNB solutions show that the observed spin is mainly confined to a nitrogen site.[112, 113] The identification of the protonated pair of imine sites as a bipolaron assumes the two spins will cancel each other. If the two adjacent lone π electrons are not severely overlapping, the Pauli-like susceptibility could be explained without rearranging the protonated sites. In other words, even without rearrangement, the two protonated sites adjacent to a previous quinoid ring can be regarded as two polarons.

3.4.2 Pernigraniline Base

In fully oxidized pernigraniline base (PNB), every nitrogen is at an imine site. Since it was shown that the imine sites in EB accept protons, PNB was expected to show the same behavior, resulting in the protonation of all imine sites. But when PNB was treated with aqueous HCl, not only protonation but also reduction occurred.[85, 114] While the protonation occurs at some imine sites, hydrogens in benzenoid rings are substituted with Cl atoms, giving other imine sites hydrogen atoms, not protons. As a result, the HCl protonated pernigraniline becomes emeraldine salt (ES) with Cl
Figure 19: Number of spins vs. EB doping level. From [110].
substitution in the rings. When the protonated pernigraniline is deprotonated, EB with Cl substitution remains, not PNB.\[85, 114\]

PNB is n-doped by Na-naphthalde solution in THF.\[85\] It is believed that the sodium atom becomes the Na\(^+\) ion, giving the electron to an imine site. The n-doped pernigraniline becomes undoped when exposed to the air. The sodium atom is washed out in the form of NaOH. The water molecule, H\(_2\)O, will leave a hydrogen atom behind in the dedoping procedure. The remaining material shows an absorption curve matching to a half-and-half mixture of PNB and EB, suggesting one out of four nitrogen sites experienced doping.\[85\]

3.4.3 Leucoemeraldine Base

The fully reduced leucoemeraldine base (LEB) can be doped by any of many oxidizing agents, like Cl\(_2\), (NO\(^+\))(PF\(_6\))\(^-\), FeCl\(_3\), SnCl\(_4\), or tetracyanoquinodimethane (TCNQ).\[109\] Some of the electrons are drained out of the polymer in this case. The final conducting form is believed to be emeraldine salt (ES).\[107, 109\] Again, this doping process is not reversible.

3.4.4 Chemical Doping and Optical Pumping

Here the similarities and differences between chemical doping and optical pumping are considered. As shown in chapter II, low level chemical doping and optical pumping give qualitatively the same results in many conjugated polymers, like polyacetylene and polythiophene. In other words, both electron- and/or hole-doping methods may create the same kind of electronic defects in conducting polymers. Under this premise, the differences between the two methods are described below.
Differences between Chemical Doping and Optical Pumping

There are some differences between the chemical doping and optical pumping. While chemical doping gives only one kind of charge to the polymer system, optical pumping has the same effect as doing both n-doping and p-doping at the same time. The net charge of the system remains neutral in optical pumping unlike chemical doping.

Chemical doping always places counter ions very near to the injected charge. As a result, the created electronic defects are generally under Coulomb interaction with the counter ion and cannot move away. In optical pumping, the excited electrons jump inside the same polymer chain or to other chains, leaving holes behind. When electronic defects are created due to the electrons or holes, generally they are not pinned by a static Coulomb potential, except possibly by that of the oppositely charged electronic defects in a neighboring chain.[34] Obviously, if pinning occurs due to the Coulomb interaction between two optically-created, oppositely-charged defects, the two will very easily annihilate each other to the ground state. Still, optically-created defects can be pinned, due to intrinsic low mobility or structural disorder in the system.

The electronic defects induced by chemical doping will never decay, while the ones by optical doping need not be permanent. As for the chemically induced electronic defects, they cannot lose the net charge, since the electron affinity difference between the polymer and the counter ion resulted in the charge transfer. In the optical pumping case, the situation is different. Though the separated and isolated electrons and holes may create such electronic defects to lower the energy, still those are excited states compared to the ground state. As a result, the photoinduced defects usually have finite decay time. One dramatic comparison can be done in the
situation where the electronic defects of the two different origins are optically probed. When an electronic defect is optically probed, there is a change in the numbers of electrons in the intragap electronic states belong to the defect. If the defect is due to optical pumping, such disturbance may easily destroy or change the defect state and it may not go back to the state before the optical probing. But, as for a chemically induced defect, the defect excited by the absorption of the probe photon will end up with the the original defect state, since that is the most energetically favoured state.

**Photoinduced Absorption**

Another difference comes from the practical point of view. It is interesting to measure directly the time evolution of electronic defects in the conducting polymers. When chemical doping is used, it is very hard to monitor the creation and evolution of electronic defects within a time scale shorter than a few seconds. However, these observations can be done in an optical pumping situation, due to the development of modern electronics and laser technology.

Photomodulation (PM) spectroscopy[115] is a method to optically monitor the dynamics of the optical signatures of electronic defects created by optical pumping. In PM experiment, two light sources are used, one is for the optical pumping and the other for the probing of the state change. When an electronic state or infrared active vibrational (IRAV) mode is created upon optical pumping, the absorption of the probe light may increase due to the newly created states. This is called photoinduced absorption (PIA). Since optical pumping does not change the total density of electrons in the system, from the sum rule,[115]  

\[
\int_0^\infty \Delta \alpha(\omega) d\omega = 0 ,
\]  

(3.24)
it is expected that there will be photoinduced bleaching (PIB) to keep the total absorption constant. The primary concern of PM is PIA. As a result, in many literatures, the word PIA is used in two ways. Sometimes PIA means the PM measurement. When it is used with PIB, it has the narrow meaning: absorption increase due to optical pumping. When ultrafast-time-scale dynamics are emphasized, sometimes it may be called transient absorption.

The basic idea of photoinduced absorption (PIA) is to optically monitor the absorption change of a sample caused by an optical pumping. Many variations of PIA measurement are possible depending on factors including time scale, optical pump intensity, and probing range. The result of PIA can be strikingly different depending on the time scale involved. There are three distinctive photoinduced absorption (PIA) measurements generally available. They are picosecond, near-steady-state, and long-time photoinduced absorption experiments. To interpret experimental results properly, it is important to understand the relationships of the three methods.

Polyaniline

In polyaniline, there is an additional difference between chemical doping and optical pumping. As pointed out above, polyaniline is classified as a conducting polymer, mainly because the emeraldine base form of it can be reversibly doped to become the highly conducting emeraldine salt form. But this chemical doping procedure does not include electrons or holes. As for the two other oxidation states of polyaniline, pernigraniline and leucoemeraldine, there is no known way of reversible doping. In other words, photoinduced absorption in polyaniline is not a simulation of chemical doping.
3.5 Near-Steady-State Photoinduced Absorption

In some materials, including conducting polymers, the excitation of an electron from the valence band to the conduction band can create a defect state inside the bandgap. For example, as explained above, when an electron is excited in a conjugated polymer, creation of a soliton or polaron state is energetically favored over staying in the conduction band.

Suppose that a sample is exposed to an intense light beam whose energy exceeds the energy gap of the sample. Then most photons will be absorbed, or will excite electrons in valence band to conduction band. If some portion of the excited electrons form defect states inside the energy gap, the absorption of the probe photons whose energy is below the energy gap will increase depending on the energy.

Figure 20 shows the schematics of a near-steady-state photoinduced absorption (NSSPIA) experiment. Typically a laser is used as a pump, since a massive photon flux within a narrow energy range is needed. The color of the pumping laser is chosen where the sample absorption is high, usually at the absorption peak just above the energy gap, to have efficient electron excitation. As a probe beam, usually a weak white light source is used. The probe beam is analyzed by a monochromometer, before or after passing through the sample. Since the probe itself is weak and the change of the transmission is very small, to detect the transmission difference with and without the pump beam, the pump beam is time modulated by a mechanical chopper and the modulated signal is measured by a detector attached to a lock-in amplifier (LIA).

In this section, time dependence and intensity dependence of near-steady-state PIA (NSSPIA) are described in detail. The polyaniline NSSPIA results are shown.
Figure 20: A typical experimental setup for measuring the near-steady-state photoinduced absorption. From [116].
3.5.1 Time Dependence

An optical detector connected to a preamplifier is usually used to convert the probe light intensity to voltage. A lock-in amplifier (LIA) is a very sensitive AC voltmeter, which can measure the amplitude and phase of a signal in a noisy environment if the frequency of the signal is known. To use a LIA, time modulation of the signal is needed. In NSSPIA, a mechanical chopper or an equivalent optical shutter is used as a time modulator. The LIA knows the modulation frequency by receiving a trigger from the modulator. If the optical pumping of the sample creates some electronic defect states which have intragap energies, when the pump beam is time modulated, the probe beam intensity transmitted through the sample will be modulated with the same frequency because of PIA. When photoinduced bleaching (PIB) occurs at a given probe photon energy, the probe beam intensity transmitted through the sample will be increased when the pump beam is on. The intensity will decrease if there is photoinduced absorption (PIA).

To determine the zero of phase, the LIA should be initialized. In the NSSPIA experiment, the time modulated pump beam is used for the phase initialization. The signal phase is read as 0° if it is in phase with the pump beam. Traditionally, the normalized transmittance variation, \(-\Delta T/T\), is reported for PIA experiment. Because of the negative sign, generally, a positive value denotes PIA and a negative value PIB from equation 3.23. But this is not always true, as will be shown below.

Suppose that the pump beam is modulated with frequency \(f\) or period \(P = 1/f\), such that the pump beam is on for the first half of the period and off for the rest half as in figure 21 (a). If the LIA measures the x-component and y-component of the signal, after initialization, the x-component is proportional to the cross correlation between
the signal and \( \sin\left(\frac{2\pi t}{P}\right) \) (figure 21 (b)), while the \( y \) component is proportional to the cross correlation between the signal and \( -\cos\left(\frac{2\pi t}{P}\right) \) (figure 21 (c)). The \( x \)-component is the component which is in phase with the reference. The phase of \( y \)-component follows the reference phase with 90° delay.

The use of a LIA has another advantage. Since the signal is time modulated, the modulation frequency dependence of the photoinduced absorption can give more information about the defect states. Before developing a quantitative model, some extreme cases can be considered. For convenience, PIB is assumed. Then the transmitted probe beam intensity will be increased when the pump beam is on. The PIA case is obtained when the sign of the signal is reversed. Though there is a fundamental difference between the origins of PIA and PIB, in the following model, they can be treated the same way except for the sign.

Suppose an electronic defect can be introduced by optical pumping. If the decay time constant \( \tau \) of the defect is very small compared to the modulation period \( P \), as shown in figure 21 (d), the signal will rise to equilibrium soon after the pump beam is on and decay away very fast as soon as the pump beam is off. As a result, the signal time dependence is very similar to the pump beam and the phase of the signal will be nearly 0°. On the other hand, if \( \tau \) is extremely large compared to \( P \), the number of defects will increase while the pump beam is on but will not noticeably change when the pump beam is off, as in figure 21 (f). In this case, the \( x \)-component measured by the LIA will have negative value, while the \( y \)-component is positive. As a result, the phase will be between 90° and 180°. In other words, like PIA with very short decay time, the measured \( x \)-component value will be negative. In the intermediate region between the two extreme cases, when \( \tau \) is comparable to \( P \), the phase will be around 90°.
Figure 21: (a) Pump beam modulated with frequency $f = 1/P$ (b) $\sin \left( \frac{2\pi t}{P} \right)$ (c) $-\cos \left( \frac{2\pi t}{P} \right)$ (d) $P \gg \tau$ (e) $P \sim \tau$ (f) $P \ll \tau$. 
For the time being, it will be assumed that the ratio between the number of pumping photons and the number of defects created remains constant, independent of the sample history or pump beam intensity. This assumption is valid as long as the average number of existing defects is much less than the maximum capacity of the sample. The detailed discussion is in the next subsection.

Suppose a pump beam of constant intensity $I$ is turned on for a duration of $P/2$, as in figure 21 (a), to a sample which was not previously exposed to the pump beam. Then, for a given time $ds$ which is very short compared to the characteristic time scales related to the decay of the defect but much longer than the defect creation time, the change in the intensity or the transmittance of the probe beam will be linearly proportional to $Ids$. This assumption is justified since the creation time is usually no longer than psec scale and the decay time constants related to the defects which can be detected by a NSSPIA measurement are in the range of $\mu$sec or longer, as will be shown later.

Let $D(t)$ be the time dependence of the number of defects created at $t = 0$, s.t. $D(0) = 1$ and $D(t)$ never increases for $t \geq 0$. Then, for $0 \leq t \leq P/2$, the transmitted probe beam intensity change, $R_0(t)$, can be described as

$$R_0(t) = \int_0^t \gamma I ds D(t - s).$$  \hspace{1cm} (3.25)

It is assumed that the probe beam intensity change will be proportional to the change of the number of defects, following equation 3.23. Likewise, for $t \geq P/2$, the temporal behavior of the transmitted probe beam intensity change, $F_0(t)$, becomes

$$F_0(t) = \int_0^{P/2} \gamma I ds D(t - s).$$ \hspace{1cm} (3.26)

The subscript '0' means there is no previous optical pumping. Here

$$\gamma = \eta \zeta(\omega)$$  \hspace{1cm} (3.27)
where $\eta$ indicates the efficiency of creating defects from the optical pumping and $\zeta(\omega)$ is proportional to the optical coefficient change at the probe beam photon energy $\hbar \omega$ due to the creation of defects. As mentioned above, $\eta$ is assumed constant in this subsection. Practically, $\eta$ depends on the number of already existing defects. This will be discussed in the next subsection. When there is PIB, $\zeta$ and $\gamma$ are positive and when there is PIA, both of $\zeta$ and $\gamma$ are negative.

Suppose that there are $N$ precedent optical pumpings, where a pump beam of intensity $I$ has been turned on for the first half of period $P$. The effect is that the transmitted probe beam intensity changes are given by

$$R_N(t) = R_0(t) + \sum_{n=1}^{N} F_0(t + nP)$$

$$F_N(t) = F_0(t) + \sum_{n=1}^{N} F_0(t + nP).$$

Again, $R_N(t)$ is valid when the pump beam is on $(0 \leq t \leq P/2)$ and $F_N(t)$ is for $t \geq P/2$. The continuity requirements

$$R_N(P/2) = F_N(P/2)$$

$$R_N(0) = F_{N-1}(P)$$

are obviously satisfied.

Now, the $x$- and $y$-component values recorded by a LIA, $X_N$ and $Y_N$, will be

$$X_N = \frac{2}{P} \int_0^{P/2} R_N(t) \sin\left(\frac{2\pi t}{P}\right) dt + \frac{2}{P} \int_{P/2}^{P} F_N(t) \sin\left(\frac{2\pi t}{P}\right) dt$$

$$Y_N = -\frac{2}{P} \int_0^{P/2} R_N(t) \cos\left(\frac{2\pi t}{P}\right) dt - \frac{2}{P} \int_{P/2}^{P} F_N(t) \cos\left(\frac{2\pi t}{P}\right) dt.$$

The amplitude and the phase angle, $A_N$ and $\phi_N$, are obtained from the relations

$$A_N = \sqrt{X_N^2 + Y_N^2}$$

$$\phi_N = \arctan(Y_N/X_N).$$
In principle, $A_N$ and $\phi_N$ above can be found for any decay function $D(t)$ by numerical methods. If total $M$ different defects are created, the factor $\gamma D(t - s)$ in equations 3.25 and 3.26 is changed into

$$\gamma D(t - s) = \sum_{i=1}^{M} \gamma_i D_i(t - s) \tag{3.36}$$

due to the superposition principle. In the simplest case where there is only one kind of defect which decays exponentially with time constant $\tau$,

$$D(t) = \exp(-t/\tau). \tag{3.37}$$

With this, a straightforward calculation gives

$$R_N(t) = \gamma I \tau \left(1 - \frac{e^{P/2\tau} + e^{-NP/\tau}}{e^{P/2\tau} + 1} e^{-t/\tau}\right) \tag{3.38}$$

$$F_N(t) = \gamma I \tau \left(\frac{e^{P/\tau} - e^{-NP/\tau}}{e^{P/2\tau} + 1}\right) e^{-t/\tau} \tag{3.39}$$

$$X_N = 2\gamma I \tau \left\{ \frac{1}{\pi} - \frac{2\pi}{(P/\tau)^2 + 4\pi^2} \left(2 + e^{-\frac{1}{2}NP/\tau} - e^{-(N+1)P/\tau}\right) \right\} \tag{3.40}$$

$$Y_N = \frac{2\gamma IP}{(P/\tau)^2 + 4\pi^2} \left(2 + e^{-\frac{1}{2}NP/\tau} - e^{-(N+1)P/\tau}\right). \tag{3.41}$$

Decay Time VS. Phase

Consider a typical NSSPIA measurement with modulation frequency $f = 1$ kHz or $P = 1$ msec. If the experiment started $\sim 15$ minutes ago, $N$ can be set to be $N = 10^5$. Under the assumption that only one kind of defect is created which decays exponentially with decay time constant $\tau$, the values of $X_N$, $Y_N$, $A_N$, and $\phi_N$ calculated as a function of $\log(\tau)$ are shown in figure 22, using equations 3.37 – 3.41. Here the PIB case is shown, by using a positive $\gamma$. In PIA, $\gamma$ is negative and, as a result, the $X_N$ and $Y_N$ change sign and $180^\circ$ is added to $\phi_N$. $A_N$ remains same.
Figure 22: A PIB simulation. $D(t) = \exp(-t/\tau)$ with $P = 1$ ms and $N = 10^5$. (a) $X_N$, $Y_N$, and $A_N$. (b) $\phi_N$. 
Figure 23: Log-log plot of NSSPIA signal amplitude as a function of modulation frequency. $NP = 1000 \text{ sec and } \tau = 10 \text{ ms}$. 
When the decay time \( \tau \) is less than the pump beam modulation period \( P \), the in-phase reading of the LIA, \( X_N \), shows the correct sign. \( X_N \) has a peak when \( \tau \) is \( \sim 10 \) times shorter than \( P \). If the decay time \( \tau \) is within the range of \( \sim P \) to \( \sim 10^4 P \), the \( X_N \) value is suppressed and the phase \( \phi_N \) becomes \( \sim 90^\circ \). When \( \tau \) is longer than \( \sim 10^5 P \), a very interesting phenomenon occurs. The phase grows beyond \( 90^\circ \) and the \( X_N \) value becomes negative. \( Y_N \) is smaller than \( X_N \) when \( \tau \) is very short, but when \( X_N \) has a peak, the size of \( Y_N \) exceeds that of \( X_N \) and remains constant when \( \tau \) becomes longer. From equations 3.35, 3.40, and 3.41, it is easily seen that \( \phi_N \) depends only on the ratio \( P/\tau \), while \( X_N \) and \( Y_N \) have \( \tau \) and \( P \) as independent factors, respectively. These results in figure 22 fit into the intuitive expectation in figure 21.

Another interesting result is that the sizes of \( X_N \) and \( Y_N \) are reduced dramatically when the decay time \( \tau \) becomes much shorter than the modulation period \( P \). This explains why \( \mu \text{sec} \) or shorter time scale effects cannot be detected by the NSSPIA measurement.

**Decay Time VS. Modulation Frequency**

The above equations show a strong relationship between the decay time \( \tau \) and modulation frequency \( f = 1/P \), through the signal amplitude change. Figure 23 shows a log-log plot of the NSSPIA signal amplitudes measured by a LIA as a function of the pump beam modulation frequency \( f \) for a fixed decay time \( \tau \). Again, equation 3.37 is assumed and \( \tau \) is set to 10 msec. To simulate exposure of the sample to the pump beam for about 15 minutes, \( N P (= N/f) \) is kept constant at 1000 second. In figure 23, the slope of \( \log(X_N) \) changes when the chopping period \( P \) becomes several times longer than the defect decay time \( \tau \). While \( X_N \) levels off when the chopping
frequency becomes smaller, $Y_N$ decreases fast. Apparently, when $P$ becomes shorter than $\tau$, the signal size reduces dramatically.

### 3.5.2 Optical Pumping Intensity Dependence

For a sample, since the number of molecules is finite, there exists the upper limit on the number of localized electronic defects the sample can accommodate. When optical pumping is started, most of the photons are absorbed and some portion of them create defect states. In this subsection, it is assumed that the optical pumping intensity is constant, without any time modulation.

As the optical pumping is continued, the number of defects increases. At the same time, generally, the defects decay with finite decay time. When the number of defects become appreciable compared to the maximum defect capacity of the sample, for an incoming photon, the chance of creating defects is reduced. Initially, the increasing slope will be stiff. Later it gradually levels off as the number of defects approaches an equilibrium point. Eventually, the number of defects will reach an equilibrium value.

This relation is formulated as

$$\frac{dn}{dt} = A(n_{\text{max}} - n)I - \gamma(n) \quad (3.42)$$

where $n$ is the defect number density. The first term in the right hand side of equation 3.42 increases $n$. $A$ is an appropriate constant and $I$ is the pump beam intensity, which is proportional to the number of incoming photons per unit time. The maximum defect density $n$ the sample can have is $n_{\text{max}}$. The number of defects created in a unit time is proportional to the number of photons and the number of available defect sites.
The second term in the left side of equation 3.42 is non-zero when the defects decay or diffuse away. Here, diffusion effect is ignored and only two simple decay mechanisms will be considered. In the case that the defect decays alone, this term will be proportional to \( n \) and if it decays by combining with another defect of same kind, the term will be proportional to \( n^2 \). In other words,

\[
T(n) = B_k n^k
\]

(3.43)

where \( B_k \) is again an appropriate coefficient and \( k \) is 1 or 2 depending on the nature of the decay, unimolecular or bimolecular, respectively.

When equilibrium is achieved, \( \frac{dn}{dt} \) vanishes in equation 3.42, giving

\[
A(n_{\text{max}} - n_{\text{eq}})I = \Upsilon(n_{\text{eq}}).
\]

(3.44)

Only when \( \Upsilon = 0 \), \( n_{\text{eq}} \) becomes same as \( n_{\text{max}} \). For \( k = 1 \) in equation 3.43, from the equation 3.44, \( n_{\text{eq}} \) becomes

\[
n_{\text{eq}} = \frac{AI}{AI + B_1} n_{\text{max}}.
\]

(3.45)

If \( AI \gg B_1 \), \( n \) grows close to \( n_{\text{max}} \). For \( k = 2 \), the exact solution of equation 3.44 is

\[
n_{\text{eq}} = \frac{1}{2} \left( \sqrt{\frac{AI}{B_2}^2 + 4 \frac{AI}{B_2} n_{\text{max}} - \frac{AI}{B_2}} \right).
\]

(3.46)

The light intensity cannot be increased indefinitely, since the sample itself will be destroyed. To increase \( n_{\text{eq}} \), not only \( I \) but also the coefficients \( A \) and/or \( B_k \) should be manipulated by some proper way such as temperature adjustment.

If the decay channel is large relative to the defect creation rate, \( n_{\text{eq}} \) may become very small compared to \( n_{\text{max}} \) and equation 3.44 can be approximated to

\[
A n_{\text{max}} I = \Upsilon(n_{\text{eq}}).
\]

(3.47)

From this, \( n_{\text{eq}} \) is proportional to \( I \) for \( k = 1 \) and proportional to \( \sqrt{I} \) for \( k = 2 \).
If saturation is defined as the situation where the number of defects reaches the maximum capacity of the sample so that there are no more defect sites available, from above equations it is apparent that saturation cannot be achieved as long as there is a finite decay time or a non-zero chance that a defect disintegrates into the next stage. The two concepts, saturation and equilibrium, should be distinguished.

From equation 3.42, when it is assumed that $T = 0$ or there is no decay or diffusion at all,

$$\frac{dn}{dt} = A(n_{\text{max}} - n)I. \quad (3.48)$$

This differential equation is easily solved to give

$$n(t) = n(0) \exp(-t/\tau_{eq}) + n_{\text{max}}\{1 - \exp(-t/\tau_{eq})\}, \quad (3.49)$$

with the time constant $\tau_{eq}$

$$\tau_{eq} \equiv 1/(AI) \quad (3.50)$$

which is the measure of the time needed to reach the equilibrium. If the sample has not been previously exposed to the pump beam, $n(0) = 0$. When $t \ll \tau_{eq}$, equation 3.49 can be approximated to give

$$n(t) - n(0) \simeq \frac{n_{\text{max}} - n(0)}{\tau_{eq}}t. \quad (3.51)$$

Under constant pumping, the number of defects $n$ grow proportional to time only when the sample was optically pumped in a very short period compared to $\tau_{eq}$. Otherwise, even without any decay mechanism, the growth rate of the defect population will gradually approach to zero.

In the previous subsection, under the assumption that $\eta$ is constant, by using equation 3.51 with $n(0) = 0$, the decay time $\tau$ and the modulation period $P$ were compared. But there can be a case such that $\tau_{eq}$ is not longer than the time scale
of the experiment and the density of defects is around the equilibrium value \( n_{eq} \).
Practically, the sample can be annihilated to prevent the drift of the signal during the measurement.

From the arguments above, \( \eta \) and \( \gamma \) in the previous subsection are proportional to \( n_{\text{max}} - n \). With same sample and same condition, while \( n_{\text{max}} \) is a constant, \( \tau_{eq} \) and \( n_{eq} \) are the functions of the pump intensity \( I \). As \( I \) becomes larger, \( \tau_{eq} \) shortens and \( n_{eq} \) increases.

### Temporal Growth Behavior

In practice, when there is virtually no decay mechanism, under a constant optical pumping, the growth of number density of defects are slower than the exponential form shown in equation 3.49 and often fits to stretched exponential form

\[
n(t) = n_{\text{max}}[1 - \exp\{-(Ct)^\beta\}],
\]

with a constant \( C \). Here \( \beta \) has value between 0 and 1. One important example is the population growth of the optically excited electronic defects in polyaniline.[93, 112]

To explain this slow growth, many possibilities were sought from various decay mechanisms which show stretched exponential time dependence.[93] Here, it will be argued that such slow defect growth is at least partly due to a universal property coming from the bulkiness of sample, independent of the microscopic sample-dependent mechanism.

Strictly speaking, equation 3.48 is true only when the sample is made up of one monomolecular layer. Otherwise, sample thickness effects should be considered. The formulation is straightforward. Consider a film of thickness \( d \). The excited
state number density \( n \), the optical coefficient \( \alpha \), and the pump beam intensity \( I \) are functions of time \( t \) and position \( x \) with \( 0 \leq x \leq d \). The pump beam comes from negative \( x \)-axis with intensity \( I(x = 0, t) = I_0 \) for any \( t \). If the maximum or saturation number density is \( n_{\text{max}} \), their relations can be expressed as

\[
\alpha(x, t) = \alpha_0 - (\alpha_0 - \alpha_1) \frac{n(x, t)}{n_{\text{max}}} \tag{3.53}
\]

\[
I(x, t) = I_0 \exp\left\{-\int_0^x \alpha(\rho, t) \, d\rho\right\} \tag{3.54}
\]

\[
\frac{dn(x, t)}{dt} = A\{n_{\text{max}} - n(x, t)\} I(x, t) \tag{3.55}
\]

where \( \alpha_0 \) is the pristine sample optical coefficient, \( \alpha_1 \) is the electronic defect saturated portion optical coefficient, and \( A \) is same constant as the one in equation 3.48. Above equations can be put to one integrodifferential equation

\[
\frac{dn(x, t)}{dt} = A\{n_{\text{max}} - n(x, t)\} I(x, t) \exp\left\{-\alpha_0 x + \frac{\alpha_0 - \alpha_1}{n_{\text{max}}} \int_0^x n(\rho, t) \, d\rho\right\}. \tag{3.56}
\]

The photoinduced absorption at a probe energy or the number of spins in the system will be proportional to \( 1 - \exp\{C \int_0^d n(\rho, t) \, d\rho\} \) with a constant \( C \).

The most important difference between equations 3.48 and 3.56 is the optical pump intensity. Equation 3.48 assumes that all the excitation cites are exposed to the same pump intensity. But, in equation 3.56, the sample is regarded as a collection of many thin layers perpendicular to the pump beam direction and the pump intensity is reduced gradually as the pump beam is partly absorbed by front layers. From equations 3.49 and 3.50, this means that the solution of equation 3.56 will be approximately in the form of a summation of exponential growths with a wide spectrum of time constant. It is known that the spread of the time constant in the exponential growth results an overall stretched exponential growth.[117] Though it is not explicitly shown here, the numerical solutions of equation 3.56 fits to equation 3.52 very well.
3.5.3 Emeraldine Base

Two near-steady-state photoinduced absorption (NSSPIA) spectra of EB are shown in figure 24. In the top figure, the sample at temperature 15 K was pumped by an Ar laser at 2.54 eV with intensity 250 mW/cm², and the pump beam was mechanically chopped with frequency 21 Hz. The bottom figure shows the result of NSSPIA with a pump energy of 3.8 eV. The chopper frequency was 22.5 Hz, and the pump intensity was 100 mW/cm². The sample was held at 10 K.[99] The results show that there is no qualitative difference between pumping at the exciton peak and the \( \pi - \pi^* \) transition peak. There are three dominant PIA peaks at 0.9, 1.4, and 3.0 eV. Two PIB peaks, at 1.9 eV and at an energy higher than the probe range, are evident.[99] The NSSPIA absorption and bleaching peak positions are close to the doping-induced absorption and bleaching peaks shown in figure 17.

The pump intensity dependence and modulation frequency dependence of the EB PIA and PIB peaks are shown in figures 25 and 26. The spectrum in figure 25 was measured at 10 K, with a pump energy of 3.8 eV. In the top portion of figure 25, the maximum intensity \( I_0 \) was 130 mW/cm² and chopping frequency was 22.5 Hz. The frequency dependence measurement at the bottom of figure 25 was done with pump intensity 130 mW/cm².[99] The spectrum in figure 26 was measured at 300 K, with pump energy at 2.54 eV. In the top portion of figure 26, the pump energy was modulated with frequency 21 Hz. While all other peaks are proportional to \( \sqrt{I} \), the PIB peak at 1.8 eV is proportional to \( I \).[118]

Comparison of figures 25 and 26 shows much difference in pump intensity and modulation frequency dependences. One possible explanation is the population density difference of the electronic defect which causes 1.4 eV PIA. As will be shown in
Figure 24: NSSPIA of EB, 2.54 eV pumping at 15 K (top) and 3.8 eV pumping at 10 K (bottom). From [99].
Figure 25: Pump intensity and chopper frequency dependence of NSSPIA of EB at 10 K with pump energy 3.8 eV. From [99].
Figure 26: Pump intensity and chopper frequency dependence of NSSPIA of EB at 300 K with pump energy 2.56 eV. From [118].
Figure 27: NSSPIA of LEB at 10 K with pumping at 3.8 eV of intensity 190 mW/cm². The modulation frequency was 22.5 Hz (top) and 10 Hz (bottom). From [99].
Figure 28: Pump intensity and chopper frequency dependence of NSSPIA of LEB at 10 K with 3.8 eV pumping. The modulation frequency 22.5 Hz with $I_o = 400$ mW/cm$^2$ (top) and pump intensity 200 mW/cm$^2$ (bottom). From [99].
the next section, the population density of the defect is a strong function of temperature. At the same time, the electronic defects directly causing NSSPIA signal may have strong temperature and/or pump energy dependence.

3.5.4 Leucoemeraldine Base

The NSSPIA spectrum of LEB shown in figure 27 have features very similar to those of EB. Since there remain some quinoid rings in LEB, they are possibly responsible for the result. Especially, the presence of 1.9 eV PIB peak is impossible without the involvement of quinoid rings. Figure 28 shows the pump intensity and modulation frequency dependences of the NSSPIA peaks. While all other peaks show same behavior as the 1.9 eV PIB peak, the 1.35 eV PIA peak shows the possibility that it may be from two different species; one same as others and the other which has decay time in the range of ~ 1 msec, from the implication of simulations shown in figure 23.

3.5.5 Pernigraniline Base

In figure 29, two NSSPIA spectra of PNB measured at 10 K and 300 K are shown. For both spectra, the sample was pumped at 2.41 eV with pump intensity 100 mW/cm² and chopping frequency 22.4 Hz. The probe range was 0.5 – 3.3 eV. At 300 K, three major PIA peaks are identified at 1.0, 1.5, and 3.0 eV and named as low energy (LE), middle energy (ME), and high energy (HE) peaks, respectively. Two PIB peaks at the Peierls' energy gap and \( \pi - \pi^* \) absorption peaks are apparent. PIA crosses into PIB at \( \sim 1.63 \) eV.[97, 101, 119, 120]. When the sample is cooled down to 10 K, as in figure 29, the peaks are shifted to higher energy and an additional energy peak
appears at 1.3 eV. The LE and ME peaks are \( \sim 4 \) times larger than the 300 K case. The two low energy peaks at 10 K are named as LE1 (1.0 eV) and LE2 (1.3 eV). The crossover from PIA to PIB occurs at \( \sim 1.71 \) eV.\[97, 101, 119, 120\].

In figure 30, the PNB sample was kept at 10 K and pumped at 3.8 eV with intensity 140 mW/cm\(^2\). The chopper frequency was 22.4 Hz. When the two measurements at 10 K in figures 29 and 30 are compared, the 3.8 eV pumped result is blue shifted relative to the one pumped at 2.41 eV. The 3.8 eV pumping has about 4 times larger signal than 2.41 eV pump case, though the pump intensity is increased by \( \sim 40\% \) and as a result the number of pump photons per unit time is about 20 \% smaller.\[97, 120\]

Figure 31 shows the pump intensity and chopper frequency dependence of PIA and PIB peaks in NSSPIA measurement at 300 K pumped at 2.41 eV. The peaks grow proportional to \( I^{0.7} \).\[120\] The pump intensity and chopper frequency dependence of NSSPIA peaks at 10 K are shown in figure 32. The PNB sample was optically pumped at 2.41 eV.\[97, 120\] From the comparison of the frequency dependences, it seems that the decay time of the defects at 10 K is longer than the decay time at 300 K, which is in the range of a few msec, at least 1.1, 1.5, and 2.0 eV peaks are concerned, due to the model calculation shown in figure 23.

The upper curve of figure 33 is the NSSPIA measurement of PNB at 10 K. The probe range was \( 0.1 - 1.6 \) eV (1000 – 12500 cm\(^{-1}\)) and the sample was pumped at 2.41 eV with intensity 250 mW/cm\(^2\). The ratio between the sizes of the electronic PIA peaks and IRAV PIA peaks are strikingly different from the results of polyacetylene and polythiophene, in figures 5 and 12.\[97, 120\] The lower curve in figure 33 is the result of frequency-domain long-time PIA (F-LTPIA) measured at 80 K with 100 mW/cm\(^2\) intensity optical pumping at 2.41 eV, which will be discussed in the next
Figure 29: NSSPIA of PNB. Pumped at 2.41 eV. From [120].
Figure 30: NSSPIA of PNB. Pumped at 3.8 eV. Sample temperature was 10 K. From [120].
Figure 31: Pump intensity (top) and chopper frequency (bottom) dependence of NSSPIA of PNB at 300 K, pump energy 2.41 eV. From [120].
Figure 32: Pump intensity (top) and chopper frequency (bottom) dependence of NSSPIA of PNB at 10 K, pump energy 2.41 eV. From [120].
section. For comparison, the F-LTPIA result was $\sim 400$ times reduced relative to the NSSPIA result.

The details of the IRAV part of figure 33 are shown in figure 34. The upper curve is the NSSPIA result and quite different from the F-LTPIA result. The NSSPIA result shows no bleaching. The F-LTPIA result shows PIA peaks at 1153, 1477, and 1554 cm$^{-1}$. PIB peaks are shown at 1219, 1323, 1487, and 1591 cm$^{-1}$.[97, 120] Apparently, the UV/VIS and IR range NSSPIA and F-LTPIA results are much different.

Figure 35 shows the chopper frequency dependence of electronic and IRAV PIA peaks in NSSPIA measurement at 10 K. The PNB sample was pumped at 2.41 eV.[120] The result strongly implies that the electronic PIA peaks are correlated to the IRAV PIA peaks. In other words, the electronic defect has net charge.

### 3.6 Long-Time Photoinduced Absorption

Long-time photoinduced absorption (LTPIA) is a method of optically probing long-lived electronic excitations. The conventional way of monitoring long-lived defects in conducting polymers is the near-steady-state photoinduced absorption (NSSPIA). The details of NSSPIA method is in previous section. The modulation frequency range in NSSPIA is practically confined to $1 - 10000$ Hz. If the decay time of a defect is in msec order, NSSPIA is a very powerful method to investigate the properties of the defect.

When the decay time is longer than a few seconds, however, the optical signature of the defect goes beyond the resolution of NSSPIA. The reasons have already been mentioned in the previous section. First, when the modulation period is much longer than the decay time, the phase of the signal changes severely, as demonstrated...
Figure 33: Comparison of low temperature NSSPIA result (upper curve) and F-LTPIA result (lower curve) of PNB. The F-LTPIA result is ~ 400 times reduced compared to the NSSPIA result. From [120].
Figure 34: Comparison of NSSPIA (upper curve) and F-LTP1A (lower curve) IRAV modes of PNB. The F-LTP1A result is \( \sim 250 \) times larger than shown here. From [120].
Figure 35: Chopper frequency dependence of electronic and IRAV peaks in PNB NSSPIA at 10 K, pump energy 2.41 eV. From [120].
in figure 22. Second, figure 23 shows that the magnitude of the signal is reduced very dramatically when the modulation period becomes shorter than the decay time. Third, in addition to the above, since there are only finite number of possible defect sites in a sample and the equilibrium number density of defects $n_{eq}$ becomes very large due to long life, according to the arguments in subsection 3.5.2, the magnitude of signal becomes even smaller when the equilibrium state is reached.

To remedy the problem, the LTPIA method is used to study the long-lived defects. Since the decay mechanism of such long-lived defects is very poor and the equilibrium density of defects $n_{eq}$ is very large, with high pump beam intensity and/or long exposure time, the signal-to-noise ratio can be easily improved. Furthermore, the large signal does not vanish quickly. As a result, the signal is easily measured with detectors of relatively poor sensitivity.

There are two different methods in LTPIA. The first method is to measure the PIA over a wide spectral range. The transmittance or optical density of the sample is measured twice, before and after the optical pumping, by using a conventional spectroscopy. The difference gives the needed information. By convention, this is called frequency-domain LTPIA (F-LTPIA). Another method, time-domain LTPIA (T-LTPIA), monitors the transmittance of the sample at a given probe energy, throughout the optical pumping. While F-LTPIA easily gives the spectral signature of the defects, the dynamics of the defect population is directly recorded in T-LTPIA.

Most of all, these methods are meaningful only when there are such long-lived defects. Indeed, polyaniline is the first conducting polymer in which such defects were found.[99, 121]
3.6.1 Frequency-Domain LTPIA

At low temperature, polyaniline of any oxidation level shows very long-lived and optically-detectable excited states. Their spectral and temporal behavior is measured by frequency-domain long-time photoinduced absorption (F-LTPIA).

Emeraldine Base

McCall et al.[99, 122, 123] measured F-LTPIA of emeraldine base (EB). The EB KBr pellet was pumped for 20 seconds at 3.8 eV with intensity 175 mW/cm² or at 2.54 eV with intensity 200 mW/cm². Before and after the pumping, the 0.06 – 2.0 eV (500 – 16000 cm⁻¹) spectral range was probed by using a Nicolet 60SX FTIR spectrometer.[99] The resultant normalized transmittance changes are shown in figure 36. There is one very strong electronic PIA peak at 1.4 eV (11200 cm⁻¹) and many IRAV peaks. Like NSSPIA of PNB as shown in figure 33, the IRAV PIA amplitudes are much smaller than the electronic PIA amplitude.

The decay time of the EB F-LTPIA signal is strongly dependent on temperature. It was measured to be ~ 6 minutes at 250 K, ~ 45 minutes at 200 K, and longer than 2 hours at 80 K.[122]

The details of the IRAV F-LTPIA of EB are shown in figure 37. There is little pump energy dependence. The main features include PIA peaks at 1144 and 1574 cm⁻¹ and very sharp PIB peaks at 1510 and 1599 cm⁻¹.[99]
Figure 36: F-LTPIA of EB. Pumped at 3.8 eV (top) and 2.54 eV (bottom). From [99].
Figure 37: IRAV F-LTPIA of EB. Pumped for 20 seconds at 3.8 eV (top), 2.54 eV (middle), and 2.0 eV (bottom), with intensities 175, 200, and 180 mW/cm², respectively, at 80 K. From [99].
Leucoemeraldine Base

Figure 38 shows the F-LTPIA results of leucoemeraldine base (LEB). The LEB KBr pellet was pumped at 3.8 eV for 20 seconds, while kept at liquid N₂ temperature, ~ 80 K. There is a PIA peak at 1.4 eV. Another feature is the small peak at 0.75 eV (6000 cm⁻¹). The small peak is seen in the top of figure 36, which corresponds to a pump energy of 3.8 eV.[99] The bottom portion of figure 38 shows the detailed IRAV comparison of EB (lower curve) and LEB (upper curve). The 1599 cm⁻¹ PIB peak is suppressed in LEB.

Generally, the LEB samples are not fully reduced. As shown in figure 15, a few percent of phenyl rings remain as quinoid rings neighboring to imine sites. The NSSPIA results in figures 24 and 27 are very similar to each other. At the same time, the F-LTPIA results in figures 36 and 38 are the same, except for the amplitude. The LEB signal is about 10 times smaller than EB signal. The signal magnitude is proportional to the number of quinoid rings they have. These results strongly suggest that there are little optically detectable photoinduced excitations inherent in LEB.

Pernigraniline Base

The pernigraniline base (PNB) F-LTPIA result in the range of 0.06 — 1.6 eV is shown in figure 33, with the NSSPIA result. The sample was at a temperature of 80 K and pumped at 2.54 eV with intensity 100 mW/cm² for 20 seconds. The F-LTPIA signal amplitude was ~ 400 times reduced to compare with the NSSPIA signal. The IRAV mode magnitude is smaller than the electronic PIA peaks in the NSSPIA result. In the F-LTPIA result, the ratio of IRAV mode magnitude to electronic PIA peak intensity becomes even smaller. The PNB F-LTPIA result is very similar to the results of EB.
Figure 38: F-LTPIA of LEB. Pumped for 20 seconds at 3.8 eV at 80 K. The overall spectrum (top) and detailed IRAV comparison with EB result (bottom) are shown. From [99].
Figure 34 shows the details of the F-LTPIA result for IRAV modes compared to the NSSPIA result. The relative magnitude of the NSSPIA result is ~ 250 times enlarged for easy comparison. While the NSSPIA result shows no PIB peak, the F-LTPIA result shows relatively sharply developed PIA and PIB peaks. Figure 39 shows the pump intensity dependence of the PNB F-LTPIA peaks at 1.5 eV and 1155 cm\(^{-1}\). From this, it is concluded that the IRAV modes are related to the 1.5 eV peak. In other words, the 1.5 eV peak corresponds to an electronic defect which has net charge.\[120\]

One comment should be made on the electronic peak position. The strong LTPIA peak is at ~ 1.4 eV in all oxidation levels. The peak position is slightly blue shifted when the oxidation level grows.\[123\] Though it has been called 1.4 eV peak\[99, 122\], because of a tentative attempt to relate this peak to the ME peak (~ 1.5 eV) in the NSSPIA measurement, it is frequently referred as the 1.5 eV peak.

Coplin et al.\[121\] measured F-LTPIA of polyaniline with a probe range of 0.4 – 7.2 eV. It was found that under controlled conditions, a 1.8 eV F-LTPIA peak is shown in PNB. This 1.8 eV peak was not detected in any other oxidation level of polyaniline. At the same time, unlike the 1.5 eV peak, the 1.8 eV peak does not accompany any IRAV mode.\[121\]

The top portion of figure 40 shows the full F-LTPIA spectrum of PNB at 80 K with pump energy 2.54 eV. From equation 3.23, the \(\Delta A\) value can be easily converted to \(-\Delta T/T\). There are three PIB peaks at 2.3, 3.8, and 4.3 eV, as expected from the direct absorption spectrum in figure 15. Three PIA peaks are shown at 1.5, 1.8, and 3.0 eV. No reduction of the PIA peaks was detected 24 hours after the pumping.\[121\]
Figure 39: Pump intensity dependences of the PNB F-LTPIA electronic PIA peak at 1.5 eV and IRAV PIA peak at 1155 cm\(^{-1}\). From [120].
Figure 40: PNB F-LTPIA at 80 K result over 0.4 – 6 eV (top) and the pump intensity dependence (bottom). Pumped at 2.54 eV. From [121].
The intensity dependence of the 1.5 and 1.8 eV peaks appears at the bottom of figure 40. While the pump energy (2.54 eV), pumping time (120 seconds), and sample temperature (80 K) are held constant, the power of the pump beam from a Ar laser was adjusted from 3 to 300 mW/cm\(^{-1}\). After obtaining each curve, the sample was heated to room temperature to erase the history of previous measurement.[121, 124]

It was found that the 1.8 eV peak is dominant when the pumping power is weak, the temperature is intermediate (~ 150 K), and the polymer has side chains.[124] These results strongly suggest the 1.8 eV peak comes from relatively more isolated species than the 1.5 eV peak. The crossover from PIA to PIB in PNB F-LTPIA appears at ~ 2.1 eV, as shown in figure 40. From figure 36, the crossover occurs at ~ 1.6 eV in EB F-LTPIA measurement.

3.6.2 Time-Domain LTPIA

As mentioned above, time-domain long-time photoinduced absorption (T-LTPIA) monitors the temporal behavior of absorption change at a given probe photon energy. An Ar laser of emission energy 2.54 eV (488 nm) was employed as a pump. A Nicolet 60SX FTIR spectrometer was used to probe the sample. Instead of the peak amplitude, the integration of the area belong to the 1130 cm\(^{-1}\) peak was monitored.[93, 125] Since the shape of the F-LTPIA did not change, this integrated value was proportional to the magnitude of the PIA peak.

In figure 41, the temperature dependence of the EB 1130 cm\(^{-1}\) PIA peak is shown. The Ar laser power was kept constant at 320 mW for all measurements.[93, 125] While the number of excited states was continuously growing at 90 K even after two and half hours, the number reached an equilibrium in a few tens of minutes at 240 K. At 260
Figure 41: Temperature dependence of integrated 1130 cm$^{-1}$ PIA peak of EB T-LTPIA. From [93].
Figure 42: Pump intensity dependence of integrated 1130 cm$^{-1}$ PIA peak of EB T-LTPIA (top). Bottom shows redrawing of top figure as a function of pump photon number. From [93].
Figure 43: T-LTPIA of EB at 90 K. IRAV mode at 1130 cm$^{-1}$ (top) and electronic PIA peak at 1.4 eV (bottom). From [93].
K, no LTPIA signal was detected. From the arguments in subsection 3.5.2, it is apparent that the equilibrium density of excited states decreases as temperature decreases. There is a decay channel with finite decay time and the decay time increases as temperature increases. When the temperature goes below some range, virtually the decay mechanism stops.

The pump intensity dependence in the top portion of figure 42 was measured at 90 K. When the optical pumping starts, initially there is very fast growth of excited states. Though the growth levels later, the equilibrium state is not reached even after 150 minutes of intense pumping. At the bottom of figure 42, the PIA signal size is shown as a function of total pumping energy, which is proportional to the number of pumping photons. This implies that the signal size primarily depends on the number of input photons, not the intensity of pump beam. This is another evidence that there is practically no decay mechanism at 90 K.

Figure 43 shows IRAV mode at 1130 cm\(^{-1}\) (top) and electronic PIA peak at 1.4 eV (bottom) of EB T-LTPIA as a function of time. The solid lines are fits to a stretched exponential function in equation 3.52. \(\beta \approx 0.4\) is obtained from the fitting. From subsection 3.5.2, it is probable that the stretched exponential growth is a mere reflection of the bulkiness of the sample.

3.7 Third Harmonic Generation

The unusually large \(\chi^{(3)}\) of \textit{trans}-polyacetylene, even compared to the \(\chi^{(3)}\) of \textit{cis}-polyacetylene, seemed to be explained by the degenerate ground state on which solitons can occur. Halvorson \textit{et al.} suggested that the criteria, (i) energy gap greater than 2 eV (ii) no side chains (iii) processible (vi) oriented and ordered,
are essentially required for a material to be a good candidate for the third harmonic generation applications, in addition to the presumably obvious requirement of having degenerate ground states. As a result, the third harmonic generation of PNB was very promising, since it is the only known degenerate ground state conjugated polymer other than trans-polyacetylene and its energy gap is larger than 2 eV.

Osaheni et al.[126] measured the third-order optical susceptibilities of the polyaniline family and their derivatives in the range of 0.5 — 1.4 eV (2.4 — 0.9 μm). Their measurements and the measurements of Halvorson et al.[127] reveal interesting results as shown in figure 44. Among the three oxidation states, EB shows the largest $\chi^{(3)}(3\omega;\omega,\omega,\omega)$, not PNB. LEB has the lowest value.[126, 127] For the oxidation states where quinoid rings exist, the $\chi^{(3)}$ has a resonance peak at around $3\omega = 2$ eV.[126, 127] There is no noticeable contribution from resonance at around $3\omega = 4$ eV for EB and PNB.[126] But the three photon resonance to the energy gap at $\omega = 1.18$ eV is claimed in LEB.[127]

To explain the result, several factors can be considered. Since trans-polyacetylene showed very high $\chi^{(3)}$ value compared to other conjugated polymers including cis-polyacetylene, the role of virtual solitons was emphasized.[62, 63] But in polyaniline this is not the case, since PNB has smaller $\chi^{(3)}$ than EB, which has only one possible ground configuration. The soliton mass of PNB is much heavier than that of trans-polyacetylene. As a result, the nonlinear zero-point motion is suppressed in PNB.[127]

The suppression of the nonlinear zero-point fluctuations cannot explain why EB has a larger $\chi^{(3)}$ than PNB. The simple argument comes from the energy gap. The lowest electronic absorption peak of EB is at around 2 eV, while the energy gap of PNB is at around 2.3 eV. If $\chi^{(3)}$ is simply anti-proportional to the sixth power of energy gap, factor of 2 is explained from this. The peak values of the $\chi^{(3)}$ of the two
oxidation states show about factor of 3 difference at peak.[126, 127]

Obviously, the $\chi^{(3)}$ peak at 0.6 eV indicates the presence of the quinoid rings. But as the number of quinoid rings increases, the $\chi^{(3)}$ value has a peak and further increment of quinoid rings reduces the value. In other words, while the presence of quinoid rings is essential for large $\chi^{(3)}$, the quinoid rings should be separated to each other to a some degree to maximize $\chi^{(3)}$.

3.8 Electron Spin Resonance

As mentioned in chapter II, the information on the spin status is critical in the classification of the electronic defects. Electron spin resonance (ESR) and light-induced electron spin resonance (LESR) measurements are very important tools for the purpose. ESR uses the Zeeman effect. Under a magnetic field, the degeneracy of the spin energy levels is broken. When the magnetic field intensity is changed while a microwave field is applied, there occurs absorption of the microwave whenever the microwave photon energy matches the difference of two spin energy levels where a transition is allowed.

3.8.1 Ground States

Like polyacetylene[9], spins are found in pristine polyaniline. They are detected by electron spin resonance (ESR) experiments.
Figure 44: The $\chi^{(3)}$ spectra of three possible oxidation states of polyaniline; PNB (filled triangle), EB (filled circle), and P4PAB (filled square). P4PAB is similar to LEB. From [126].
Polyaniline Solution

Figure 45 shows the derivative of the absorbed microwave intensity with respect to the applied magnetic field. The top portion of figure 45 shows the ESR spectrum of PNB in dioxane. Dioxane is chosen because of its very low dielectric constant. There are three absorption peaks and each absorption peak contains many fine absorption peaks.[112, 113] The three absorption peaks are due to the nitrogen atom, which has nuclear spin 1. At the same time, the small peaks are believed to be from hydrogen atoms at the two adjacent rings. This result implies that the spin is strongly localized at a nitrogen atom and spread over the two adjacent phenyl rings.[112, 113]

EB solution has exactly the same features appeared in PNB solution. The bottom part of figure 45 shows the detailed comparison of EB and PNB in dioxane. The EB result is slightly shifted upward for comparison. Again, this is interpreted as due to the presence of a PNB segment coming from excessive oxidation.[113]

Solid State

The top portion of figure 46 shows the ESR signal of a PNB KBr pellet. The two positive and two negative peaks imply three peaks in the microwave absorption, with one large peak at the center and two small peaks at each side of the peak. In relation to the well resolved solution ESR results, these broad peaks can be interpreted in terms of an anisotropic g value and anisotropic hyperfine interactions with a nitrogen nuclear spin.[112, 113]
Figure 45: Solution ESR spectrum of PNB in dioxane (0.3 g/l) (top). Comparison of PNB and EB in dioxane (bottom). From [113].
Figure 46: ESR spectrum at 60 K of PNB in KBr pellet (top). Bottom figure compares LESR (solid line) pumped at 2.54 eV with intensity 100 mW/cm$^{-1}$ for one hour and ESR (broken line, magnified 50 times). From [112].
\subsection*{3.8.2 Light-induced Electron Spin Resonance}

The light-induced ESR (LESR) method resembles T-LTPIA experiment in that it monitors the change of the sample status while the sample is continuously pumped by a constant laser beam. While T-LTPIA measures the change of optical absorption, LESR records the change of spins.

The integral of the microwave absorption peak in ESR is regarded as being proportional to the magnetic susceptibility $\chi$ and the number of spins. Figure 47 shows the temperature dependence of the PNB LESR results. PNB in KBr was optically pumped at 2.51 eV with intensity 100 mW/cm$^{-1}$. The susceptibility is normalized by the dark susceptibility. The comparison of figures 41 and 47 strongly implies the defect responsible for the LTPIA absorption peak at 1.5 eV has spin 1/2. When the pump beam is blocked, the spin density decays very slowly, if there is any decay. Like the LTPIA signal, the spin density growth fits to a stretched exponential form.[112, 128]

\subsection*{3.9 Theoretical Models}

The complicated structure of polyaniline makes it hard to theoretically predict and calculate its physical properties. In the case of polyacetylene, the SSH hamiltonian and consequent variations based on carbon-backbone bond-length alternation related to the $\pi$ electron band explained most of physical observations. But polyaniline has many other important characteristics. The backbone has not only carbon but nitrogen atoms. The number of $\pi$ electrons coming from nitrogen varies upon three possible oxidation levels. The amine state possesses two $\pi$ electrons, while there is only one in imine state. The carbon atoms form phenyl rings between nitrogen atoms.
Figure 47: Temperature dependence of the magnetic susceptibility in PNB. From [112].
As a result, not only the bond-length alternation but also the rotation of the ring with respect to the carbon-nitrogen axis plays an important role in the geometrical deformation from ground state. At the same time, the interchain interaction is more important because of the large crosssection of a chain. Obviously, ring-torsion will cause more interchain reaction than bond-length alternation.

Theoretical models of possible localized excited states in leucoemeraldine base and pernigraniline base are described below. In leucoemeraldine base, the ring torsion angle is the main concern. Both bond-length and ring-torsion angle are considered in pernigraniline base. Because of the complexity in structure, emeraldine base is not yet theoretically well modeled in spite of the abundant data on its physical properties.

### 3.9.1 Leucoemeraldine Base

Leucoemeraldine base (LEB) has wide bandgap of \(~ 3.6\) eV, as shown in figure 15. Each nitrogen has two electrons in \(p_z\) orbital. Since there is no double bond between carbon and nitrogen atoms, LEB is not a conjugated polymer. Only one ground state bond configuration is possible and no conventional localized electronic defect can be created by bond-length alternation changes in LEB.

Still the NSSPIA experiment shows intragap defects in LEB as seen in figure 27. Poly-paraphenylene sulfide (PPS)[129], whose electronic structure is isomorphic to LEB, also shows PIA peaks in the energy gap. These results suggest the possible importance of the ring-torsion angle change in these polymers.[129, 130, 131, 132, 133, 134, 135]

Ginder et al.[130, 131] investigated the role of the ring-torsion in the creation of electronic defects in LEB, by using a Hamiltonian based on the two contributions, a
π electronic term and a steric term. Since each nitrogen atom in LEB provides two π electrons, the valence band is fully filled and there is no Peierls's gap opening. LEB still has two degenerate ground states, due to the ring-torsion.

The energy of the π electron system becomes minimum when all the carbon and nitrogen atoms are in a plane, since all the π orbitals become parallel each other to make the π electrons delocalized. But the steric hindrance[136] pushes the carbon rings to make the angular distance between the neighboring rings become as large as possible. As a result, a ring will be rotated out of the nitrogen plane in the opposite direction to its nearest neighbors until the total energy is minimized. After numbering the carbon rings and nitrogen atoms in a LEB chain such that rings are odd numbered and nitrogens are even numbered, an order parameter

$$\psi_{2m+1} = (-1)^m \phi_{2m+1}$$  (3.57)

can be introduced, with integer m. Here $\phi_{2m+1}$ is the rotation angle of the $(2m+1)$-th ring with respect to the plane possessing nitrogen atoms. The order parameter $\psi_{2m+1}$ will become a constant, either $\psi_o = |\psi_o|$ or $\psi_o = -|\psi_o|$, at the ground state of a perfect chain.[130, 131]

The electronic part of the Hamiltonian is constructed using a tight-binding approximation. Different site potentials are used for nitrogen and carbon atoms, respectively. Since the $p_z$ electron orbitals in nitrogens and rings have angle $\phi_{2m+1}$ to each other, it is assumed that the transfer integral between them is proportional to $\cos \phi_{2m+1} (= \cos \psi_{2m+1})$. The steric hindrance potential is series-expanded to several low-order terms. The resultant Hamiltonian is

$$H = H_{el} + H_{steric}$$  (3.58)

$$H_{el} = -\sum_{i,s} \left[ \frac{\alpha N}{2} + \frac{\alpha_{eff}}{2} \cos^2 \psi_{2l+1} (h_{2l+1}^h h_{2l+1}^s + h_{2l+1}^s h_{2l+1}^h) \right]$$
\[ H_{\text{steric}} = \sum \frac{I}{2} \left( \frac{\partial \psi_{2l+1}}{\partial t} \right)^2 + \sum [V_{i,i}(\sin \psi_{2l+1} - \sin \psi_{2l-1})^2 - V_{2,0} \sin^2 \psi_{2l+1} + V_{4,0} \sin^4 \psi_{2l+1}] \quad (3.60) \]

Where \( \alpha_N \) and \( \alpha_{\text{eff}} \) are the nitrogen site energy and the phenyl ring effective site energy, respectively. The operator \( h^\dagger(h) \) creates (annihilates) a hole in the valence band. The first term of \( H_{\text{steric}} \) is the kinetic energy of the ring rotation with rotational moment of inertia \( I \). \( V_{i,j} \) are constant coefficients.\[130, 131\]

Starting from this Hamiltonian, two possible defect states, hole polaron and soliton, are deduced. The hole polaron is described as

\[ \sin^2 \psi_{2m+1} = \sin^2 \psi_0 - A \text{sech}[(m - m_0)/l] . \quad (3.61) \]

With the depth \( A \simeq 0.19 \) and length \( l \simeq 1.5 \), the hole polaron at \( m_0\)-th site will have binding energy \( \epsilon_B \simeq 0.6 \) eV and the effective mass \( M_{\text{pol}} \simeq 50m_e \), where \( m_e \) is the free electron mass. This hole polaron will have only one intragap electron state which is occupied by an electron. A neutral soliton is anticipated to have the structure

\[ \sin^2 \psi_{2m+1} = \sin^2 \psi_0 \tanh[(m - m_0)/l] . \quad (3.62) \]

The solitons are predicted to follow the conventional spin-charge statistics.\[131\] This is obvious since there is no creation of an unpaired \( \pi \) electron, unlike the solitons from the bond-length alternation.\[130, 131\]

From the symmetry of the phenyl rings, the steric potential \( V = V(\psi_{2m+1}) \) has symmetries

\[ V(\psi_{2m+1}) = V(-\psi_{2m+1}) \quad (3.63) \]
\[ V(\psi_{2m+1}) = V(\psi_{2m+1} + n\pi) , \quad (3.64) \]

\[ + t_{\text{eff}} \sum \cos^2 \psi_{2l+1}(h_{2l,s}^\dagger h_{2l,s} + h_{2l+2,s}^\dagger h_{2l+2,s}) \quad (3.59) \]
Figure 48: Steric potential of leucoemeraldine base. From [133].
for any integer $m$. Hence, from figure 48, there are two possibilities of connecting the two degenerate ground states, $\psi_o$ and $-\psi_o$, over $V(0)$ or $V(\pi/2)$, unless

$$V(\psi_o + \psi) = V(\psi_o - \psi), \quad (3.65)$$

and obviously this is not the case. After ignoring the kinetic part in $H_{steric}$ of equation 3.60, a continuum limit was introduced to be

$$H = 2V_{1,1} \int dx \left[ \frac{1}{2} \left( \frac{d\sigma}{dx} \right)^2 + \frac{\lambda}{4} (\sigma^2 - v^2)^2 \right], \quad (3.66)$$

where $x$ is a dimensionless variable, $\sigma = \sin \psi$, $\lambda = 2V_{4,0}/V_{1,1}$, and $v^2 = V_{2,0}/(2V_{4,0})$. The system has two possible ground states,

$$\sigma = \pm v = \sin \pm \psi_o. \quad (3.67)$$

The equation of motion becomes

$$\frac{d^2\sigma}{dx^2} = \lambda \sigma(\sigma^2 - v^2), \quad (3.68)$$

and, from this, the two possible solitons are obtained,[133]

$$\sigma_1(x) = v \tanh(x/\xi) \quad (3.69)$$

$$\sigma_2(x) = v \coth((|x| + \xi)/\xi). \quad (3.70)$$

Here, $\xi = (2V_{1,1}/V_{2,0})^{1/2}$ is the soliton decay length and the constant $\xi_o$ satisfies

$$v \coth(\xi_o/\xi) = 1. \quad (3.71)$$

With $V_{1,1} \simeq 0.2$ eV, $V_{2,0} \simeq 2.0$ eV, and $V_{4,0} \simeq 1.45$ eV, the creation energy and the kinetic mass of the tanh soliton are $\sim 0.82$ eV and $\sim 17$ amu, respectively. The coth soliton creation energy is $\sim 0.055$ eV and its kinetic mass goes to infinity in this model.[133]
3.9.2 Pernigraniline

Otto and Dupuis[137] calculated the energy band structures for PNB using the \textit{ab initio} Hartree-Fock crystal orbital method. They concluded that the perpendicular orientation of the two rings, benzenoid ring and quinoid ring, leads to the most stable structure.

Based on the SSH Hamiltonian, or using a simple Hückel Hamiltonian with \(\sigma\) bond compressibility, dos Santos and Bredas[10, 11] calculated the ground state and electronic defect states of PNB. Here, ring-torsion was not explicitly included. Following the A-B polymer theory[138], the lattice dimerization and the site energy difference were considered. The valence band which mainly comes from the benzenoid ring states has larger bandwidth than the conduction band which comes from the nitrogen and quinoid rings. There is a 1.4 eV energy gap and the sum of the two band widths and the band gap is 2.9 eV.[10, 11]

They found that there can be not only two types of solitons due to the broken charge conjugation symmetry, but also positive and negative polarons. Bipolarons are not found. The geometry of the defects are shown in figure 49 and the energy levels, net charge, and spin are shown in figure 50. A pair of polarons decay into a pair of charged solitons. A type-I soliton has a symmetric wave function centered at a nitrogen atom between rings possessing aromatic geometry. It creates a localized electronic state at 0.11 eV below the Fermi level. A type-II soliton has an antisymmetric wave function. It is centered at a nitrogen atom between quinoid-like rings and creates a localized electronic state 0.06 eV above the Fermi level. A neutral pair of solitons, whose creation energy is 0.64 eV, includes a type-I soliton with two electrons and a type-II soliton with no electron. They carry charges \(-0.52|e|\) and \(+0.52|e|\) each.
Figure 49: Optimized defect geometries in PNB; (a) type-I soliton, (b) type-II soliton, and (c) polaron. Solitons are symmetric w.r.t. the nitrogen atoms at the left hand side. Polaron has no symmetry. From [11].
Figure 50: Possible intragap defects in PNB; (a) neutral soliton pair, (b) positive polaron, (c) negative polaron, (d) positive soliton pair, and (e) negative soliton pair. From [11].
and no net spin. The most stable excitation upon addition of an electron or a hole to PNB is a polaron with two localized levels at 0.38 eV below and 0.30 eV above the Fermi level. The binding energy of a positive (negative) polaron is 0.14 eV (0.21 eV). A pair of positive (negative) polarons is unstable with respect to a pair of positively (negatively) charged solitons by 0.37 eV (0.28 eV).

Ginder and Epstein[131] considered the role of the ring-torsional angle, adding to the model above. From the introduction of a dimensionless electron-ring-angle coupling constant, they concluded that ring-angle dimerization contributes to the formation of the Peierls’ gap in PNB. The effective masses of the electronic defects from bond-length alternation and ring-torsion alternation were estimated to show that the latter is much bigger than the former. Since the ratio of IR part of the signal amplitude to electronic part of the signal amplitude in the PNB NSSPIA was small compared to those of other conjugated polymers which do not possess the ring torsional freedom, it was argued that the role of the ring-torsion part will be dominant in the creation of charge-storing defect states in PNB.[131]

Su and Epstein[139] constructed a simplistic Hamiltonian describing PNB. They started from a SSH model-like Hamiltonian,

\[
H_0 = \sum_{<i,j>} \{-t_o - \alpha \delta r_{ij}\} \sum_{\sigma} [c_{i,\sigma}^{\dagger} c_{j,\sigma} + H.c.] + \frac{K}{2}(\delta r_{ij})^2
+ V_0 \sum_{n,\sigma} c_{n,\sigma}^{\dagger} c_{n,\sigma}.
\]

Here carbon and nitrogen are treated as the same, except for the on-site potential difference \(V_0\) on the nitrogen atoms. The prime on the last summation means it is over the nitrogen atoms only. The \(c_{i,\sigma}^{\dagger}\) (\(c_{j,\sigma}\)) operator creates (annihilates) an electron with spin polarization \(\sigma\) in an atomic \(2p_z\) orbital on the \(i\)-th backbone atom, carbon or nitrogen. The symbol \(<i,j>\) denotes summation over bond sites, where \(j\) is a
nearest neighbor of \( i \). Like the SSH model, the bond-length change \( \delta r_{ij} \) requires the mechanical potential term with spring constant \( K \) and the modulation in interatomic hopping integral with electron-phonon interaction coefficient \( \alpha \).[139]

With values \( t_D = 1.6 \) eV, \( \alpha = 7 \) eV/Å, \( K = 60 \) eV/Å\(^2\), \( K' = K/\alpha^2 = 1 \) /eV, and \( V_o = -2 \) eV, the energy gap is calculated to be \( \sim 1 \) eV, much smaller than the observed \( \sim 2.3 \) eV. Su and Epstein added another parameter, ring-torsion, following Ginder and Epstein.[131] Since the ring-torsion is promoted by the steric repulsion and suppressed by the \( \pi \) electron system delocalization, they added the steric potential, which is the potential term of equation 3.60,

\[
V_s = \sum_k [V_{11}(\sin \psi_k - \sin \psi_{k-1})^2 - V_{20} \sin^2 \psi_k + V_{40} \sin^4 \psi_k]
\]  

(3.73)

to the Hamiltonian above and multiplied the hopping integral term in the Hamiltonian by cosine of the staggered order parameter \( \psi_k = (-1)^k \theta_k \). Here \( \theta_k \) is the torsional angle of the \( k \)-th phenyl ring away from the C–N–C plane. The values of the three parameters \( V_{11}, V_{20}, \) and \( V_{40} \) are chosen to be 0.185 eV, 4.5 eV, and 2.5 eV, respectively, to fit the observed spin density distributions and the energy gap.[139]

The Hamiltonian gives two degenerate ground states. In the ground states, the quinoid rings twist small (12°) compared to the benzenoid rings (53°). This means, the two order parameters \( \delta r_{ij} \) and \( \psi_k \) are not independent to each other. The calculated energy gap is approximately the experimental value. This shows not only the bond-length alternation but also the ring-torsion contributes to the energy gap.[139]

There are three possible excitations, neutral soliton, charged soliton, and polaron, supported by the Hamiltonian constructed above.[139] A neutral soliton pair, \( S^o \) and \( \tilde{S}^o \), have degenerate gap state energy levels, as shown in figure 51 (a). The effective charges of \( S^o \) and \( \tilde{S}^o \) are very small and they have spin 1/2. As in figure 51 (a),
(a) Pernigraniline: Neutral Soliton Pair

![Graph showing absorbance vs. photon energy for neutral soliton pair.](image)

Photon Energy (eV)

(b) Pernigraniline: Charged Soliton Pair

![Graph showing absorbance vs. photon energy for charged soliton pair.](image)

Photon Energy (eV)

Figure 51: Solitons in Pernigraniline. (a) Neutral soliton pair and (b) charged soliton pair. From [139].
(a) Neutral Soliton: Bond Orders and Torsion Angles

\[
\theta = 53^\circ \quad \theta = -12^\circ \quad \theta = 44^\circ \quad \theta = -44^\circ \quad \theta = 12^\circ \quad \theta = -53^\circ
\]

(b) Neutral Soliton: Gap State Wave Function

\[
\theta = -12^\circ \quad \theta = 44^\circ \quad \theta = -44^\circ \quad \theta = 12^\circ
\]

Figure 52: Neutral Soliton in Pernigraniline. (a) Neutral soliton: bond orders and torsion angles and (b) neutral soliton: gap state wave function. From [139].
(a) Pernigraniline: Charged Polaron Pair

(b) Electron Polaron: Gap State Wave Function

Figure 53: Polaron in Pernigraniline. (a) Charged polaron pair and (b) polaron structure. From [139].
absorptions at 0.9 eV and 1.5 eV are expected from the lack of the charge conjugation symmetry. When the Hubbard repulsion of $U = 4$ eV is included, the midgap absorption peaks are shifted to higher energy. From this, the 1.5 eV and 1.8 eV long-time photoinduced absorption (LTPIA) peaks[101, 121] of PNB are recognized as neutral soliton peaks. This designation is encouraged since no infrared active vibrational (IRAV) mode related to 1.8 eV LTPIA peak was observed[121].

At the same time, EPR measurements indicate the existence of localized spins in ground state PNB.[113, 128] The calculated neutral soliton structure is shown in figure 52 (a). The central two rings are benzenoid rings. $S^0$ and $S^0$ have exactly the same structure, within mirror symmetry. Figure 52 (b) shows the gap state wave function, whose square is the spin density. The calculated spin density matches the measured spin density distribution.[113, 128]

Charged solitons have different structures, depending on the charge.[139] The torsional angle in the vicinity of a negatively charged soliton goes ..., $+53^\circ$, $-12^\circ$, $+54^\circ$, $-54^\circ$, $+12^\circ$, $-53^\circ$, ..., and it is denoted as $S^{BB}_-$. On the contrary, the positive soliton, $S^{QQ}_+$, runs like ..., $+12^\circ$, $-52^\circ$, $+16^\circ$, $-16^\circ$, $+52^\circ$, $-12^\circ$, ... centered on two quinoids. Figure 51 (b) shows the calculated absorption peaks of charged solitons, with and without the presence of the Hubbard term, $U = 4$ eV. The NSSPIA peaks at 1.0 eV and 1.3 eV[101] are interpreted to be from charged solitons.

Another possible excitation is the polaron. The calculated absorption curves under the presence of polaron structure is shown in figure 53 (a). While the hole polaron, $P^+$, contributes to the upper and lower peaks of the subgap absorption, the electron polaron, $P^-$, is responsible for the middle peak. The ring-torsional angle around a hole polaron goes like ..., $+12^\circ$, $-50^\circ$, $+15^\circ$, $-41^\circ$, $+15^\circ$, $-50^\circ$, $-12^\circ$, ..., showing it is less strongly bound than an electron polaron as shown in figure 53 (b).
The creation energy of an oppositely charged polaron pair, 1.9 eV, is much larger than that of a soliton pair, shown in the inlet of figure 51 (a). As a result, if polarons are not pinned down or located on different chains, it is expected that they will decay into solitons.[139]
CHAPTER IV

EXPERIMENTAL TECHNIQUE

4.1 Sample Preparation

The polyaniline samples were mainly provided by the Professor MacDiarmid group in University of Pennsylvania. The powder form of sample was made into pellet or film for the optical measurements.

4.1.1 Synthesis of PNB

The methods of polyaniline synthesis are well described in many literatures.[85, 114, 140] Especially Sun[85] documented the manufacturing procedure of pernigraniline base (PNB) in detail. The procedure is qualitatively summarized below.

The synthesis of polyaniline starts with aniline. Aniline is mixed in 1 M HCl solution. This solution is again mixed with ammonium peroxydisulfate, \((\text{NH}_4)_2\text{S}_2\text{O}_8\), at \(\sim 0^\circ\text{C}\). While the solution is stirred, aniline is polymerized and emeraldine salt (ES) is precipitated. The precipitate is repeatedly washed with 1 M HCl solution.[85]

To convert ES into emeraldine base (EB), the precipitate is treated with 0.1 M
NH₄OH solution. During the procedure, to prevent over-oxidation, the solution is purged with N₂ gas. EB powder is obtained by drying and pulvarizing the resultant precipitate.[85]

PNB is made from EB. EB powder is desolved into N-methyl pyrrolidinone (NMP). Meta-chloroperoxybenzoic acid (mCPBA) is dissolved in glacial acetic acid (HAc). The mCPBA/HAc solution is slowly added into EB/NMP solution. To neutralize the acid, triethylamine is later added. The result is put to acetone and washed by acetone and ethyl ether to remove NMP and mCPBA. After vacuuming and pulvarizing, PNB powder is obtained.[85]

4.1.2 KBr Pellet

In optical measurements light is used to stimulate or to probe a sample. For that purpose, in many cases, the sample is required to be free standing and optically flat, homogeneous, not too opaque at a given wavelength, and the heat caused by the absorption of light should dissipate well. There are many materials which can hardly be processed to meet these requirements. To get rid of the difficulty, two basic methods are used. The first idea is to make a film on a substrate. This works well if the material can easily be processed as a thin film on a proper substrate. The other method is to mix the sample material to a powder and make a pellet. In both cases the substrate or the powder should be chosen based on their optical, mechanical, and chemical properties. In the experiment, KBr pellet[73] of pernigraniline base (PNB) was used. The pellet manufacturing method is described below.
Pellet Manufacturing Procedure

Since PNB degrades when exposed to the air and KBr absorbs moisture, both are kept in a glove box filled with Ar gas. First, PNB powder is mixed with KBr in 1:99 weight ratio to make 1% sample. Then 10 mg of the 1% mixture is added to 490 mg of KBr powder. Every time the sample is diluted, the powder is thoroughly mixed by using an automatic mechanical shaker. The 500 mg 0.02% sample is put into a vacuum sealed pellet press and taken outside the glove box. The press is evacuated for 20 minutes at $10^{-5}$ mbar. While pumping is continued, the mortar is pressed by a press with the pressure at 1000 psi for 10 minutes. The resultant pellet is pillbox shape with $\sim 1$ mm height and 12.7 mm diameter. The pellet is kept in the glove box or in an evacuated cryostat.

4.1.3 Synthesis of LEB

Polyaniline (emeraldine hydrochloride salt) powder was obtained by polymerization of aniline in 1M HCl solution using ammonium peroxydisulfate as the oxidizing agent. It was subsequently converted to the emeraldine base (EB) form by treatment with ammonium hydroxide.[141] To obtain a solution of reduced leucoemeraldine base (LEB), EB was dissolved in N-methyl pyrrolidinone (NMP) and reduced by hydrazine hydrate.[142]

4.2 PSPIA: Experimental Set-Up

In many materials, when electrons are excited from the ground state, they may create defect states with associated energy levels inside the band gap before all the
energy absorbed is dissipated and the ground state is resumed. It will be very interesting to trace the creation and evolution of the defect states inside the bandgap in the energy and time domains. Creation of the defects means deformation of the density of states from the ground state and the redistribution of the electron population. The change of the density of states and the change of the electron distribution alter the absorption of light spectrum. Hence, by measuring the absorption changes as a function of energy and time, the dynamics of the defects can be investigated. Picosecond photoinduced absorption (PSPIA) is a very powerful tool for this purpose.

In PSPIA, the absorption of the probing light pulses is monitored before and after the injection of a pulse of pumping light, whose photon energy generally exceeds the bandgap energy of the sample to excite electrons. The absorption difference as a function of probe beam photon energy and the elapsed time between the arrivals of the pump pulse and the probe pulse will give the needed information for the defect classification and dynamics.

Only lasers can realize the practical creation and manipulation of such short light pulses in psec range. Two cavity dumped dye lasers are used for the purpose, which are pumped by the second harmonics of a mode locked Nd:YLF laser. The temporal pulse shapes are monitored by an autocorrelator. The probe pulse arrival time relative to the pump pulse arrival is varied through a time delay line. The synchronization of the pump and probe pulses is monitored by a fast photodiode. Spatial beam shapes are manipulated by lenses and adjustment of path length. The cross section of the beams are directly measured by a moving pinhole at the sample position. A sample holding cryostat attached to a vacuum station is employed for the temperature and environment control of the sample. A shutter is adapted to manipulate the pump beam. To overcome poor signal to noise ratio, the signal is
time modulated by mechanical chopping or electronic temporal hopping method, and lock-in amplifiers are used to detect the signal. The overall measuring procedure is automated and controlled by a personal computer and software.

The optical set-up is shown schematically in figure 54. The electronic block diagram is in figure 55. The properties and functions of the lasers will be described below. The spatial and temporal behaviors of laser pulses and the control of them will follow.

4.2.1 Lasers

Since a laser generally emits photons of a well defined energy, two lasers are needed to probe defects at energy levels different from the pumping energy. It is desirable to have tunable probe beam photon energy to monitor the energy spectral characteristics of the defects. The lasers should produce carefully synchronized short pulses to measure the temporal behavior. To satisfy these requirements, two cavity dumped dye lasers were used as pump beam and probe beam sources. The dye lasers were pumped by the second harmonics of a mode-locked Nd:YAG or a mode-locked Nd:YLF laser.

Nd:YLF Laser

Initially a Quantronix Model 416 Nd:YAG laser was used, and it was replaced by a Coherent Antares 76-YLF Nd:YLF laser. These lasers are mode-locked to generate pulses at 76 MHz repetition rate. The neodymium (Nd) ion is responsible for the emission of both types of lasers. The main difference between the two lasers comes from the host crystals. One uses yttrium aluminum garnet (YAG) and the other yttrium lithium fluoride (YLF) as the host crystal. YAG is optically isotropic and
Figure 54: The schematic diagram of the optical set-up of the picosecond photoinduced absorption experiment.
Figure 55: The schematic diagram of the electronic set up of the picosecond photoinduced absorption experiment.
has a strong thermal lensing effect. YLF is uniaxial and has small thermal lensing effect.[143] The Nd:YLF laser shows superior stability and easy control of output power by adjustment of the pump lamp current. The average power can be up to 22 watt in continuous emission and 18 watt or more for the mode-locked case. While the Nd:YAG laser emits infrared (IR) beam of wavelength 1064 nm (1.165 eV), the Nd:YLF laser produces wavelength 1053 nm (1.178 eV).[143]

Second Harmonic Generation

Dye lasers use the photoluminescence of dyes as light sources. Since the bandgaps of the concerned dyes are in the range of 2 eV or larger, the photon energy (frequency) of the Nd:YAG laser or Nd:YLF laser IR output is doubled by a crystal which has very high second harmonic generation (SHG) efficiency.

As for the Nd:YLF laser, a lithium triborate (LBO) crystal was used to generate the second harmonics. The crystal is temperature-tuned to the non-critical phase matching (NCPM) condition. When the crystal size was $3 \times 3 \times 8 \text{ mm}^3$, at 167.3 C, up to $\sim 3 \text{ W}$ of green colored output, photon energy $2.356 \text{ eV} (\lambda = 527 \text{ nm})$, was obtained out of the IR input of 18 watts. When a $3 \times 3 \times 15 \text{ mm}^3$ LBO crystal was used, under identical condition, $\sim 7 \text{ W}$ of the green laser beam was produced. Usually the power of the Nd:YLF laser was reduced to generate less than 2 W of green beam, which was enough to pump the two dye lasers. The green beam is split by a variable beam splitter to pump the two dye lasers simultaneously.
Dye Lasers

Two Coherent 702 dye lasers were employed. A dye laser is made up of a dye jet and an optical cavity, which is composed of a set of mirrors of various curvature. The biggest advantage of dye laser is frequency tunability. The dyes are chosen, among other conditions, based on their photoluminescence emission wavelength range.

When the dye molecules are optically pumped by a proper external laser, they will emit photons of various energy to all directions. The dye laser cavity end mirrors reflect back some of the photons and it starts the stimulated emission. Since the stimulated emission has the same direction as the stimulation, the light amplification starts.

Inside the dye laser optical cavity, there is an optical filter which chooses the desired wavelength out of the broad photoluminescence. As for the Coherent dye lasers, the birefringent filter tuning method is adapted. Three flat and parallel crystalline quartz plates make a Brewster’s angle with the laser beam inside the optical cavity. The wavelength is tuned by adjusting the optical axis direction of the plates by rotation of the plates with respect to the surface normal of the plates. The rotation is made by an attached micrometer.

In the experiment, Rhodamine 6G (R6G) dye was used for the pump beam and Styryl 9M (S9M) dye was for the probe beam. The R6G dye laser in the experimental set-up emitted laser beam in the range of 1.97 – 2.22 eV (559.5 – 630.8 nm), which is visible. From the S9M dye laser, 1.32 – 1.60 eV (774.2 – 937.2 nm) near infrared (NIR) range emission was obtained. These were measured by a CVI Digikrom 240 monochrometer. The practically available ranges are narrower than these, since the lasers become very weak and unstable at the edges.
4.2.2 Spatial Alignment

The eventual goal of spatial alignment is to provide high quality pump and probe beams, where the probe beam is probing the area of the sample which the pump beam is evenly illuminating. The laser system itself is made up of many optical pieces, such as mirrors, prisms, and crystals. The tuning of the optical components in the laser system is very important to ensure the good quality of laser, including the beam shape and the strong and stable intensity.

Once the lasers are optimized, the beams pass through various optical components to reach the sample and after that the probe beam is monitored. The basic principle of laser beam propagation and the methods of alignment, in addition to how the spatial alignment can be monitored quantitatively, are described below.

Gaussian Beam Properties

In general, various transverse electromagnetic modes (TEM) occur in the laser cavity. Among them, the TEM$_{00}$ mode is strongly preferred in most optical experiments, since TEM$_{00}$ mode is easily controllable and has relatively even intensity at the beam center. To filter out higher modes, a proper size pinhole inside the laser cavity is usually used because the divergence of the higher mode beams are larger than the fundamental TEM$_{00}$ mode.[144]

The TEM$_{00}$ mode has a Gaussian shape intensity distribution crosssection. For a TEM$_{00}$ mode laser beam, polarized along z-axis and propagating along positive z-axis direction with beam waist $w_o$ at $z = 0$, the electric field can be expressed as:[145]

$$E_z = E_{z0} \left( \frac{w_o}{w} \right) \exp \left\{ -i(kz + \phi) - (x^2 + y^2) \frac{ik}{2} \left[ \frac{1}{R} - \frac{2i}{kw_o^2} \right] \right\}, \quad (4.1)$$
with $\phi = \arctan\left(\frac{kw_0^2}{2z}\right)$ and wavevector $k = 2\pi/\lambda$.

The parameters in the above equation are very useful to describe a laser beam. The beam radius $w$ is

$$w^2(z) = w_0^2\left[1 + \left(\frac{2z}{kw_0^2}\right)^2\right], \quad (4.2)$$

the radius of curvature $R$ of the wavefront is

$$R(z) = z\left[1 + \left(\frac{w_0^4k}{2z}\right)^2\right], \quad (4.3)$$

and the angle of divergence $\theta$ of the Gaussian beam at large $z$ comes from the relation

$$\tan \theta = \frac{w}{R} \sim \theta \text{ such that}[145]$$

$$\theta = 2/kw_0. \quad (4.4)$$

These relations are visualized in the top portion of figure 56.

The Rayleigh range $z_R$ is defined as

$$z_R = \frac{\pi w_0^2}{\lambda} \quad (4.5)$$

so that $w(\pm z_R) = \sqrt{2}w_0$. Since the beam radius does not exceed $\sqrt{2}w_0$ in $-z_R < z < z_R$, the Rayleigh range is sometimes used to describe the focal status of a beam, instead of the beam waist $w_0$.[145, 146]

The thin lens formula for spherical beam is well known,

$$\frac{1}{s} + \frac{1}{s'} = \frac{1}{f}, \quad (4.6)$$

where $s$ and $s'$ are the object and image distances, respectively, and $f$ is the focal length of the lens. The Gaussian beam satisfies a slightly complicated form,

$$\frac{1}{s + z_R^2/(s-f)} + \frac{1}{s'} = \frac{1}{f}. \quad (4.7)$$
Figure 56: The propagation properties of TEM$_{00}$ mode spherical Gaussian laser beam (top) and its focusing with a magnifying lens (bottom). From [146].
The propagation of a Gaussian beam through a lens is shown in the bottom portion of figure 56. The magnification of the lens, $m$, becomes,

$$m \equiv \frac{w'_o}{w_o} = \frac{1}{\left[1 - (s/f)\right]^2 + \left(z_{R/f}\right)^2}^{1/2}.$$  \hspace{1cm} (4.8)

Obviously, when the Rayleigh range or the beam waist approaches zero, the formula for a Gaussian beam becomes that for the spherical beam.[146]

Beam Collimation and Telescope

There are two basic requirements for the beam collimation between the lasers and the sample. First, the beam diameter should not exceed the finite sizes of the effective areas of the optical components that the beams are passing through or being reflected from. Second, since the probe beam size at the sample should be smaller than the pump beam at the same point, the diameter of the probe beam at the focusing lens in front of the sample should be larger than that of the pump beam.

These requirements were achieved by employing a telescope made up of a pair of magnifying lenses at the early part of each of the pump beam and/or probe beam paths. More care was taken for the telescope or beam expander installment at the probe beam, since the path length varies appreciably to delay the pulse arrival time. The pump beam telescope was not essential in this particular set-up. Only probe beam telescope (beam expander) is shown in figure 54.

The Time Delay Line

The time delay line is made up of a retroprism on a ~ 1 m long straight rail. The retroprism is moved back and forth by a stepper motor. Since the light velocity is 3
Figure 57: The schematic diagram of the time delay line alignment.
× 10^8 m/s and the probe light makes a roundtrip on the rail, the time delay line can
delay the arrival of a light pulse up to ~ 6 nsec. The unit movement of the stepper
motor gives a 43.3 fs delay. While the pump beam path is fixed, the probe pulses
are passing through the time delay line. The beam paths are adjusted in such a way
that when the delay is minimum, the probe pulse arrives at the sample a few hundred
ps earlier than the pump pulse. This is essential to obtain the background level
and zero time delay position.

The beam reflected by the retroprism is parallel to the incident beam. If the
incident beam is not parallel to the time delay line, while the retroprism is moving,
the reflected beam will translate to its side. This results in the beam walk at the
sample. There are some known methods to align the delay line, like using a razor
blade. But a simpler and accurate method was devised.

Figure 57 summarizes the method. In the ideal alignment, when the incident
probe beam is parallel to the moving direction of the retroprism, the reflected beam
hits point E on screen, independent of the position of the retroprism. Suppose that
the probe beam has an angle $\theta$ from the ideal path, as shown in figure 57. Then the
reflected beam will hit points F and N, when the position of the retroprism is at the
farthest point and nearest point, respectively. Let the length of the delay line is $L$,
the distance between F and N be $x$, and the distance between N and E be $y$. If the
distance between the nearest position of the retroprism to the last reflecting mirror
before the time delay line is $a$ and to the screen which is set up for the alignment is
$b$, the relations among them are

\[ x + y \simeq (a + 2L + b)\theta, \]  \hspace{1cm} (4.9)
\[ y \simeq (a + b)\theta. \]  \hspace{1cm} (4.10)
From these, the relation

\[ y = \frac{a + b}{2L} x \]  \hspace{1cm} (4.11)

is obtained. After marking points F and N on the screen and extending the straight line which passes the two points, point E is on the line at the side of point N. Since \( a, b, L, \) and \( x \) are easily measured, the position E is directly obtained on screen. By adjusting the last reflecting mirror, the beam can be readily made to meet the point E. The procedure is repeated until the the F and N points are indistinguishable on the screen.

A quantitative test of the alignment can be done by the direct beam position measurement at the sample position, with the retroprism at various points on the delay line. As shown in figure 58, with the beam diameter \( \sim 30 \, \mu m \), less than 10 \( \mu m \) deviation of the probe beam position between the maximum and minimum time delay was observed when the method above was repeated two or three times.

**Focused Beam Size and Position Measurement**

The cross sectional pump and probe beam shapes and their coincidence are very crucial in the experiment. A system which directly measures the detailed profile of the beams at the sample position was developed. The sensoring head is composed of a 10 \( \mu m \) diameter pinhole attached in front of a United Detector Technology UV 100 silicon detector. Let the \( x \)-axis be the direction of the laser beam at the sample position. The position of the head in the \( yz \)-plane is controlled by two micrometers attached to stepper motors. The sensoring head position in the \( x \)-axis direction can be moved by another micrometer. The stepper motors are controlled by the computer to get the contour of the beam cross section. Since the measurement is reproducible,
Figure 58: Typical crosssections of the pump beam (top) and probe beam (bottom). The intensity was measured at every 10 $\mu$m movement of pinhole in $y$ and $z$ directions covering $100 \times 100 \ \mu$m$^2$. 
the system can determine not only the beam profile but also the beam position with less than 10 μm resolution. In figure 58, typical profiles of the probe beam and the pump beam are shown. It is obvious that the probe beam is probing at the center part of the pump beam.

### 4.2.3 Temporal Alignment

Temporal alignment is made up of synchronization of the pump and probe pulses and the optimization of the time resolution of the system. Unlike spatial alignment, temporal alignment is mainly achieved by various optical components actively controlled by electronic systems. The principles of mode-locking and cavity-dumping are briefly described. The method by which the ultrafast pulse width is monitored and optimized is summarized. The determination of the time resolution of the system is explained.

#### Mode-Locking

Mode-locking is a method to generate short pulses with a constant repetition rate. In the Nd:YLF laser, it is achieved by putting a piezoelectric crystal inside the laser cavity, near to an end mirror. A 38 MHz electric field is applied to the crystal and the crystal vibrates at a rate of 76 MHz, because there are two power peaks in one cycle. The change of the lattice constant of the crystal caused by the acoustic wave results in bending of the beam path by Bragg diffraction.[144] The net effect is blocking and opening of the laser cavity 76 million times a second. The optical cavity length is adjusted so that light can travel 76 million round trips per second. Though the Nd:YLF rod is continuously pumped by two Krypton lamps, only the discrete light
pulses can be amplified. As a result, the mode locked Nd:YLF laser emits 76 million pulses per second or one pulse every 13 nsec. The pulse width is \( \sim 50 \, \text{ps} \).\[143\]

**Cavity-Dumping**

When both of the cavity end mirrors of a laser are perfectly reflecting, the laser beam cannot emerge from the cavity. Many lasers including the Nd:YLF laser use a partial reflector (output coupler) as one of the two cavity end mirrors to overcome this problem. In the synchronized dye lasers, a cavity-dumping method is used. Like the mode locking system described above, a piezoelectric crystal or Bragg cell is placed inside the cavity. If an ac electric field is applied while a laser pulse is passing through the crystal, the laser beam path is bent and the pulse escapes from the dye laser cavity.

The Coherent 7210 dye laser cavity-dumper head (CDH) is controlled by the Coherent 7200 cavity-dumper driver (CDD), as illustrated in figure 55. The CDD receives the 38 MHz signal from the mode-locker for the synchronization. The CDD was set so that one dye laser pulse escapes from the dye laser cavity out of every 79 pulses. As mentioned above, the time interval between the pulses inside the dye laser is 13 nsec. But since 38 MHz instead of 76 MHz is used as a reference, the laser pulses are considered to be a sum of two groups. In each group the time interval between pulses are 26 nsec apart. One group is delayed 13 nsec to the other. Because only one group of the two is chosen, the time interval between emitted dye laser pulses becomes \( 26 \, \text{nsec} \times 79 = \sim 2 \, \mu\text{sec} \).
Autocorrelation

Usually, when the dye lasers are tuned to maximum CW power, the pulse width is up to several times wider than the optimal pulse width. It is very important to monitor directly the pulse width for the optimization.

A Femtochrome Research FR-103 autocorrelator was used to measure the pulse widths. The autocorrelator uses second harmonic generation (SHG) in a conventional Michelson interferometer set-up for pulse width measurement. A laser beam of repeated pulses is split by a beam splitter. The two beams go through two different optical paths and meet at a SHG crystal with an angle to each other. After the crystal, the two beams are blocked. The optical detector for the second harmonics is between the beam blocks. Consequently, only the second harmonics created by the frequency summation of the photons from the two different paths are detected.

While one beam path is fixed, the other path length is periodically varied. Since the light velocity and the variation of the path deviation are known, the pulse width is determined from the measurement of the second harmonics. The oscillation frequency of the varying optical path is 20 Hz and a synchronized pulse is provided to the oscilloscope as a trigger. The pulse width can be minimized by adjusting the cavity length of the dye laser while monitoring the pulse width displayed on an oscilloscope attached to the autocorrelator. Usually, the oscilloscope display is in msec scale. It is converted to the real time scale by the conversion ratio 63.8 psec/msec.

The resultant autocorrelation or pulse shape can be recorded by a boxcar. An EG&G Princeton Applied Reach PAR4420 boxcar is set up in parallel to the oscilloscope and GPIB controlled by the computer for this purpose. Figure 59 shows typical results of autocorrelation of the pump and probe pulses. The x-axis is converted from
the direct reading in msec unit to real time scale unit psec, by using the conversion ratio.

**Synchronization**

Since two cavity-dumped dye lasers are used, the synchronization of the laser pulses is important. The delay toggle switch at the CDD shifts the relative time delay 26 nsec at a time, allowing any of the 79 pulses in the ~ 2 μsec cycle to be chosen. The fine delay knob at the CDD can choose one of the two groups explained above, to make a 13 nsec shift.

A fast diode of less than 1 nsec rising time is installed to monitor the pump and probe pulses, as shown in figures 54 and 55. The beam path lengths to the fast diode were adjusted so that the relative time delay between the pump and probe pulses is close to that at the sample. The signal is monitored by an oscilloscope. The ~ 2 μsec period synchronization output from a CDD is used as a trigger. To synchronize the two pulses, the CDD delay toggle switch and the phase control knob are adjusted while monitoring the relative arrival times of the pulses.

**Crosscorrelation**

The autocorrelator can also measure the crosscorrelation of two different wavelength laser pulse beams.[147] As shown in figure 54, the autocorrelator is positioned after the time delay line. The position of the retroprism was adjusted to optimize the synchronization of the pump and probe pulses and the top portion of figure 60 shows an ordinary result recorded by the boxcar. Usually, full width half maximum (FWHM) of the crosscorrelation is quoted as the time resolution of the system.
Figure 59: Typical optimized autocorrelation results of pump (top) and probe (bottom) pulses.
Figure 60: The time resolution of the system; a crosscorrelation of the pump and probe pulses (top) and the differentiation of the rising slope of the PSPIA signal of an a-Si:H sample w.r.t. the delay time (bottom).
The final way of measuring the system time resolution is by doing a picosecond photoinduced absorption (PSPIA) using a sample whose signal rising time or the defect creation time is known to be much shorter than the expected system time resolution. A hydrogenated amorphous silicon (a-Si:H) film was adapted for the purpose. The bottom portion of figure 60 shows the result and the differentiation of the result with respect to the delay time. This test measurement not only tells the time resolution but also the status of the time delay line alignment, including the exact position of the retroprism on the time delay line where the pump and probe pulses arrive at the sample simultaneously.

4.2.4 Time Modulation of Signal

The typical intensity change of the probe beam due to the absorption change caused by the photoinduced electronic defects is in the order of 0.01 % of the probe beam intensity. In spite of experienced care of the lasers, the temporal fluctuation of the laser beam intensity is larger than the signal size. To measure the signal under such a noisy environment, like the near-steady-state photoinduced absorption (NSSPIA) measurement, lock-in amplifiers are used.

The signal is time modulated and the trigger, which is synchronized to the time modulation, is provided along with the signal to the lock-in amplifier. From the input, the lock-in amplifier band passes only the component which has the same frequency as the trigger and measures its phase and amplitude. Since the phase is a relative concept, the phase initialization should be completed prior to the usage of a lock-in amplifier.

Two EG&G Princeton Applied Research PAR5209 lock-in amplifiers were em-
ployed to measure the signal. As this model can read only the projected amplitude of the signal to the initialized phase, one lock-in amplifier was phase delayed 90° relative to the other to measure the phase and the amplitude of the signal at the same time.

The Si detector which monitors the probe beam intensity after the sample is slow enough to regard the probe beam as a continuous wave, though it is actually a stream of ≤10 psec pulses repeated with 500 kHz frequency. Even when the detector has a better time resolution, the lock-in amplifier filters out all the higher frequencies. The modulation frequency, ~ 1.5 kHz, was chosen such that the period is much longer than the rising time of the Si detector and at the same time the environmental electromagnetic interference was relatively calm at the frequency. Two different signal time modulation methods, used in the measurements, are described below.

**Mechanical Chopping**

Mechanical chopping is the time modulation method where the pump beam is blocked periodically. Since the half period of the adapted time modulation frequency ~ 1.5 kHz is ~ 0.33 msec, when the pump beam is blocked, practically the psec or nsec order photoinduced absorption vanishes. For the other half of the period, a pump pulse is precedent to a probe pulse in the amount of time delay set by the time delay line. As a result, the probe beam is time modulated and measured by the lock-in amplifiers. A Stanford Research Systems SR540 optical chopper was used for the experiment. The chopper head was placed so that the chopping blade cut where the pump beam diameter is narrow compared to the openings on the chopping wheel. The chopper controller provided a trigger to the lock-in amplifiers.

The chopped pump beam is used for the phase initialization of the lock-in ampli-
fiers. Attenuated chopped pump beam is temporarily rerouted to the optical detector attached to the lock-in amplifiers through preamplifiers, for the phase initialization procedure. The interim pump beam path for the phase initialization need not have same length as the probe beam path, since the path length difference will cause at worst a few nsec deviation, while the chopping period is $\sim 0.66$ msec.

The mechanical chopping method is also adapted in the near-steady-state photoinduced absorption (NSSPIA). The samples for picosecond photoinduced absorption (PSPIA) usually show finite NSSPIA signal. Obviously, like the NSSPIA measurement, the pump beam is chopped while the sample is probed. Rosenberg et al.[148] interpreted the background of their mechanically chopped PSPIA measurement as NSSPIA signal. Another possibility is the thermal signal. The optical absorption of many materials varies as a function of temperature and the sample temperature can be modulated by the chopping of the pump beam.

This unwanted background problem is investigated in figure 61. Without losing generality, it is assumed that all three photoinduced phenomena increase the absorption of the pump beam. First, the NSSPIA signal is considered. As previously explained, the time delay line can vary the time delay $\Delta t$ from $\sim -0.5$ nsec to $\sim 6$ nsec. There are two possible situations. In the top portion of figure 61, the time delay line makes a negative time delay, by positioning the retroprism nearer than the zero time point, or $0 > \Delta t > \sim -0.5$ nsec. As a result, for a probe pulse, the most recent pump pulse was $\sim 2$ $\mu$sec earlier. If the probe pulse arrives while the pump beam is blocked, the time delay becomes even longer. The probe can be modulated as shown in the figure, but none of the PIA in time scale of $\sim 2$ $\mu$sec or shorter exists since no pump pulse is followed by a probe pulse within $\sim 2$ $\mu$sec.

The bottom portion of figure 61 shows the case with positive time delay. When
Figure 61: Mechanical chopping of negative time delay (top) and positive time delay (bottom) in delay line.
the pump beam is unblocked, each probe pulse follows a pump pulse with delay time $\Delta t$, which is between 0 and $\sim 6$ nsec. Clearly, when the pump beam is blocked, the probe pulses arrive $\sim 2$ $\mu$sec to 0.33 msec later than the last pump pulse.

Like the NSSPIA signal, the thermal signal decay time is relevant to the adapted chopping frequency. As in the top portion of figure 61, when the time delay is negative, the lock-in amplifier measures the background signal including photoinduced absorption of time scale longer than $\sim 2$ $\mu$sec and thermal signal. If the time delay is zero or positive, the photoinduced absorption of the given time delay $\Delta t$ is added to the same background signal. Figure 63 (a) shows a typical case.

From figure 61, it is obvious that the PSPIA signal is either in phase or out of phase with the pump beam, in the bleaching or absorption case, respectively. But the background signal will generally have a phase different than $0^\circ$ or $180^\circ$. Ideally, when the phase of the lock-in amplifier is shifted $90^\circ$ after the initialization by using the modulated pump beam, the lock-in amplifier will detect only the background.

**Electronic Temporal Hopping**

Electronic temporal hopping is another way of time modulation.[149, 150] As mentioned earlier, a CDD can delay or advance the pulse stream of a cavity-dumped dye laser in the unit of 26 nsec. The CDD for the R6G dye laser is electronically modified and receives a $\sim 1.5$ kHz signal from a Hewlett Packard pulse generator. As a result, the pump pulses are advancing and delaying 26 nsec, with the $\sim 1.5$ kHz frequency. At the same time, the pulse generator delivers a trigger of the same frequency to the lock-in amplifiers.

The schematic diagram explaining electronic temporal hopping is in figure 62. In
Figure 62: Electronic temporal hopping of negative time delay (top) and positive time delay (bottom) in delay line.
Figure 63: The results of the two time modulation methods. (a) mechanical chopping (b) electronic temporal hopping. From [149].
the bottom of figure 62, the time delay line makes a positive delay of \( 0 \leq \Delta t < \sim 6 \) nsec. when the pump pulses are 26 nsec delayed, a probe pulse sees the \( \sim 2 \mu\text{sec}, \sim 4 \mu\text{sec}, \sim 6 \mu\text{sec}, \sim 8 \mu\text{sec}, \ldots \) old effects of the pump pulses. If the pump pulses are advanced in 26 nsec, a probe pulse sees the \( \Delta t, \sim 2 \mu\text{sec}, \sim 4 \mu\text{sec}, \sim 6 \mu\text{sec}, \sim 8 \mu\text{sec}, \ldots \) old effects of the pump pulses. Consequently, the lock-in amplifier detects only the photoinduced absorption of \( \Delta t \) time delay between pump and probe.

The top portion of figure 62 shows the situation when the time delay \( \Delta t \) is negative. All the probe pulses see virtually same traces of the pump pulses throughout a time modulation period, since 26 nsec is much shorter than \( \sim 2 \mu\text{sec} \). The two background signals in mechanical chopping, NSSPIA signal and thermal signal of the given time modulation frequency, can not be detected in this case, since the pump beam is always on. Figure 63 compares the two time modulation methods. The background signal in mechanical chopping method vanishes when electronic temporal hopping method is used.

In electronic temporal hopping, the phase initialization of the lock-in amplifiers are done by using a sample whose PSPIA result is known. Again, the a-Si:H film was used, since it shows strong photoinduced absorption. As a result, if the signal of a sample is out of phase, the sample shows photoinduced bleaching. Like the mechanical chopping case, the PSPIA signal phase should be either 0° or 180°.

4.2.5 Other Components and System Control

Many more instruments are needed in the experiment. Below are some of important ones.
Optical Detector and Preamplifier

United Detector Technology model 101C transimpedence amplifiers are used to amplify the signal detected by United Detector Technology UV 100 silicon detectors. The amplifiers converted current from the detectors to voltage with ratio $10^3$ or $10^4$ V/A.

A/D Converter

The photoinduced absorption is defined to be the negative of the normalized variation of the transmitted intensity of probe. Real time normalization is important because the probe beam intensity varies widely as a function of time. The PAR5209 lock-in amplifiers include A/D converters. While the two lock-in amplifiers measure phase 0° and phase 90° values of the probe intensity variation, one A/D converter measures the magnitude of the probe intensity after the sample and the other A/D converter measures the probe intensity before the sample, as in figures 54 and 55. The probe intensity after the sample is used to normalize the variation, to get PSPIA signal. At the same time, by dividing the probe intensity after sample with the probe intensity before sample, the transmission of probe beam is monitored throughout the measurement. The detail is discussed in chapter V.

Voltmeter

A Keithley model 195A digital multimeter is used to monitor the signal which goes to the lock-in amplifiers. This is very useful to estimate the optical thickness of the sample and to monitor the probe beam intensity. At the same time, when the beam
profiles are to be measured, this voltmeter is essential to make the beam meet the pinhole.

**Power Meter**

The Nd:YLF laser has an internal power meter. The second harmonics intensity is measured by a Coherent model 201 power meter. Its full scale runs from 0.3 W to 10 W. A Spectraphysics model 404 power meter was used to measure the pump and probe powers, since its full scale runs from 0.02 mW to 5 W, in the range of 450 — 900 nm (1.38 — 2.76 eV).

**Vacuum Station and Temperature Controller**

While the home made cryostat is pumped to $\sim 10^{-5}$ mbar by a CIT Alcatel vacuum station with diffusion pump, a Lake Shore Cryotronics DRC82C temperature controller monitored and controlled the temperature of the sample.

**4.3 PSPIA: Measurement**

As shown in figure 55, a Hewlett Packard Vectra personal computer controls the experiment via GPIB connections. The controlling software, KK.DMO, was written in Macmillan Software Asyst version 2.0, a language designed for control, data collection, and data analysis. KK.DMO is in appendix A. After setting up the system, normal measurement procedure is automatically accomplished by the controlling software. KK.DMO offers nine different measurement routines. They can be classified in two categories. The first seven routines are for PSPIA. They are different
in the way of varying delay time, by controlling the x stepper motor. Among them, FREE.CONST.STEP and FREE.EXP.STEP are most versatile. In these routines, the y and z stepper motors are not used. The two routines BEAM.PROFILE and SAMPLE.CHECK include the manipulation of the y and z stepper motors, to measure the beam profile and sample condition, respectively.

4.3.1 PSPIA Routines

The only difference among the seven PSPIA routines is the way the time delay $\Delta t$ is set. Among data points, $\Delta t$ can be varied linearly with constant interval or exponentially. The intervals can be preset or given at the beginning of measurement. When one of these routines is chosen, at the beginning, the name of sample, the name of data file where data will be saved, the powers of pump and probe, and the pulse repetition rate are asked. When the time delay line manipulation is not preset in the routine, information like initial move, unit step and number of data should be given. After that, questions like how many samplings are done at a data point and how many lock-in amplifiers are used is given and lastly a comment is required.

While the measurement is in progress, whenever a new data point is added, the $\Delta T$, which is measured by the lock-in amplifier, the $T$, which is from the A/D converter, and the ratio $-\Delta T/T$, all three are plotted on screen with all the information including chopping frequency and other parameters. When a scan is done, the time delay line is reset to the nearest position and the screen is printed with starting and ending time. The data are saved under the given name.
FREE.CONST.STEP

This is the most versatile linear delay routine. Any unit step can be chosen, including negative value and zero. When unit step is negative, all the procedure is the same as the positive case, except that the time delay is maximum at the beginning and decreases. When unit step is zero, the time delay is fixed. In this case, the routine repeats the same measurement with a given time interval. By this option, the second or minute range change of PSPIA can be easily monitored.

ROUGH.CONST.STEP and FINE.CONST.STEP

These two are special cases of FREE.CONST.STEP. Especially ROUGH step is good for checking over the full extent of the time delay line.

EXPONENTIAL.STEP Routines

Like the linear step case, the time delay line parameters can be chosen in the FREE routine. This is very useful when the details around delay time zero are needed while covering a wide time delay range. The other two, ROUGH and FINE routines are not used like the LINEAR.STEP, where the unit step itself increases linearly.

4.3.2 BEAM.PROFILE and SAMPLE.CHECK

These two routines manipulate the y and z stepper motors at the sample holder. The stepper motors move the position of sample holder on the plane orthogonal to the pump and probe beams. Initial move, unit step, and number of steps are asked for
each direction. At each position, a lock-in amplifier and/or an A/D converter collects data. After finishing data collection, the 2-D and 3-D profiles are displayed on screen and hardcopied, with all other information. The data is saved in a file whose name is given at the beginning.

**BEAM.PROFILE**

The basic purpose of this routine is to measure the position and profile of the pump and probe beam. The sensor head with a 10 μm pinhole in front of an optical detector is used at the sample holder. It is not a trivial task to make a laser beam hit the pinhole to start the measurement. The tightly focused laser beams are either invisible or too bright and the pinhole itself is virtually invisible. Since the optical detector is connected to the preamplifier which is connected to the lock-in amplifiers in figure 55, by watching the voltmeter, the alignment can be confirmed.

**SAMPLE.CHECK**

Practically, many samples have uneven optical density distribution. This routine measures sample transmittance and/or photoinduced absorption of given area to find proper point for the experiment. At the same time, this routine can be used to monitor a diffusion of a long-lived defects, created in a localized area.

**4.4 PL: Experimental Set-Up**

To measure the decay time, \( \tau \), of leucoemeraldine base (LEB) photoluminescence (PL), frequency doubled Rhodamine 6G (R6G) dye laser was used. The experimental
Figure 64: The experimental set-up of leucoemeraldine base in NMP decay time measurement.
Figure 65: A typical fitting result of the LEB in NMP PL decay time $\tau$. The solid line is the fitting to the measured signal ($\bullet$) from the impulse response of the measuring system ($+$). This gives $\tau = 1.91$ nsec.
set-up is shown in figure 64. Like picosecond photoinduced absorption (PSPIA) case, the dye laser is pumped by a Quantronix 416 frequency doubled mode locked Nd:YAG laser. A Coherent 7210 cavity-dumper head (CDH) is attached to the Coherent 702 dye laser with Rhodamine 6G (R6G) dye. A Coherent 7200 cavity-dumper driver (CDD) controls the CDH to generate 2.13 eV (583 nm) 10 psec pulse width laser pulses every 2 μsec (500kHz). The CW power of the dye laser was adjusted to be ~ 5 mW. The dye laser beam is focused to a 25 mm KDP crystal by a lens with focal length 100 mm, to be frequency doubled. Two Hoya U-330 high pass filters (HPF) block the fundamental 2.13 eV beam, only passing the newly generated 4.26 eV (292 nm) beam. The sample, LEB dissolved in NMP, is in a 2 mm Uvonic cuvette and hung inside a cryostat, making 45° to the incoming ultraviolet (UV) beam, as shown in figure 64. The home built cryostat is vacuumed by a CIT Alcatel vacuum station and temperature controlled by a Lake Shore Cryotronics DRC82C temperature controller.

After the sample, a Hoya L-34 or L-42 low pass filter (LPF) blocks the reflected or scattered 4.26 eV photons. A Hamamatsu type R928 photomultiplier tube (PMT) collects the PL photons. DC 1000 V is supplied to the PMT, from a home assembled DC voltage supplier. The PMT is attached to a Tektronix oscilloscope and a EG&G PAR 4400 boxcar averager (BA), triggered by the 500 kHz signal from the CDD. The gate width of the boxcar was 2 nsec and signal was averaged 10 times. A Hewlett Packard Vectra personal computer (PC) with a line printer is connected to the BA through a general purpose interfacing bus (GPIB) cable, to handle the data.

Since the nominal rising time of the PMT was 2.2 nsec, exceeding the decay time τ of the sample, the decay time was obtained by the convolution of the impulse response of the measuring system, under the assumption of a single exponential decay.[151] To get the impulse response, a neutral density filter (NDF) of optical density 1.5 was
placed before the SHG crystal, as shown in figure 64, while removing the HPF which will block the 2.13 eV photons. Since the 2.13 eV beam is very much weakened by the NDF, the KDP crystal can hardly generate 4.26 eV photons. As a result, no detectable PL occurs and the PMT will see only the 10 psec pulse width 2.13 eV pulse. Since the measuring system response time is in nsec scale, the 10 psec pulse can be treated as an impulse with Dirac delta function shape. The measured signal response was fitted by a least square method to a convolution of the impulse response and a single exponential decay function, exp(−t/τ), to get the decay time τ. Figure 65 shows a typical fitting result.
CHAPTER V

DATA AND DISCUSSION

In this chapter, the polyaniline picosecond photoinduced absorption data is analyzed in relation with other time range results summarized in chapter III. The polyaniline photoluminescence result is shown.

5.1 Picosecond Photoinduced Absorption

In this section, the picosecond photoinduced absorption (PSPIA) results of pernigraniline base (PNB) are described and a model for the dynamics of the electronic defects is suggested.

5.1.1 Hysteresis

In a normal PSPIA, it takes a few seconds to measure a data or a value of $-\Delta T/T$ for a given time delay. The detail may vary from set-up to set-up, but it includes movement of the retroprism to change the time delay, waiting period for the lock-in amplifier (usually the time constant of the lock-in amplifier is set in the order of 1 sec and the waiting period is about five times of the time constant), and data acquisition time
(generally the data is read many times and the average of the readings is calculated to reduce the noise). Since PSPIA measurement includes many data points of different time delay, the total time for a scan in PSPIA is in the range of a few minutes or longer. Throughout the measurement time, the pump beam illuminates the same point on the sample.

In many conducting polymers like polyacetylene and polythiophene shown in chapter II, no excited state with decay time longer than a few msec is reported. As a result, it is assumed that the averaged number of excited states in the sample reaches a steady state or becomes a perfect periodic function with the same period as the pump beam time modulation, within a few seconds of optical pumping or the first waiting period for the lock-in amplifier (LIA). In other words, the PSPIA measurement will give the same results independent of the sample's history. Usually, with such samples, several scans of PSPIA measurement are done consequently and the results are averaged to give better signal-to-noise ratio. Here one scan means one set of data collection covering the intended delay time range.

**Probe at 1.38 eV**

In that sense, pernigraniline base (PNB) shows very peculiar behavior in PSPIA. Figure 66 is the result of PSPIA measurement of PNB in KBr pellet, pumped at 2.1 eV and probed at 1.38 eV at room temperature. The pump power was 12 mW at the sample. Since the pump beam was mechanically chopped with frequency ~ 1.5 kHz, the average power at the sample was 6 mW. As shown in chapter IV, the pump beam diameter at the sample was ~ 100 μm. If even illumination over the area is assumed, this gives pump beam intensity $12 \text{ mW}/(\pi (50 \ \mu\text{m})^2) \approx 1.5 \times 10^2 \ \text{W/cm}^2$ when the pump beam is unblocked. Since the pump beam is made up of ~ 6 psec
Figure 66: PSPIA of PNB, pumped at 2.1 eV and probed at 1.38 eV.
pulses emerging every 2 \( \mu \text{sec} \), the peak intensity of the pump laser at the sample is \( 1.5 \times 10^2 \text{ W/cm}^2 \times (2 \ \mu \text{sec} / 6 \text{ psec}) \approx 0.05 \text{ GW/cm}^2 \). Each pump pulse contains 12 mW \times 2 \ \mu \text{sec} = 24 \text{ nJ} of energy or \( 24 \text{ nJ}/(2.1 \text{ eV}) \approx 7.1 \times 10^{10} \) photons. The average pump photon input is \( 12 \text{ mW}/(2.1 \text{ eV}) \approx 3.6 \times 10^{18} \) photons/sec.

Two scans are shown in figure 66. The sample point was not previously exposed to the pump beam. The first PSPIA scan was done while increasing the time delay constantly, starting at \( \sim -70 \text{ psec} \) time delay. The time constant of the LIA was set to 0.3 sec and one scan took \( \sim 5 \) minutes to obtain 40 data points. Because mechanical chopping was used, the phase of the LIA was initialized with the modulated pump beam. There is a strong photoinduced absorption (PIA) peak at delay time zero (practically, the peak was set to decay time zero) and it decays rapidly as the delay time increased. A long PIA tail remains. The next scan was done at the same sample point. This time, the delay time starts from maximum delay time and decreases as the measurement progresses. The arrows in the parentheses show the direction of measurement. The same long PIA tail is shown in the second scan. But the sharpness of the PIA peak intensity near delay time zero is reduced nearly by half. Between the first scan and the second scan around the delay time zero point, the sample was exposed to the pump beam for more than \( \sim 5 \) minutes.

**Probe at 1.50 eV**

Figure 67 shows the result of PNB PSPIA, pumped at 2.1 eV and probed at 1.50 eV. Same pump beam was used as in figure 66. The first scan was made from \( \sim -70 \text{ psec} \) time delay and the delay time was increased. There is a strong photoinduced absorption, at the beginning of the first scan. PIA tail remains until \( \sim 300 \text{ psec} \). But the tail intensity is smaller than the 1.38 eV probe case in figure 66. The measurement
Figure 67: PSPIA of PNB, pumped at 2.1 eV and probed at 1.50 eV.
Figure 68: PSPIA of PNB, pumped at 2.1 eV and probed at 1.50 eV. This shows the details of the PIA peak.
time for a scan and the pump power at the sample in figure 67 were same as those in figure 66. When the same sample point was scanned a second time, already the long absorption tail disappeared and the PIA peak decayed very fast. Between the first and second scan in figure 67, the sample was exposed to the pump beam for a few minutes. When the scan was repeated further, the long tail disappeared completely and only the short PIA peak remained.

The detail of the PSPIA behavior around delay time zero with probe beam at 1.5 eV is shown in figure 68. The same pump beam intensity (12 mW with diameter 100 μm) was used and mechanically chopped. This time, the delay time interval was not held constant and increased exponentially. Though only upto ~ 40 psec delay time is shown in figure 68, the measurement covered the full extent of the delay line, reaching upto ~ 4.5 nsec. Each scan took ~ 10 minutes. All the scans were made while increasing the delay time. The PIA in the first scan disappeared when the delay time became 2–3 nsec. From the second scan, repeating the result shown in figure 67, there was no long-lived tail. The PIA signals rose in ~ 6 psec, showing the temporal resolution of the measuring system. In other words, this proves that the PIA rising time of PNB at 1.5 eV is much shorter than psec time scale, because the recorded rising time is approximately the summation of the measuring system resolution and the actual rising time of the sample. After more than 10 minutes of optical pumping, for the second and later scans, no PIA slowly decaying component is observed. The PIA peak decays very fast, several times slower than the measuring system temporal resolution. In other words, the decay time of the PIA peak is in the range of ~ 20 psec.
Probes at 1.58 eV

Figure 69 was measured under same condition as the measurements in figures 66 and 67, except the pump power and the probe energy. This is the result of 14 mW pump power at the sample and 1.58 eV probing. In this case a most striking result is obtained. When a fresh sample point is scanned, initially a large PIA is observed. Even when the time delay is negative, PIA is observed in the first scan as shown in figure 69. The dye lasers emit pulses every 2 µsec. Since the time delay is negative, the probe pulse reaches the sample about 2 µsec after the arrival of the latest pump pulse. This means the photoinduced absorption is appreciably strong even after 2 µsec. It should be pointed out that the mechanical chopping was used. As explained in chapter IV, the electronic temporal hopping method does not measure signal with 2 µsec delay time.

With this probe energy, a most dramatic change is occurring. The strong PIA changes to photoinduced bleaching (PIB), during the first scan. Like the scans in figures 66 and 67, the full scan takes ~ 5 minutes. In the second scan, already there is a very short initial PIA peak around delay time zero and soon a strong PIB peak shows up as delay time is increased. No measurable signal is shown at 2 µsec delay (negative delay time in the figure) in the scans made after the first scan in figure 69. When the same sample point is repeatedly measured, the PIA peak is gradually wiped out. After three scans or ~ 15 minutes of optical pumping, no PIA peak remains.

The PIB starts at delay time ~ 10 psec and the rising time is ~ 20 psec, exceeding the resolution of the system, ~ 6 psec. In the measurements, the delay time interval was set to a constant, ~ 10 psec. Even when the sharp PIA peak was wiped out after long time exposure to the pump beam, the PIB rising shape does not change.
Figure 69: PSPIA of PNB, pumped at 2.1 eV and probed at 1.58 eV. The first scan was measured while increasing delay time.
Figure 70: PSPIA of PNB, pumped at 2.1 eV and probed at 1.58 eV. The first scan is measured while decreasing delay time.
The same measurement was repeated with fresh sample, this time starting from positive delay time in the first scan and the delay time was reduced gradually. Figure 70 shows a dramatic PSPIA behavior. Initially, there is strong PIA at large delay time. The PIA changes to PIB, as the measurement progresses. It can be seen that the strong PIA becomes PIB within about two thirds of scanning time, in both of the first scans in figures 69 and 70. In figure 70, starting from the second scan, again there appears strong PIB peak, the same as the second scan result in figure 69. From figures 69 and 70, it can be concluded that there is an initial strong PIA throughout the delay time exceeding 2 μsec. This PIA fades and disappears within a few minutes of optical pumping and strong PIB shows up.

With 14 mW pump power, the sample was optically pumped for more than 15 minutes, before the PSPIA measurement shown in figure 71. The delay time interval was exponentially increased up to ~ 4.5 nsec. The top of figure 71 shows the result in linear decay time scale and the bottom of figure 71 is the redrawing by using logarithmic decay time scale. At the bottom figure, 20 psec was added to the decay time to avoid negative argument of log function. Apparently, there is no initial sharp decay of PIB. When the decay trend of the PIB peak in the bottom of figure 71 is linearly extrapolated, the PIB vanishes within a few hundreds of nsec. Small offset is found in the figure where the decay time is negative. This is believed to be a systematic error of the measuring system. To correct this, the whole curve should be shifted downward.

5.1.2 Temperature Dependence

Since the PSPIA result shows such hysteresis, another way of measurement was devised. The delay line was fixed to give ~ 20 psec time delay. Initially the pump
Figure 71: PSPIA of PNB in linear time scale (top) and log time scale (bottom), pumped at 2.1 eV and probed at 1.58 eV. The sample was optically pumped for more than 15 minutes before measurement.
Figure 72: PSPIA of PNB, pumped at 2.1 eV and probed at 1.58 eV. The delay time was fixed at ~ 20 psec and pump beam was blocked for the first ~ 2 minutes.
beam was blocked by using the shutter shown in figure 54. The PSPIA measurement routine started only with probe beam. After a given time duration, the shutter was open and the optical pumping of the sample began. Upon the opening of the shutter, the PSPIA signal appeared as in figure 72, where the same measurement was repeated while varying the temperature.

As explained previously, there is a lower limit of time interval between data measurements due to the measuring system. For the measurements in figure 72, ~ 10 sec was set as the time interval. The PNB KBr pellet sample was pumped at 2.1 eV with power 10 mW. 1.58 eV was chosen as the probe energy and probe power was 1 mW. The lock-in amplifier (LIA) time constant was 0.3 sec. Electronic temporal hopping with frequency ~ 1.5 kHz was used. Hence, not like mechanical chopping, there was no reduction of pumping power by half at the sample. To initialize the phase of the LIA's, PSPIA signal of an a-Si:H film was adapted as a standard. The material shows strong PIA peak at the given probe energy.

The value $-\Delta T/T$ will be zero, without optical pumping. When the pump beam is on, $-\Delta T/T$ starts to have finite value. The value is stabilized when the sample reaches a steady state where the number of defects becomes perfectly periodic with respect to the ~ 2 $\mu$sec period of the pump pulse arrivals and as a result the ~ 1.5 kHz modulation. In other words, the value $-\Delta T/T$ will vary until the sample forgets the sudden starting of the optical pumping. If all the excited states created by the optical pumping decay thoroughly in a time scale shorter than the pump beam modulation period, the result of this measurement with constant delay time will show a step function-like shape. The deviation of the result from the step function-like shape indicates the presence of a mechanism with longer time scale.

Figure 72 shows six measurements with different temperatures from 150 K to
400 K. The moment when the pump beam shutter was opened is evident from the figure. For the first \( \sim 2 \) minutes, until the shutter was open, the measured results were identically zero within background noise. All curves except 150 K case were shifted upward for clarity. Two trends were obvious. As temperature went up, the measured initial PIA peak amplitude became larger. The change from PIA to PIB went faster as the temperature decreased.

5.1.3 Pump Exposure Time Dependence

The top portions of figures 73 and 74 are redrawing of the curves measured at 150 K and 400 K in figure 72. The bottom portions of the two figures show the transmitted probe intensity changes during the process of the measurement. If the probe beam intensity can be kept constant, the intensity detected by the detector 1 in figure 54 will be proportional to the transmittance of the sample. In reality, the probe beam intensity fluctuates severely. Since photoinduced absorption measures the quotient \(-\Delta T/T\), such temporal fluctuation can be mostly ignored. But to monitor the transmittance \(T\), detector 2 in figure 54 was employed. Detector 2 monitored the probe beam intensity before the sample. The two detectors were connected to different A/D converters, respectively. As a result, the variation of the original probe beam intensity was separated from the transmittance change of the sample by calculating the ratio between them.

The bottom portion of figure 73 shows \(\sim 20\%\) decrease of transmittance after the turning on of the pump beam by opening the shutter. The change occurred in \(\sim 30\) second. After the reduction of the intensity, the new transmittance seems to be stabilized. At the top of figure 73, while the transmittance is dramatically decreasing, PIA peak is shown. But \(-\Delta T/T\) continues to go down for the next \(\sim 250\) sec while
Figure 73: PSPIA of PNB at 150 K, pumped at 2.1 eV and probed at 1.58 eV. The delay time was fixed at ~ 20 psec and pump beam was blocked for the first ~ 2 minutes. $-\Delta T/T$ (top) and probe intensity after sample (bottom).
Figure 74: PSPIA of PNB at 400 K, pumped at 2.1 eV and probed at 1.58 eV. The delay time was fixed at ~ 20 psec and pump beam was blocked for the first ~ 2 minutes. $-\Delta T/T$ (top) and probe intensity after sample (bottom).
the transmittance shows little change.

The result at 400 K appears in figure 74. The transmittance of the probe beam reduces a few % when the pump beam is on. While the absorption increment (or transmittance reduction) is small compared to 150 K case, the peak magnitude of \(-\Delta T/T\), which is a normalized differentiation of the transmittance with respect to the influx of optical pumping, is several times larger than that of 150 K case. This can be explained by the fact that the data was taken every ~ 10 sec. The probe beam intensity was measured by an A/D converter. As a result, the reading reflects the absolute value of the probe beam intensity at the measuring moment. The value \(\Delta T\) was measured by the LIA's with time constant 0.3 sec. The pump beam was turned on several seconds before the measurement, to give enough waiting period for the LIA's. But, if the value \(-\Delta T/T\) decays very much after the initial rise in shorter time scale than a few seconds, the peak value cannot be recorded by the LIA's. Only from the second measurement after turning on the pump beam, the reading of LIA's more or less reflects correct magnitude of \(-\Delta T/T\).

From this argument and figure 72, it can be concluded that as temperature goes down the initial magnitude of \(-\Delta T/T\) becomes larger contrary to the shown results in figures 72, 73, and 74. But as shown in the figures, their decay time gets longer as temperature goes up.

5.1.4 Analysis

It has been shown that there is a hysteresis in PSPIA results of PNB in KBr pellet. The way the sample responds to optical pumping within picosecond time scale undergoes a dramatic change during several hundred seconds of optical pumping. Initially,
there is a strong PIA throughout the probe range, $1.38 - 1.58$ eV. This PIA signal rises faster than the measuring system resolution ($\sim 6$ psec). While part of the PIA signal decays rapidly within $\sim 30$ psec upon creation, the rest part decays slowly and lasts into the nsec range. But, after a few minutes of optical pumping, the overall PIA intensity is weakened and PIB peak appears at the higher energy side of the probe range. This PIB signal rising time is longer than the measuring system resolution.

**Thermal Effect**

It was mentioned in chapter IV that there may be thermal effect in mechanical chopping modulation and it will be removed by the electronic temporal hopping. When PSPIA data of PNB in KBr pellet with the two modulation methods were compared, there seemed not to be any of noticeable thermal effect in the adapted modulation frequency ($\sim 1.5$ kHz). This will be partly because of the fact that 99.98 weight% of the sample pellet is made up of KBr, acting as a heat sink.

More serious question goes to the possibility of chemical disintegration of PNB due to the optical pumping. The time averaged pump beam intensity used was $\sim 150$ W/cm$^2$ and peak intensity reached up to $\sim 0.05$ GW/cm$^2$.

There are reasons against this possibility. First, the sample was pumped at 2.1 eV, the lower slope of the bandgap. If there occurred such chemical disintegration, most probably the end product would have wider energy gap than PNB since some bonds will be disconnected. As a result, the new product would hardly absorb the pump photons and the observed strong PIB signal cannot be explained by such chemical disintegration. If such chemical disintegration occurs, it will cause only reduction of the PIA signal magnitude.
Second reason against the possibility of chemical disintegration comes from the temperature dependence. As summarized in chapter III, in LTPIA, huge PIA signal was observed in the spectral range covering the probe range used in the PSPIA measurement. In the LTPIA experiments, the PIA signal increased as the sample was cooled down and the signal was wiped out when the sample was heated.[88, 90, 93, 99, 121] If the absorption change is due to the disintegration of chemical bonds, it should be promoted when the ambient temperature goes up.

PIA and PIB Components in PSPIA

As shown in figures 29, 30, and 40, in the probe range used in the PSPIA measurement, both of NSSPIA and LTPIA results show large PIA peaks. But in the PSPIA measurement, though initially only PIA signal is observed in the range 1.38–1.58 eV, there appears PIB at the higher energy side after a few minutes of optical pumping. From figures 66, 67, and 69, three components can be identified from the PSPIA signal.

First, there is an initial PIA peak. From figures 67, 69, and 70, its rising time is sub-ps and decay time is within ~ 30 psec. When the sample is exposed to the 2.1 eV pumping for more than ~ 20 minutes, this initial large PIA peak remains at probe energies 1.38 eV and 1.50 eV, but eventually disappears at 1.58 eV.

Second, a slow component of PIA, which lasts longer than ~ 400 psec, is shown. Initially this long tail appears in all of the probe energy range. After ~ 10 minutes of optical pumping with power of ~ 10 mW, the long PIA tail remains only at low energy side of the probe range.

Third, a PIB peak appears when the transmittance of the sample reaches a steady
state after a large reduction upon optical pumping repeating the LTPIA results. The PIA signal intensity gradually reduces and PIB starts to show only after $\approx +10$ psec delay time. The rising time of the PIB peak is $\approx 30$ psec, much longer than the time resolution of the measuring system and matches to the decay of the initial PIA peak. The decay time of the PIB is estimated to be in the range of $\approx 100$ nsec.

**Dynamics of Photoexcited States in PNB**

The PSPIA results should be understood in relation with the NSSPIA and LTPIA results. An explanation of the behaviors of the three components, fast and slow PIA peaks and PIB peak observed in the PSPIA measurements, is given below.

The PSPIA result shows that for a pristine sample there appears slowly decaying long PIA tail after the strong and short-lived PIA peak. After a few minutes of optical pumping, the long PIA tail is replaced by a PIB tail at high energy part of the probe range. The PIB peak in spectral domain locates at $\geq 1.58$ eV.

It was pointed out in chapter III that NSSPIA signal is mainly from those electronic states whose decay time is in $\mu$sec to msec range. As a result, it can be concluded that the appearance of the PIB in PSPIA measurement is not related to the NSSPIA signal but has a strong connection with the observed LTPIA signal.

For convenience, the NSSPIA signals are assumed due to state B and the LTPIA signals are from state C. The NSSPIA and LTPIA signals may reflect more than one species of electronic defects in each case. In the PSPIA results, a fast component is shown within $\sim 30$ psec of optical pumping. This is named as state A. State D is responsible for the appearance of PIB peak after a few minutes of optical pumping.
Figure 75: The dynamics of electronic defects in PNB.
A possible scenario is shown in figure 75. The left side of figure 75 depicts the evolution of excited states in PNB at the initial stage of optical pumping. When a photon is absorbed, it may create an excited state A. This state is very unstable and may go back to the ground state or create state B or C. State B has a µsec to msec range decay time and observed by the NSSPIA measurement. The decay time of state C is very long, if finite. When the temperature goes down, it may never decay. This electronic defect is measured by the LTPIA method. The slowly decaying PIA tail which is observed in all the probe energy range of PSPIA measurement comes from both of B and C states.

When the optical pumping is continued, the number density of state C reaches the maximum at some parts of sample. There, when a state A tries to decay into state C, a conflict between a pre-existing C state and the new excitation may occur. As a result, the state C is deformed to state D and it no more has a same electronic structure as state C. This causes PIB, since the PSPIA measurement sees only the change of the transmission compared to the transmission a few msec ago (due to the time modulation explained in chapter IV) and obviously the number of state C, which is responsible for the strong PIA signal in LTPIA, is reduced. The state D has finite decay time of ~ 100 nsec and possibly goes back to state C.

Due to the bulkiness effect discussed in chapter III and possibly by the fact that the pump beam intensity slightly depends on the position (Gaussian distribution) at the probing area, the sample saturates unevenly. While the state D starts to be created at the saturated portion, still some parts of the sample have room for state C. Hence, while overall saturation is increasing, the long-lived PIA tail slowly decreases.

The right side of figure 75 shows the situation when the population of state C is saturated. Upon optical pumping, still state A is created and it may decay through
state B. At the same time, the interaction between state A and pre-existing state C may create state D. This interaction picture is supported by two observations. First, state D is observed only after creation of extensive amount of state C. Second, the decay time of state A and the rising time of state D match, resulting \( \sim 30 \) psec delay of PIB peak compared to the initial PIA peak in PSPIA result.

It has been reported that the time scale of the geometrical settlement due to photo-excitation of \textit{trans}-4,4'–diphenylstilbene in solvent, which has benzene rings, is in the order of a few 10’s of psec.[152] From this, the slow rising of the PIB peak or the state D can be explained by ring-torsion and consequently inevitable interchain interaction. Furthermore, from figure 75, the creation of both of B and C states may include ring-torsion, though the geometrical configurations of the three states will be necessarily different.

State C is responsible for the LTPIA peaks shown in figure 40. There are two PIA peaks at 1.5 and 1.8 eV below the Peierls' gap. From the observations of Coplin \textit{et al.}[121] and the calculation of Su and Epstein[139], the 1.8 eV peak was assigned as a neutral soliton. When figures 42 and 73 are compared, it is evident that the relatively very intense optical pumping in PSPIA measurement caused rapid creation of concentrated state, or neutral soliton lattice. Since it seems that the peak of the PIB in PSPIA measurement lies near to 1.8 eV, it is probable that state D is due to the portion of state C which causes the 1.8 eV PIA peak in LTPIA measurement or the neutral soliton lattice.

The reason that all the decay times slow down in polyaniline compared to other conducting polymers like polyacetylene and polythiophene can be at least partly found from the consideration of the ring-torsion and the interchain interaction. Though it was theoretically demonstrated that PNB can accommodate solitons like \textit{trans}-
polyacetylene,[139] while the solitons in trans-polyacetylene can easily move by the translation of carbon atoms in the order of $\sim 0.03 \, \text{Å}$, to move the solitons in PNB, not only the translations of many carbons and nitrogen atoms but also the rotation of phenyl rings are needed. Mere translation of carbon atoms in polyacetylene may have little effect from the interchain interaction. But the ring rotation in solid PNB is inevitably interfered by the interchain interaction. This is not limited to solitons but all other electronic excitations undergo same situation in PNB, since all electronic defects in PNB are involved with both of bond length change and ring torsion.[139] While the basic translation unit of electronic defects in trans-polyacetylene is two (CH) units, in PNB, it takes two ($\text{C}_8\text{H}_6-\text{N}$) units. The relatively low $\chi^{(3)}$ values of PNB even compared to EB shown in chapter III may be another evidence of the slower motion of the electronic defects in PNB.

5.1.5 Emeraldine Base

Figure 76 shows the PSPIA result of emeraldine base (EB) with pump at 2.11 eV and probe at 1.5, 2.1, and 2.9 eV.[153] While the PIB at 2.1 eV and PIA at 2.9 eV show long tail, the PIA at 1.5 eV has short decay time similar to the PNB result shown in figure 67. The PIB peak at 2.0 eV can be fit to $\sim t^{-0.11}$ in the delay time range of 40 psec to 4 nsec.[154] The result was independent of temperature, from 40 to 300 K.[154] At probe 2.9 eV, while the solid film shows long-lived PIA tail, EB solution in NMP shows very fast decay.[153] This suggests the importance of ring-torsion and the interchain interaction in the decay time of electronic defects in polyaniline.
Figure 76: EB PSPIA. Pump at 2.1 eV and probe at 2.9 eV (solid line, PIA), 2.0 eV (broken line, PIB), and 1.5 eV (dot line, PIA). The 2.9 eV curve was kindly provided by L.B. Lin and 2.0 eV curve is after [154]. From [153].
5.2 Photoluminescence

Photoluminescence (PL) of polyaniline was first reported by Son et al.[155] A polyaniline film was electrochemically deposited to a flat Pt plate electrode and optically pumped at 4.2 eV (295 nm), while varying the potential relative to the Ag/AgCl standard cell electrode (SCE) in 1 M HCl. When fully reduced (−200 mV versus SCE), the luminescence was most intense and has a single peak at 2.85 eV (455 nm). As the polyaniline film was oxidized, the PL intensity was weakened and the peak shifted to higher energy, to give 2.85 eV (435 nm) at 100 mV versus SCE. The shift of the peak was attributed to the increase of the energy gap due to the shortening of undoped chain lengths.[155]

The PL spectra of polyaniline solution in NMP was measured at room temperature, as shown in figure 77.[156] The oxidation level was determined by monitoring the 1.94 eV (637 nm) absorption peak.[84] The PL shape was independent of the excitation energy[156, 157] and the peak energy 2.95 eV (420 nm) did not change while oxidation was varied. The absorption peak of LEB in NMP is at 3.61 eV (343 nm). The PL became undetectably weak when LEB was oxidized to EB.[84, 156]

The PL of leucoemeraldine base (LEB) oligomer was measured. The NMP solution of N, N' diphenyl-1,4-phenylene diamine, which has three phenyl rings and two nitrogen atoms, has absorption peak at 4.01 eV (309 nm) and PL peak at 3.0 eV (412 nm).[156] Aniline, the monomer with one phenyl ring and one nitrogen atom, shows absorption peak at 4.31 eV (288 nm) and PL peak at 3.68 eV (337 nm), in ethanol solution. The decay time under the assumption of single exponential decay is 3.1 nsec in room temperature.[151] When cyclohexane was used as a solvent, the aniline PL peak was at 3.91 eV (317 nm) and decay time was 3.4 nsec, though the absorption
Figure 77: The PL spectra of polyaniline in NMP as a function of oxidation state \((1-y)\). From [156].
The temperature dependence of the LEB in NMP decay time \( \tau \) was measured, as shown in figure 78. The instrumentation is explained in chapter IV. The decay time in room temperature was \( \sim 1.5 \) nsec, appreciably shorter than that of aniline solution. This can be explained by the presence of residual quinoid rings present in most LEB.\[99, 118\] It is well known that the quinoid ring is a strong quencher of radiative decay. As evident from figure 15, quinoid rings absorb the LEB PL spectrum.

In the measurement of the temperature dependence of the decay time, two different optical low pass filter was used between the sample and photomultiplier tube (PMT). While one passes the whole range of the PL spectrum, the other blocks PL photons whose energy is larger than 2.95 eV (420 nm), the peak energy of the PL. As shown in figure 78, no temporal behavior deviation was found between the two spectral range, implying that only one PL mechanism is involved.\[158\]

The decay time was reduced, as the temperature increased. This corresponded to the observation that the PL intensity decreased as the temperature increased.\[156\] Figure 79 is the Arrhenius plot fitting of the decay time, to get the Arrhenius activation energy.\[159\] The Arrhenius equation can be written as

\[
\ln \frac{1}{\tau} = C - \frac{\Delta}{k_B T}
\]

where \( C \) is a constant, \( \Delta \) is the Arrhenius activation energy, and \( k_B \) is the Boltzmann constant. The activation energy was in the range of 0.084 to 0.12 eV, depending upon the choice of the slope. This is in the range of the backbone vibrational energy, suggesting the backbone vibration is important in this PL decay mechanism.

In LEB, the PL emission seems to originate from the geminate decay of a polaron-
Figure 78: The temperature dependence of PL decay time for LEB in NMP solution. Under the assumption of single exponential decay, the decay time was obtained. From [153].
Figure 79: An Arrhenius plot fitting all $\tau$ data points gives an activation energy $\Delta = 0.084 \text{ eV}$ (broken line); exclusion of the lowest temperature data points gives $\Delta = 0.12 \text{ eV}$ (solid line). From [153].
The PL emission spectrum of LEB in NMP, like that of aniline in solution, has only one peak and does not show any vibrational structure, unlike the PL emission spectra of, for example, polythiophene (PT) or polyphenylenevinylene (PPV). The similarity between the PL of aniline and LEB strongly supports the confinement of the excitation to a single ring and adjacent nitrogen unit. The activation energy for the decay time constant of the PL of LEB in NMP is approximately ten times greater than the estimated ring rotational energy barrier in LEB and is in the range of backbone vibrational energies, suggesting that intra-ring vibrations play an important role in the PL emission.

The fact that all the PL spectra reported above had identical single peak form except for the shift due to the energy gap change strongly suggests that a polaron-exciton confined in the basic unit including a ring and adjacent nitrogen atoms is responsible for the PL, whose decay is determined by backbone vibrations.
CHAPTER VI

Conclusions

Among the conducting polymers, polyaniline has very distinctive properties. Its backbone is made up of alternating benzene rings and nitrogens. There are three oxidation states in polyaniline. The fully reduced state leucoemeraldine base (LEB) shows photoluminescence (PL).\[155, 156] The PL intensity reduces as the number of quinoid rings increases and in the half oxidized emeraldine base (EB), PL is hardly measured. Comparison of figures 15 and 77 shows the PL emission will be reabsorbed when oxidation occurs.

EB can be reversibly protonated by acids including HCl to become a highly conducting state emeraldine salt (ES). Since it does not involve oxidation or reduction (p-doping or n-doping), optical pumping is not direct simulation of doping process, unlike all other known conducting polymers.

The fully oxidized state pernigraniline base (PNB) is the first known conjugated polymer which can accommodate solitons, after \textit{trans}-polyacetylene. The quinoid ring and benzenoid ring connecting nitrogen atoms are equivalent to the double and single bonds of \textit{trans}-polyacetylene.[11, 139] Adding to the bond-length alternation, PNB has another important order parameter, ring-torsion.[131] In PNB, the two order
parameters are strongly correlated.\[139\] Ring-torsion seems to play a very important role in the evolution of electronic defects in all oxidation states of polyaniline.

Below the Peierls’ gap, PNB has near-steady-state photoinduced absorption (NSSPIA) peaks and they are interpreted as polarons and charged solitons, due to the involvement of infrared active mode (IRAV).\[97, 119\] Long-time photoinduced absorption (LTPIA) shows 1.5 eV and 1.8 eV photoinduced absorption (PIA) peaks below the Peierl’s gap. The 1.8 eV peak is believed due to neutral solitons.\[121, 139\] Interestingly, the doping-induced absorption resembles the NSSPIA results, not LTPIA results. NSSPIA and LTPIA measurements of dilute polyaniline solution may verify the role of interchain interaction.

In the picosecond photoinduced absorption (PSPIA) measurement of PNB with pump at 2.1 eV and probe range from 1.38 eV to 1.58 eV, a hysteresis was found. Initially, only PIA was observed. After a few minutes of optical pumping, there appeared a photoinduced bleaching (PIB) at the higher energy side of the probe range. While the PIA peak rose within the resolution of the measuring system, $\sim 6$ psec, the PIB peak rose in $\sim 20$ psec and the peak was $\sim 30$ psec delayed compared to the PIA peak. From the comparison of the results of NSSPIA and LTPIA, it was strongly suggested that the PIB in PSPIA comes from the interaction of the neutral solitons which are responsible for the 1.8 eV PIA peak in LTPIA. The excited states which create the NSSPIA are not directly involved in the process.

Due to the relatively narrow probe range of the PSPIA measurement whose results are reported here, the electronic structures of fast decaying electronic states remain unclear. An effort is being made to widen the range. Since the PSPIA signal shows very large hysteresis, instead of one color pump and one color probe method, one color pump and white light probe method is strongly recommended.
The PSPIA of EB was studied. With 2.1 eV pumping, a PIA peak was observed at 1.5 eV with decay time ~ 50 psec. The relatively fast decay compared to the results at probe energies 2.0 eV and 2.9 eV may imply a hysteresis similar to the one shown in PNB.

The PL decay time of LEB was measured as a function of temperature. When temperature was increased from ~ 290 to ~ 370 K, the decay time decreased from ~ 1.5 nsec to ~ 0.7 nsec. The Arrhenius plot gave ~ 0.1 eV activation energy, which is in the range of carbon-carbon backbone vibrational energy, suggesting the importance of backbone vibration in the PL decay mechanism.
Appendix A

KK.DMO

This software is for the picosecond photoinduced absorption and written in ASYST version 2.0.

Program to run the picosecond photoinduced absorption experiment

Small portion of this program is a modification of example programs supplied by the S/W and H/W companies.

Program name: KK.DMO
Written by: Kwangjoon Kim
Date: 08/14/89
Last revision: 08/21/92

KK1, KK2, and KK3.DMO are originally just one program. It is divided to three only because it is too large to be handled by the editing software editor sov in ASYST.

When KK1.DMO is loaded, other two are automatically loaded.
\ YOU CAN USE CTRL-BREAK TO GO BACK TO OK PROMPT OF ASYST.
ECHO.OFF \ TO SPEED UP, NO DISPLAY ON SCREEN, WHEN LOADED.
\ MODULE TO INITIALIZE GPIB
\ : GPIB.INIT
    ERROR.TRACE.ON
    BUS.INIT
    SENDINTERFACE.CLEAR
    REMOTE.ENABLE.ON

" 8 GPIB.DEVICE STEPPERS " "EXEC
10 EOS.CHARACTER
EOS.ON
1000 TIMEOUT

" 10 GPIB.DEVICE LOCKIN10 " "EXEC
13 EOS.CHARACTER
EOS.ON

" 11 GPIB.DEVICE LOCKIN11 " "EXEC
13 EOS.CHARACTER
EOS.ON

; INITIALIZE GPIB

GPIB.INIT

\ MODULE TO INITIALIZE STEPPER8
STEPPER8.INIT

STEPPER8

" Y.E.Z.E." GPIB.WRITE \ TURN OFF Y AND Z MOTORS
" X.D.M-129000.G.J170.E." \ TURN ON, MOVE TO THE NEAREST PT
GPIB.WRITE \ TURN OFF X MOTOR

INITIALIZATION OF STEPPER8

STEPPER8.INIT

MODULE TO INITIALIZE LOCKIN10

LOCKIN10.INIT

ME TALKER

" LOCKIN10 LISTENER " "EXEC \ LOCKIN10 NOT DEFINED YET
" ASM " \ AUTO-MEASURE
TALK
" XTC 7 " \ TIME CONST. = 3 SEC
TALK
" ADCAL " \ A/D CONVERTER CALIBRATION
TALK
UNTALK UNLISTEN

MAKE WINDOWS AND VUPORTS

2 14 17 66 WINDOW {MAIN.DISH}

1 1 25 16 WINDOW {SIDE.DISH}
VUPORT VU.TOP
0.25 0.685 VUPORT.ORIG
0.75 0.315 VUPORT.SIZE

VUPORT VU.MIDDLE
0.25 0.370 VUPORT.ORIG
0.75 0.315 VUPORT.SIZE

VUPORT VU.BOTTOM
0.25 0.055 VUPORT.ORIG
0.75 0.315 VUPORT.SIZE

VUPORT VU.FOR.LABELS
0 0 VUPORT.ORIG
1 1 VUPORT.SIZE

\ MODULE FOR LABELS AND LINEAR/SEMILOG GRAPHICS \ 
DP.INTEGER SCALAR UNIT.STEP
INTEGER SCALAR LINEARO.SEMILOG1
INTEGER SCALAR TRANSO.REFLEC1
: WRITE.LABELS.ALL

LINEARO.SEMILOG1 1 = \ 0:LINEAR 1:SEMilog
IF
   HORIZONTAL LOGARITHMIC
ELSE
   HORIZONTAL LINEAR
THEN

NORMAL.COORDS
UNIT_STEP 0 =
IF
" TIME PASSED (SEC) "
ELSE
" RELATIVE TIME DELAY (pS) "
THEN

LABEL

TRANSO.REFLEC1 1 =
IF
.05 .1 POSITION 90 CHAR.DIR 90
LABEL.DIR " -Delta.R/R " LABEL
.05 .42 POSITION 90 CHAR.DIR 90
LABEL.DIR " Reflec " LABEL
.05 .74 POSITION 90 CHAR.DIR 90
LABEL.DIR " Delta.R " LABEL
ELSE
.05 .1 POSITION 90 CHAR.DIR 90
LABEL.DIR " -Delta.T/T " LABEL
.05 .42 POSITION 90 CHAR.DIR 90
LABEL.DIR " Trans " LABEL
.05 .74 POSITION 90 CHAR.DIR 90
LABEL.DIR " Delta.T " LABEL
THEN

\ \\ MODULE TO POLL THE STATUS OF LOCKIN
\ INTEGER SCALAR S.POLL
INTEGER DIM[ 8 ] ARRAY S.POLL.BIT
: SER.POL
  255 SERIAL.POLL
  DUP S.POLL :=
  #>MASK
  ?DUP 128, AND MASK># S.POLL.BIT [ 8 ] :=
  ?DUP 64, AND MASK># S.POLL.BIT [ 7 ] :=
  ?DUP 16, AND MASK># S.POLL.BIT [ 5 ] :=
  ?DUP 8, AND MASK># S.POLL.BIT [ 4 ] :=
  ?DUP 4, AND MASK># S.POLL.BIT [ 3 ] :=
  ?DUP 2, AND MASK># S.POLL.BIT [ 2 ] :=
  1, AND MASK># S.POLL.BIT [ 1 ] :=
;
\ MODULE TO SEND COMMAND TO LOCKIN
  BEFORE EXECUTING THIS, YOU SHOULD CALL THE DEVICE NAME
  AND THE COMMAND SHOULD BE DOUBLE QUOTED.
  EXAMPLE :
  OK LOCKIN10
  OK " AS " \ AUTO-SENSITIVITY
  OK SEND.CMD
:
SEND.CMD
BEGIN
  SER.POL \ CHECK WHETHER
  S.POLL.BIT [ 1 ] #>MASK \ LOCKIN10 IS READY
UNTIL
  GPIB.WRITE
MODULE TO GET A NUMERICAL RESPONSE

75 STRING RESPONSE
: GET.RSP
BEGIN
SER.POL
S.POLL.BIT [ 8 ] ->MASK \ OUTPUT READY?
IF
RESPONSE GPIB.READ
13 RESPONSE \ CONVERT RESPONSE
"NUMBER \ TO NUMBER IN STACK
IF NOP THEN \ THROW OUT A LOGICAL VALUE
"DROP \ THROW OUT AFTER STRING
THEN
S.POLL.BIT [ 1 ] ->MASK \ COMMAND DONE?
UNTIL
;

MODULE TO READ A SUM.DELTA.T FROM LOCKIN

REAL SCALAR SUM.DELTA.T
: READ.A.SUM.DELTA.T
" OUT " \ ASK ONE SUM.DELTA.T
SEND.CMD
GET.RSP \ READ ONE SUM.DELTA.T
SUM.DELTA.T + SUM.DELTA.T := \ MAKE A SUM OF DELTA T
;

MODULE TO READ A SUM.T FROM LOCKIN10

REAL SCALAR SUM.T
: READ.A.SUM.T
 " ADC 1 " \ ASK ONE SUM.T
 SEND.CMD
 GET.RSP \ READ ONE SUM.T
 SUM.T + SUM.T := \ MAKE A SUM OF T
 ;

 \ MODULE TO GET THE SENSITIVITY
 \ INTEGER SCALAR SEN.CODE

 REAL DIM[ 16 ] ARRAY SENSITIVITY

 1. SENSITIVITY [ 1 ] := \ GIVE THE VALUES OF
 3. SENSITIVITY [ 2 ] := \ SENSITIVITY IN THE
 10. SENSITIVITY [ 3 ] := \ UNIT OF 10^-7 VOLT
 30. SENSITIVITY [ 4 ] :=
 100. SENSITIVITY [ 5 ] :=

 300. SENSITIVITY [ 6 ] :=
 1000. SENSITIVITY [ 7 ] :=
 3000. SENSITIVITY [ 8 ] :=
 10000. SENSITIVITY [ 9 ] :=
 30000. SENSITIVITY [ 10 ] :=

 100000. SENSITIVITY [ 11 ] :=
 300000. SENSITIVITY [ 12 ] :=
 1000000. SENSITIVITY [ 13 ] :=
 3000000. SENSITIVITY [ 14 ] :=
 10000000. SENSITIVITY [ 15 ] :=
 30000000. SENSITIVITY [ 16 ] :=

 : GET.SENSITIVITY
 " SEN " \ ASK SEN.CODE
 SEND.CMD
GET.RSP \ READ SEN.CODE
1 + SEN.CODE := \ ADDED 1 SINCE CODE STARTS FROM 0

\ MODULE TO GET THE MAXIMUM POSITIVE OUTPUT
\ : MAXIMUM.PHASE
    " ASM " \ AUTO PHASE
    SEND.CMD

\ MODULE TO DO THE DO LOOP TO AVERAGE
\
DP.INTEGER SCALAR NLP \ HOW MANY TIMES GET.A.DATAPORT?
: DO.LOOP.OF.AVERAGE
  0. SUM.DELTA.T := \ INITIALIZATION
  0. SUM.T := \ INITIALIZATION
  NLP 0 \ DO LOOP NLP TIMES
  DO
      READ.A.SUM.DELTA.T \ GET SUM.DELTA.T
      READ.A.SUM.T \ GET SUM.T
  LOOP

\ MODULE TO GET A DELTA.T AFTER THE AVERAGE PROCEDURE
\ FROM LOCKINIO
\ REAL DIM[ 1000 ] ARRAY DELTA.T10
DP.INTEGER SCALAR INDX \ POSITION INDEX OF RETROMIRROR
: GET.DELTA.T10
    GET.SENSITIVITY \ GET THE SENSITIVITY RANGE
    SUM.DELTA.T NLP / \ GET THE AVERAGE SINCE LOOPED NLP TIMES
10000. / \ NORMALIZE TO 1
SENSITIVITY [ SEN.CODE ] * \ NOW IN THE UNIT OF $10^{-7}$ VOLT
2.2 * \ TO GET THE PEAK-PEAK SIZE
DELTA.T10 [ INDX ] := \ INDX IS INDEX FOR
\ TRANSLATION OF RETROMIRROR

\ MODULE TO GET A TRANS AFTER THE AVERAGE PROCEDURE FROM LOCKIN10
\ REAL DIM[ 1000 ] ARRAY TRANS10
: GET.TRANS10
  SUM.T NLP / \ GET THE AVERAGE SINCE LOOPED NLP TIMES
  -1. * \ TO MAKE THE SIGN POSITIVE
  TRANS10 [ INDX ] := \ IN MILLIVOLT AT THE
  \ INDX PSTION OF RETROMRROR

\ MODULE TO GET A MINUS.DELTA.T.OVER.T FROM LOCKIN10
\ REAL DIM[ 1000 ] ARRAY MINUS.DELTA.T.OVER.T10
: GET.ONE.DATAP0INT10
  LOCKIN10 \ TALK TO LOCKIN10
  DD.LOOP.OF.AVERAGE
  GET.DELTA.T10
  GET.TRANS10
  -1. DELTA.T10 [ INDX ] * TRANS10 [ INDX ] /
  MINUS.DELTA.T.OVER.T10 [ INDX ] :=

\ MODULE TO GET A DELTA.T AFTER THE AVERAGE PROCEDURE FROM LOCKIN11
REAL DIM[ 1000 ] ARRAY DELTA.T11
:  GET.DELTA.T11
    GET.SENSITIVITY \ GET THE SENSITIVITY RANGE
    SUM.DELTA.T NLP / \ GET THE AVERAGE SINCE LOOPED NLP TIMES
    10000. / \ NORMALIZE TO 1
    SENSITIVITY [ SEN.CODE ] * \ NOW IN THE UNIT OF 10^-7 VOLT
    2.2 * \ TO GET THE PEAK-PEAK SIZE
    DELTA.T11 [ INDX ] := \ INDX IS INDEX FOR
    \ TRANSLATION OF RETROMIRROR

;\
\ MODULE TO GET A TRANS AFTER THE AVERAGE PROCEDURE
\ FROM LOCKIN11
\ REAL DIM[ 1000 ] ARRAY TRANS11
:  GET.TRANS11
    SUM.T NLP / \ GET THE AVERAGE SINCE LOOPED NLP TIMES
    -1. * \ TO MAKE THE SIGN POSITIVE
    TRANS11 [ INDX ] := \ IN MILLIVOLT AT THE INDX
    \ PSTION OF RETROMIRROR

;\
\ MODULE TO GET A MINUS.DELTA.T.OVER.T FROM LOCKIN11
\ REAL DIM[ 1000 ] ARRAY MINUS.DELTA.T.OVER.T11
:  GET.ONE.DATA.POINT11
    LOCKIN11 \ TALK TO LOCKIN11
    DO.LOOP.OF.AVERAGE
    GET.DELTA.T11
    GET.TRANS11
    -1. DELTA.T11 [ INDX ] *
    TRANS11 [ INDX ] /
MINUS.DELTA.T.\over.T11 [ INDX ] :=
;
\ MODULE TO MOVE STEPPER8
\\
DP.INTEGER SCALAR INTERVAL \ DELAY BTWN TWO MEASUREMENTS
DP.INTEGER SCALAR SUM.INTERVAL \ DISTANCE FROM THE ORIGIN
100 STRING MOVING.COMMAND
: CHANGE.DELAY
" X.D.M"
INTERVAL
"." \ NUMBER TO STRING
"CAT \ MAKE A COMPOSITE STRING
".G.E."
"CAT \ MAKE A COMPOSITE STRING
MOVING.COMMAND ":=
STEPPER8 \ TALK TO STEPPER8
MOVING.COMMAND GPIB.WRITE
;
\ MODULE TO CALCULATE TIME.DELAY
\\
REAL DIM[ 1000 ] ARRAY TIME.DELAY \ TIME DELAY BTWN PUMP AND PROBE
: CALCULATE.TIME.DELAY
SUM.INTERVAL \ SUM OF INTERVAL, I.E.
\ DISTANCE FROM THE ORIGIN
0.04233333 * \ TIME DELAY PER UNIT MOVE, IN PICOSECOND
1. + \ TO DRAW THE SEMILOG GRAPH,
TIME.DELAY [ INDX ] := \ TIME.DELAY STARTS AT 1.pS
;
DP.REAL SCALAR INITIAL.TIME
DP.REAL SCALAR PRESENT.TIME
12 STRING NOW :

CALCULATE.TIME.PASSED
"TIME NOW " :=

NOW 1 2 "SUB 2 "NUMBER 60 * \ HOURS
NOW 4 2 "SUB 2 "NUMBER + 60 * \ MINUTES
NOW 7 6 "SUB 2 "NUMBER + \ SECONDS
PRESENT.TIME :=

STACK.CLEAR \ TO PREVENT STACK SATURATION

INDX 1 =
IF

PRESENT.TIME INITIAL.TIME :=

THEN

PRESENT.TIME INITIAL.TIME −
TIME.DELAY [ INDX ] :=

TIME.DELAY [ INDX ] 0 <
IF

TIME.DELAY [ INDX ]
24 60 60 * * +

TIME.DELAY [ INDX ] :=

THEN

; \ MODULE TO DRAW DELTA.T \ : DRAW.DELTA.T
TIME.DELAY SUB[ 1 , INDX ]
DELTA.T10 SUB[ 1 , INDX ]
XY.AUTO.PLOT
\ MODULE TO DRAW TRANS
\ : DRAW.TRANS
  \ TIME.DELAY \ SUB[ 1 , INDX ]
  \ TRANS10 \ SUB[ 1 , INDX ]
  \ XY.AUTO.PLOT
;
\ MODULE TO DRAW MINUS.DELTA.T.OVER.T
\ : DRAW.MINUS.DELTA.T.OVER.T
  \ TIME.DELAY \ SUB[ 1 , INDX ]
  \ MINUS.DELTA.T.OVER.T10 \ SUB[ 1 , INDX ]
  \ XY.AUTO.PLOT
;
\ MODULE TO DRAW ALL SIMULTANEOUSLY
\ : DRAW.ALL

  \ VU.TOP
  \ 11 AXIS.COLOR \ LIGHT CYAN
  \ 13 COLOR \ LIGHT MAGNETA

  \ DRAW.DELTA.T

  \ VU.MIDDLE
  \ 13 COLOR \ LIGHT MAGNETA

  \ DRAW.TRANS

  \ VU.BOTTOM
13 COLOR \ LIGHT MAGNETA
DRAW.MINUS.DELTA.T.OVER.T

CURSOR.OFF
;
\ MODULE TO INITIALIZE NUMBERS
\
DP.INTEGER SCALAR TOTAL.DATA.NUMBER
DP.INTEGER SCALAR INIT.BIAS
: INITIALIZE.NUMBERS
  1 INDEX :=
UNIT.STEP 0 < IF
UNIT.STEP ABS TOTAL.DATA.NUMBER 1 \ BY GIVING NEGATIVE
- * SUM.INTERVAL := \ UNIT.STEP,
ELSE \ THE MEASUREMENT
  0 SUM.INTERVAL := \ IS DONE WITH DECREASING DELAY TIME
THEN

INIT.BIAS SUM.INTERVAL + \ THIS INITIAL VALUE
INTERVAL := \ OF INTERVAL IS
  0 TIME_DELAY := \ ONLY FOR INITIAL
  0 DELTA.T10 := \ CHANGE.DELAY
  0 TRANS10 :=
  0 MINUS.DELTA.T.OVER.T10 :=
  0 DELTA.T11 :=
  0 TRANS11 :=
  0 MINUS.DELTA.T.OVER.T11 :=

;\ MODULE TO GET THE TIME CONSTANT
\ INTEGER SCALAR TIME.CODE
DP.INTEGER SCALAR TIME.CONST.TIMES.FIVE \ IN mSEC UNIT
DP.INTEGER DIM[ 14 ] ARRAY TIME.CONST \ IN mSEC UNIT
    1 TIME.CONST [ 1 ] :=
    3 TIME.CONST [ 2 ] :=
    10 TIME.CONST [ 3 ] :=
    30 TIME.CONST [ 4 ] :=
   100 TIME.CONST [ 5 ] :=
   300 TIME.CONST [ 6 ] :=
1000 TIME.CONST [ 7 ] :=
3000 TIME.CONST [ 8 ] :=
10000 TIME.CONST [ 9 ] :=
30000 TIME.CONST [ 10 ] :=
100000 TIME.CONST [ 11 ] :=
300000 TIME.CONST [ 12 ] :=
1000000 TIME.CONST [ 13 ] :=
3000000 TIME.CONST [ 14 ] :=

: GET.TIME.CONST
  LOCKIN10 \ LOCKIN10 AND 11 ALWAYS HAVE SAME TIME.CONST
" XTC " \ ASK THE TIME CONSTANT
SEND.CMD GET.RSP
  1 + TIME.CODE := \ ADDED 1 SINCE CODE STARTS FROM 0
  TIME.CONST [ TIME.CODE ] 5 *
  TIME.CONST.TIMES.FIVE :=
;
DP.INTEGER SCALAR MOVING.TIME \ TIME REQUIRED TO MOVE RETROPRISM
INTEGER SCALAR CH.NUMBER \ NUMBER OF LOCKIN USED. MAX. 2
: GET.DATA.TIME
  GET.ONE.DATA.POINT10


```
CH.NUMBER 2 =
IF
  GET.ONE.DATA.POINT1
THEN
UNIT.STEP 0 =
IF
  CALCULATE.TIME.PASSED
ELSE
  CALCULATE.TIME.DELAY
THEN
;

RED MIX FOREGROUND INTEN.ON
CR ." NOW KK2.DMO IS BEING LOADED."
LOAD KK2.DMO

\This part is KK2.DMO: This part is mainly for
\beam.profile and sample.check. Again, to activate this,
\KK1.DMO should be loaded.
\n\Written by : Kwangjoon Kim
\Last revision : 07/15/92
\n\Module to measure at origin

: INITIAL.MEASURE
  CHANGE.DELAY \ Initial move of init.bias step
  INTERVAL ABS MOVING.TIME :=
```
MOVING.TIME
TIME.CONST.TIMES.FIVE \ TIME CONST X 5 BEFORE MEASRMNT
+ MSEC.DELAY
GET.DATA.TIME
5000 MSEC.DELAY \ DELAY TIME AS IF DRAWING
; \ GRAPHS ON SCREEN
/
\ MODULE TO MOVE, MEASURE, AND DRAW
\ REAL SCALAR TIME.INTERVAL
: MOVE.MEASURE.DRAW
CHANGE.DELAY
INDX 1 > \ WHEN WE GOT
IF \ TWO OR MORE POINTS,
DRAW.ALL \ DRAW INTERMEDIATE RESULT
THEN

UNIT.STEP 0 =
IF
TIME.INTERVAL 5. - 1000. *
MSEC.DELAY
ELSE
INTERVAL ABS 2. \ MOVING.TIME :=
MOVING.TIME
TIME.CONST.TIMES.FIVE + \ TIME CONST X 5 BEFORE MEASRMNT
MSEC.DELAY \ DELAY TO GIVE LOCKIN ENOUGH TIME
THEN
INDX 1 + INDX := \ INCREASE THE INDX BY ONE
GET.DATA.TIME
;
\ MODULE TO CHECK THE VALIDITY OF NUMBER INPUT
INTEGER SCALAR FIXEDO.FREE1
: CHECK.INPUT.NUMBER
BEGIN
  ?REL.COL ?REL.ROW \ SAVE CLO AND ROW IN CASE OF ERROR
  #INPUT \ GET NUMBER
  NOT \ VALID?
  WHILE
  BELL \ NOT A NUMBER
  ?REL.COL 3 PICK - 1 + \ GET CURRENT COL
  3 PICK 3 PICK GOTO.XY \ RETURN TO ORIGINAL POSITION
REPEAT
UNROT 2 *DROP \ GOT A GOOD NUMBER, SO DROP PSTION INFO
;

MODULE TO CHECK THE VALIDITY OF CHARACTER INPUT
:
: CHECK.INPUT.WORD
BEGIN
  "INPUT \ GET A STRING
  "LEN 0 = \ LENGTH = 0 ?
  WHILE
  BELL "DROP
REPEAT
;

MODULE TO GET THE SAMPLE AND DATA FILE NAME
/
70 STRING SAMPLE.NAME
70 STRING DATA.FILE.NAME
50 STRING PROCEDURE.NAME
10 STRING PUMP.POWER \ USED CHARACTERS INSTEAD OF NUMBERS
10 STRING PROBE.POWER \ SINCE SHOULD BE SKIPPED SOMETIMES
10 STRING DIVIDE.N \ AND WILL NOT BE USED IN CALCULATIONS
INTEGER SCALAR MECHAO.ELECT1
: ASK.NAME

CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." YOU HAVE CHOSEN "
14 FOREGROUND \ YELLOW
PROCEDURE.NAME "TYPE

CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." ENTER THE SAMPLE NAME : 
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
SAMPLE.NAME ":= 

GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." ENTER THE DATA FILE NAME : 
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
DATA.FILE.NAME ":= 

GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." 0 FOR MECHANICAL, 1 FOR ELECTRONIC CHOPPING : 
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
MECHAO.ELECT1 := 

GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." PUMP.POWER IN mW? "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
PUMP.POWER ":=

GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." PROBE.POWER IN mW? "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
PROBE.POWER ":=

GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." DIVIDE.N? "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
DIVIDE.N ":=

; \
\ \ MODULE TO GET INPUTS FOR FREE.CONST.STEP
\ 
REAL SCALAR PS.UNIT.STEP
REAL SCALAR PS.INIT.BIAS
REAL SCALAR BASE
: FREE.CONST.NUMBERS
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." UNIT.STEP? (pS) "
CR ." (NEGATIVE FOR REVERSE DIRECTION) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
PS.UNIT.STEP :=
PS.UNIT.STEP 0.04233333 /
UNIT.STEP :=
CR
UNIT.STEP 0 =
IF
  14 FOREGROUND \ YELLOW
CR ." YOU ARE MEASURING AT A FIXED DELAY. "
GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." MEASUREMENT TIME INTERVAL? (LONGER THAN "
GET.TIME.CONST
TIME.CONST.TIMES.FIVE 1000. / 5. + . \ DRAWING TIME ." SEC) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
TIME.INTERVAL :=
THEN
  CR GREEN BLUE MIX FOREGROUND INTEN.ON
UNIT.STEP 0 =
IF
   CR ." TOTAL.DATA.NUMBER? "
ELSE
   CR ." TOTAL.DATA.NUMBER? (INTEGER LESS THAN"
   128000 UNIT.STEP ABS / 2. + ." ) "
THEN
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
TOTAL.DATA.NUMBER :=
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." INIT.BIAS? (LESS THAN"
   128000 UNIT.STEP ABS TOTAL.DATA.NUMBER 1.
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
PS.INIT.BIAS :=
PS.INIT.BIAS 0.04233333 /
INIT.BIAS :=

; /
\ / MODULE TO GET INPUTS FOR FREE.EXP.STEP
\ /
: FREE.EXP.NUMBERS
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." UNIT.STEP? (pS) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
PS_UNIT_STEP :=
PS_UNIT_STEP 0.04233333 /
UNIT_STEP :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." BASE? (LARGER THAN 1.0) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
BASE :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." TOTAL.DATA.NUMBER? (INTEGER LESS THAN"
   BASE 1. -
128000. *
BASE /
UNIT.STEP /
1. +
LOG
BASE LOG /
1. + ." ) "

RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
TOTAL.DATA.NUMBER :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR." INIT.BIAS? (LESS THAN"
128000. BASE
TOTAL.DATA.NUMBER 1.
- ** 1. -
BASE 1. - / UNIT.STEP *
BASE * - 0.04233333 * ." pS) "

RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
PS.INIT.BIAS :=
PS.INIT.BIAS 0.04233333 /
INIT.BIAS :=
;
/
\ MODULE TO CALCULATE TOTAL MEASUREMENT TIME
\ DP.INTEGER SCALAR TOTAL.TIME
: CALCULATE.TOTAL.TIME
GET.TIME.CONST
LINEAR0.SEMILOG1 1 =
IF
    BASE TOTAL.DATA.NUMBER 1. \ MOVING TIME
    - ** 1. - BASE 1. - / UNIT.STEP * BASE *
ELSE
    UNIT.STEP ABS TOTAL.DATA.NUMBER *
THEN

2000. /
INIT.BIAS 1000. / +

UNIT.STEP 0 =
IF
    TIME.INTERVAL TOTAL.DATA.NUMBER * +
ELSE
    TIME.CONST.TIMES.FIVE 1000. / \ WAITING TIME
    TOTAL.DATA.NUMBER * +
    5. TOTAL.DATA.NUMBER 1. - * + \ DRAWING TIME
THEN

NLP TOTAL.DATA.NUMBER * 0.35 * CH.NUMBER * + \ MEASURING TIME
60. / \ TO CHANGE THE UNIT FROM SECONDS TO MINUTES
3. CH.NUMBER * + \ HARD COPYING AND SAVING TIME
TOTAL.TIME :=
;
/
100 STRING COMMENT10
100 STRING COMMENT11
INTEGER SCALAR HDCPO.WAIT1
INTEGER SCALAR HDCPO.SKIP1
INTEGER SCALAR TOR1.10
INTEGER SCALAR TOR1.11
; ASK.NAME.AND.NUMBERS
ASK_NAME

FIXEDO.FREE1 1 =
IF
  LINEAR0.SEMILOG1 1 =
  IF
    FREE.EXP.NUMBERS
  ELSE
    FREE.CONST.NUMBERS
  THEN
THEN

GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." HOW MANY MEASUREMENTS FOR A DATA? "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
  NLP :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." HOW MANY LOCKINS WILL YOU USE? (1 OR 2) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
CH.NUMBER :=

CH.NUMBER 1 =
IF
  CR
  GREEN BLUE MIX FOREGROUND INTEN.ON
  CR ." YOU ARE USING JUST ONE LOCKIN AMP, LOCKIN10. "
  CR CR ." 0 FOR TRANSMISSION, 1 FOR REFLECTION: "
  RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
TRANSO.REFLEC1 :=
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." COMMENT : ":
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
COMMENT10 ":=
ELSE
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." YOU ARE USING TWO LOCKINS, LOCKIN10 AND LOCKIN11."
CR CR ." YOU SHOULD USE SAME TRIGGER AND SAME TIME.CONST."
GREEN MIX FOREGROUND
CR CR ." LOCKIN10 :":
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." 0 FOR TRANSMISSION, 1 FOR REFLECTION :":
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
TOR1.10 :=
TOR1.10 TRANSO.REFLEC1 :=
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." COMMENT10 :":
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
COMMENT10 ":=
GREEN MIX FOREGROUND
CR CR ." LOCKIN11 :":
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." 0 FOR TRANSMISSION, 1 FOR REFLECTION :":
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
TOR1.11 :=
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." COMMENT11 : "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.WORD
COMMENT11 ":=
THEN

CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." TYPE 0 TO HARDCOPY THE RESULT, 1 TO DETERMINE LATER. "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
HDCPO.WAIT1 :=
CR
14 FOREGROUND \ YELLOW
CALCULATE.TOTAL.TIME
CR ." IT WILL TAKE ABOUT " TOTAL.TIME . ." MINUTES."
CR
CR ." THE MEASUREMENT STARTED... "
;
\ MODULE TO KEEP THE RECORDS
\ 50 STRING STARTING.TIME
50 STRING ENDING.TIME
REAL SCALAR FREQ :
SIDE.DISH.INGREDIENTS
GRAPHICS.DISPLAY
WRITE.LABELS.ALL
{SIDE.DISH}
GREEN MIX FOREGROUND
SCREEN.CLEAR

{BORDER}
GREEN BLUE MIX FOREGROUND INTEN.ON
CR PROCEDURE.NAME "TYPE

GREEN MIX FOREGROUND
CR ." " .DATE
CR ." FRM "

GREEN BLUE MIX FOREGROUND INTEN.ON
STARTING.TIME "TYPE
GREEN MIX FOREGROUND
CR ." TO "
GREEN BLUE MIX FOREGROUND INTEN.ON
ENDING.TIME "TYPE

GREEN MIX FOREGROUND
CR ." SAMPLE.NAME "
RED MIX FOREGROUND INTEN.ON
CR ." " SAMPLE.NAME "TYPE

GREEN MIX FOREGROUND
CR ." SAVED IN "
RED MIX FOREGROUND INTEN.ON
CR ." " DATA.FILE.NAME "TYPE

GREEN MIX FOREGROUND
CR ." P(R6G) = "
RED MIX FOREGROUND INTEN.ON
PUMP.POWER "TYPE

GREEN MIX FOREGROUND
." mW" CR ." P(S9M) = "
RED MIX FOREGROUND INTEN.ON
PROBE.POWER "TYPE

GREEN MIX FOREGROUND
." mW" CR ." DIVIDE.N = "
RED MIX FOREGROUND INTEN.ON
DIVIDE.N "TYPE

UNIT.STEP 0 =
IF
  GREEN MIX FOREGROUND
  CR ." TI="
  RED MIX FOREGROUND INTEN.ON
  TIME.INTERVAL .
  GREEN MIX FOREGROUND
  ." SEC"
ELSE
  GREEN MIX FOREGROUND
  CR ." US="
  RED MIX FOREGROUND INTEN.ON
  PS.UNIT.STEP .
  GREEN MIX FOREGROUND
  ." pS"
THEN

LINEARO.SEMILOG1 1 =
IF
  GREEN MIX FOREGROUND
CR ." BASE ="
   RED MIX FOREGROUND INTEN.ON
   BASE .
THEN

GREEN MIX FOREGROUND
CR ." DATA# ="
   RED MIX FOREGROUND INTEN.ON
   TOTAL.DATA.NUMBER .

GREEN MIX FOREGROUND
CR ." IB="
   RED MIX FOREGROUND INTEN.ON
   PS.INIT.BIAS .

GREEN MIX FOREGROUND
." pS"
   RED MIX FOREGROUND INTEN.ON
   CR NLP .

GREEN MIX FOREGROUND
." SAMPLINGS"
CR
RED MIX FOREGROUND INTEN.ON

MECHAO.ELECT1 1 =
IF
   ." E"
ELSE
   ." M"
THEN
FREQ .
GREEN MIX FOREGROUND
." Hz"

CR." TIME CONSTANT"
CR." = " TIME_CONST [ TIME_CODE ] 1000. /
RED MIX FOREGROUND INTEN.ON
.
GREEN MIX FOREGROUND
." SEC."
CR." CMNT : "
RED MIX FOREGROUND INTEN.ON
COMMENT10 "TYPE

; /
\ MODULE FOR THE STARTING INFORMATIONS
\ :
: MAIN.DISH.INGREDIENTS
  GRAPHICS.DISPLAY

{MAIN.DISH}
14 FOREGROUND \ YELLOW
SCREEN.CLEAR

{BORDER}
GREEN BLUE MIX FOREGROUND INTEN.ON
CR." I AM READY TO SERVE YOU. "
CR." PLEASE PUSH ANY OF SPECIAL FUNCTION KEYS BELOW "
CR
14 FOREGROUND
CR." MIN MAX TOTAL DATA "
GREEN MIX FOREGROUND INTEN.ON
CR." <F1> ROUGH.CONST.STEP 160 160 5120 33 "
```
CR ." <F2> FINE.CONST.STEP 10 10 500 51 "
CR ." <F3> LINEAR.STEP 10 320 5280 33 "
CR ." <F4> ROUGH.EXP.STEP 1 2048 4096 13 "
CR ." <F5> FINE.EXP.STEP 1 620 4745 48 "
CR ." <F6> FREE.CONST.STEP AS YOU WISH... "
CR ." <F7> FREE.EXP.STEP AS YOU WISH... "
CR ." <F8> BEAM.PROFILE "
CR ." <F9> SAMPLE.CHECK "

BELL
;
/
\" MODE TO CLOSE THE PREVIOUS FILE, IF OPEN.
\" SINCE THERE IS NO MESSAGE AFTER ONERR:, NO ERROR MESSAGE OR
\" INTERRUPT CAUSED WHEN NO FILE IS OPEN
\"

: CLOSE PREVIOUS FILE
   OUT> FILE CLOSE
 ONERR:
;
/
\" MODULE TO START THE MEASUREMENT PROCEDURE
\"

: START THE PROCEDURE
   CLOSE PREVIOUS FILE
   NORMAL DISPLAY
   ASK NAME AND NUMBERS
   INITIALIZE NUMBERS
   LOCKIN " FRQ " SEND CMD GET RSP 1000. /
     READ REF FREQ
   FREQ :=
   " TIME STARTING TIME " :=
   " TO BE KNOWN ENDING TIME " :=
   INITIAL MEASURE
```
\MODULE FOR THE RESULTS TO BE SAVED
\INTEGER SCALAR COUNT
: DRAW.N.WRITE
  SIDE.DISH.INGREDIENTS
  DRAW.ALL \ DRAW THE FINAL RESULT
  SCREEN.PRINT

NORMAL.DISPLAY
CR
TRANSO.REFLEC1 1 =
IF
  CR ." TIME.DELAY DELTA.R REFLEC -DELTA.R/R "
ELSE
  CR ." TIME.DELAY DELTA.T TRANS -DELTA.T/T "
THEN
CR
UNIT.STEP 0 =
IF
  ." (SEC) (10^-7 V) (10^-3 V) (10^-4) "
ELSE
  ." (pS) (10^-7 V) (10^-3 V) (10^-4) "
THEN
CR
INDX 0
DO
  I 1 + COUNT := \ COUNT = 1, 2, ..., INDX
  CR
  TIME.DELAY [ COUNT ] . ." "
  DELTA.T10 [ COUNT ] . ." "
TRANS10 [ COUNT ] . " "
MINUS.DELTA.T.OVER.T10 [ COUNT ] .
LOOP
CR
CR ." +=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+=+= "
CR CR

; /
\ MODULE TO END THE MEASUREMENT PROCEDURE AND PERMANENT RECORDS \\ :
COPY.N.SAVE
DATA.FILE.NAME DEFER> OUT>FILE \ BEGINNING OF SAVING
DRAW.N.WRITE
CH.NUMBER 2 =
IF
TOR1.11 TRANS0.REFLEC1 :=
COMMENT11 COMMENT10 " :=
DELTA.T11 DELTA.T10 :=
TRANS11 TRANS10 :=
MINUS.DELTA.T.OVER.T11 MINUS.DELTA.T.OVER.T10 :=
DRAW.N.WRITE
THEN
OUT>FILE.CLOSE
;
END.THE.PROCEDURE
"TIME ENDING.TIME ":=
STEPPER8.INIT
HDCPO.WAIT1 1 =
IF
SIDE.DISH.INGREDIENTS
DRAW.ALL
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
." DO YOU WANT HARDCOPY AND PERMANENT RECORD? "
CR
." O FOR YES, 1 FOR NO. "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
HDCPO.SKIP1 :=

HDCPO.SKIP1 O =
IF
COPY.N.SAVE
THEN
ELSE
COPY.N.SAVE
THEN
MAIN.DISH.INGREDIENTS
;

: ROUGH.CONST.STEP
" ROUGH.CONST.STEP" PROCEDURE.NAME " :=
0 LINEAR0.SEMILOG1 := \ LINEAR GRAPH
0 FIXED0.FREE1 :=
3780 UNIT.STEP := \ 160.02 pS
UNIT.STEP 0.04233333 * PS.UNIT.STEP :=
33 TOTAL.DATA.NUMBER :=
0 INIT.BIAS :=
INIT.BIAS 0.04233333 * PS.INIT.BIAS :=
START.THE.PROCEDURE
TOTAL.DATA.NUMBER 1 = 0
DO
I 1 =
IF
SIDE.DISH.INGREDIENTS

THEN
UNIT.STEP INTERVAL :=
SUM.INTERVAL INTERVAL
+ SUM.INTERVAL :=
MOVE.MEASURE.DRAW

LOOP
END.THE.PROCEDURE

FINE.CONST_STEP

"FINE_CONST_STEP" PROCEDURE.NAME " :=
O LINEARO.SEMILOG1 := \ LINEAR GRAPHICS
O FIXEDO.FREE1 :=
236 UNIT.STEP := \ 9.99067 pS
UNIT.STEP 0.04233333 * PS.UNIT.STEP :=
51 TOTAL.DATA.NUMBER :=
O INIT.BIAS :=
INIT.BIAS 0.04233333 * PS.INIT.BIAS :=
START.THE.PROCEDURE
TOTAL.DATA.NUMBER 1 - O
DO
I 1 =
IF

SIDE.DISH.INGREDIENTS

THEN
UNIT.STEP INTERVAL :=
SUM.INTERVAL INTERVAL
+ SUM.INTERVAL :=
MOVE.MEASURE.DRAW

LOOP
END.THE.PROCEDURE
: LINEAR_STEP
  " LINEAR_STEP " PROCEDURE.NAME " :=
  0 LINEAR0.SEMILOG1 := \ LINEAR GRAPHICS
  0 FIXED0.FREE1 :=
  236 UNIT_STEP := \ 9.99067 pS
  UNIT_STEP 0.04233333 * PS.UNIT_STEP :=
  33 TOTAL.DATA.NUMBER :=
  0 INIT.BIAS :=
  INIT.BIAS 0.04233333 * PS.INIT.BIAS :=
  START.THE.PROCEDURE
  TOTAL.DATA.NUMBER 1 - \ ALRDY MEASRD ONCE IN
  0 \ START.THE.PROCEDURE
  DO
    I 1 =
    IF
      SIDE.DISH.INGREDIENTS
    THEN
      INDX
      UNIT_STEP * \ 9.99066 pS UNIT
      INTERVAL :=
      SUM.INTERVAL INTERVAL + SUM.INTERVAL :=
      MOVE.MEASURE.DRAW
    LOOP
    END.THE.PROCEDURE
  ;

: ROUGH.EXP_STEP
  " ROUGH.EXP_STEP" PROCEDURE.NAME " :=
  1 LINEAR0.SEMILOG1 := \ SEMILOG GRAPHICS
0   FIXEDO.FREE1 := 
24  UNIT.STEP  := \ 1.016 pS
UNIT.STEP  0.04233333 * PS.UNIT.STEP :=
2.  BASE :=
13  TOTAL.DATA.NUMBER :=
0   INIT.BIAS :=
INIT.BIAS  0.04233333 * PS.INIT.BIAS :=
START.THE.PROCEDURE
TOTAL.DATA.NUMBER  1 - 0
DO
   I 1 =
   IF
      SIDE.DISH.INGREDIENTS
   THEN
      BASE I ** \ I = 0, 1, ..., TOTAL.DATA.NUMBER - 2
      UNIT.STEP * \ 1.016 pS UNIT
      INTERVAL :=
      SUM.INTERVAL INTERVAL + SUM.INTERVAL :=
      MOVE.MEASURE.DRAW
   LOOP
END.THE.PROCEDURE
;

:  FINE.EXP.STEP
   " FINE.EXP.STEP "  PROCEDURE.NAME " :=
   1  LINEARO.SEMILOG1 := \ SEMILOG GRAPHICS
   0  FIXEDO.FREE1 :=
   24 UNIT.STEP :=
UNIT.STEP  0.04233333 * PS.UNIT.STEP :=
   1.15 BASE :=
   48 TOTAL.DATA.NUMBER :=
0 INIT.BIAS :=
INIT.BIAS 0.04233333 * PS.INIT.BIAS :=
START.THE.PROCEDURE
TOTAL.DATA.NUMBER 1 - 0
DO
I 1 =
IF
SIDE.DISH.INGREDIENTS
THEN
BASE I ** \ I HAS VALUES 0, 1, ..., 46
UNIT.STEP * \ 1.016 ps UNIT
INTERVAL :=
SUM.INTERVAL INTERVAL \ INTERVAL IS AN INTEGER
+ SUM.INTERVAL :=
MOVE.MEASURE.DRAW
LOOP
END.THE.PROCEDURE
;

: FREE.CONST.STEP
" FREE.CONST.STEP " PROCEDURE.NAME ":=
0 LINEARO.SEMILOG1 := \ LINEAR GRAPHICS
1 FIXEDO.FREE1 :=
START.THE.PROCEDURE
TOTAL.DATA.NUMBER 1 - 0
DO
I 1 =
IF
SIDE.DISH.INGREDIENTS
THEN
UNIT.STEP INTERVAL :=
SUM.INTERVAL  INTERVAL
+  SUM.INTERVAL :=
MOVE.MEASURE.DRAW
LOOP
END.THE.PROCEDURE
;

: FREE.EXP.STEP
" FREE.EXP.STEP "  PROCEDURE.NAME " :=
1  LINEARO.SEMILOG1 := \ SEMILOG GRAPHICS
1  FIXEDO.FREE1 :=
START.THE.PROCEDURE

TOTAL.DATANUMBER 1 - 0
DO
  I 1 =
  IF
    SIDE.DISH.INGREDIENTS
THEN
  BASE I ** \ I HAS VALUES 0, 1, ..., 46
  UNIT.STEP *= \ 1.016 pS UNIT
  INTERVAL :=
  SUM.INTERVAL  INTERVAL \ INTERVAL IS AN INTEGER
+  SUM.INTERVAL :=
  MOVE.MEASURE.DRAW
LOOP
END.THE.PROCEDURE
;
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." NOW KK3.DM0 IS BEING LOADED."
LOAD KK3.DM0
\ THIS PART IS KK3.DMO : THIS PART IS MAINLY FOR
\ BEAM.PROFILE AND SAMPLE.CHECK. AGAIN, TO ACTIVATE THIS,
\ KK1.DMO SHOULD BE LOADED.
\ WRITTEN BY : KWANGJOON KIM
\ LAST REVISION : 07/15/92
\ DIM[ 41 , 41 ] REAL ARRAY TRANS.ARRAY
DIM[ 41 , 41 ] REAL ARRAY -DT/T.ARRAY
INTEGER SCALAR BEAMO.SAMPLE1
INTEGER SCALAR TRANSO.-DT/T1
INTEGER SCALAR TO.-D1
INTEGER SCALAR X.DELAY.POSITION
INTEGER SCALAR Y.INIT.MOVE
INTEGER SCALAR Y.UNIT.STEP
INTEGER SCALAR Y.STEP.NUMBER
INTEGER SCALAR Z.INIT.MOVE
INTEGER SCALAR Z.UNIT.STEP
INTEGER SCALAR Z.STEP.NUMBER
50 STRING BEAM.NAME
: ASK.INIT.MOVE

CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." Y.INIT.MOVE? (INTEGER um) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
   Y.INIT.MOVE :=
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." Z.INIT.MOVE? (INTEGER um) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
    Z.INIT.MOVE :=

: ASK.INFORMATIONS
BEAMO.SAMPLE1 1 =
IF
    GREEN BLUE MIX FOREGROUND INTEN.ON
    CR ." ENTER THE SAMPLE NAME : "
    RED MIX FOREGROUND INTEN.ON
    CHECK.INPUT.WORD
    SAMPLE.NAME ":=
    CR

    GREEN BLUE MIX FOREGROUND INTEN.ON
    CR ." ENTER THE DATA FILE NAME : "
    RED MIX FOREGROUND INTEN.ON
    CHECK.INPUT.WORD
    DATA.FILE.NAME ":=
    CR

    GREEN BLUE MIX FOREGROUND INTEN.ON
    CR ." 0 FOR TRANS ONLY, 1 FOR -DT/T : "
    RED MIX FOREGROUND INTEN.ON
    CHECK.INPUT.NUMBER
    TRANSO.-DT/T1 :=
    TRANSO.-DT/T1 TO.-D1 :=
    CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." DELAY POSITION (ps) : "
RED MIX FOREGROUND INTEN.ON
CHECK INPUT NUMBER
X DELAY POSITION :=

ELSE
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." ENTER THE BEAM NAME : "
RED MIX FOREGROUND INTEN.ON
CHECK INPUT WORD
BEAM NAME " :=
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." ENTER THE DATA FILE NAME : "
RED MIX FOREGROUND INTEN.ON
CHECK INPUT WORD
DATA FILE NAME " :=

THEN
ASK INIT MOVE
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." Y UNIT STEP? (INTEGER um) " \ SINCE 10 um HOLE OR BIGGER
RED MIX FOREGROUND INTEN.ON \ BEAM WAIST IS USED,
CHECK INPUT NUMBER \ 1 um RESOLUTION IS ENOUGH,
      Y UNIT STEP := \ THOUGH .5 um IS POSSIBLE.
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR " HOW MANY Y POINTS? (MAX 41) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
    Y_STEP_NUMBER :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR " Z_UNIT_STEP? (INTEGER um) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
    Z_UNIT_STEP :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR " HOW MANY Z POINTS? (MAX 41) "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
    Z_STEP_NUMBER :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR " HOW MANY MEASUREMENTS AT A POINT? "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
    NLP :=
CR

GREEN BLUE MIX FOREGROUND INTEN.ON
CR " COMMENT : "
RED MIX FOREGROUND INTEN.ON
    CHECK.INPUT.WORD
    COMMENT10 ":=


GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." TYPE 0 TO HARDCOPY THE RESULT, 1 TO DETERMINE LATER. "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER

HDCPO.WAIT1 :=

INTEGER SCALAR Y.COUNT
INTEGER SCALAR Z.COUNT

: MEASURE.THE.PROFILE
O TRANS.ARRAY := \ INITIALIZE
O -DT/T.ARRAY :=
O Z.COUNT :=

STEPPER8 \ INITIAL
" Y.D.M" Y.INIT.MOVE 2 * NEG "." "CAT " .G.E." "CAT \ CHANGE O F
" Z.D.M" "CAT Z.INIT.MOVE 2 * "." "CAT ".G.E." "CAT \ THE ORIGIN
GPIB.WRITE
Y.INIT.MOVE Z.INIT.MOVE + ABS 1000 + MSEC.DELAY

Z.STEP.NUMBER O
DO
Z.COUNT 1 + Z.COUNT :=

O Y.COUNT :=
Y.STEP.NUMBER O
DO
Y.COUNT 1 + Y.COUNT :=

LOCKIN10
TRANSO.-DT/T1  1 =

IF

1 INDEX :=
TIME.CONST.TIMES.FIVE MSEC.DELAY \ WAIT BEFORE MSRMNT
GET.ONE.DATA.POINT10
TRANS10 [ 1 ]
TRANS.ARRAY [ Z.COUNT, Y.COUNT ] := \ mV UNIT
MINUS.DELTA.T.OVER.T10 [ 1 ]
-DT/T.ARRAY [ Z.COUNT, Y.COUNT ] := \ 10^-4 UNIT

ELSE

0. SUM.T :=
NLP 0
DO
READ.A.SUM.T
LOOP
SUM.T NLP / NEG

TRANS.ARRAY [ Z.COUNT, Y.COUNT ] := \ mV UNIT
THEN

STEPPER8
" Y.D.M" Y.UNIT.STEP 2 * NEG "."
"CAT " .G.E." "CAT
GPIB.WRITE \ Y UNIT MOVE
Y.UNIT.STEP ABS 800 + MSEC.DELAY
LOOP
" Y.D.M" Y.UNIT.STEP 2 *
Y.STEP.NUMBER * "."
"CAT " .G.E." "CAT
GPIB.WRITE \ Y RETURN
"Z.D.M" Z.UNIT.STEP 2 * "."
"CAT " .G.E." CAT
GPIB.WRITE \ Z UNIT MOVE
Y.UNIT.STEP Y.STEP.NUMBER * ABS
Z.UNIT.STEP ABS 10 * ABS + 500 + MSEC.DELAY
LOOP
"Z.D.M" Z.UNIT.STEP 2 *
Z.STEP.NUMBER * NEG "."
"CAT " .G.E." CAT
GPIB.WRITE \ Z RETURN
;

VUPORT VU.AXON
0.25 0.75 VUPORT.ORIG
0.75 0.25 VUPORT.SIZE

VUPORT VU.CONTOUR
0.35 0.0 VUPORT.ORIG
0.48 0.75 VUPORT.SIZE

: COMMON.DISH.INGREDIENTS
GREEN MIX FOREGROUND
CR ." Y INITIAL MOVE "
CR ." = "
RED MIX FOREGROUND INTEN.ON
Y.INIT.MOVE .
GREEN MIX FOREGROUND
." um"

GREEN MIX FOREGROUND
CR ." Z INITIAL MOVE "
CR ." = "
RED MIX FOREGROUND INTEN.ON
Z.INIT.MOVE .
GREEN MIX FOREGROUND
." um"

GREEN MIX FOREGROUND
CR ." Y TOTAL LENGTH "
CR ." = "
RED MIX FOREGROUND INTEN.ON
Y.UNIT.STEP .

GREEN MIX FOREGROUND
." um *"
RED MIX FOREGROUND INTEN.ON
Y.STEP.NUMBER 1 -. 

GREEN MIX FOREGROUND
CR ." Z TOTAL LENGTH "
CR ." = "
RED MIX FOREGROUND INTEN.ON
Z.UNIT.STEP .

GREEN MIX FOREGROUND
." um *"
RED MIX FOREGROUND INTEN.ON
Z.STEP.NUMBER 1 -. 
CR NLP .

GREEN MIX FOREGROUND
." SAMPLINGS"
: BEAM.DISH.INGREDIENTS

GRAPHICS.DISPLAY

{SIDE.DISH}
GREEN MIX FOREGROUND
SCREEN.CLEAR

{BORDER}
GREEN BLUE MIX FOREGROUND INTEN.ON
CR ." BEAM PROFILE "
GREEN MIX FOREGROUND
CR ." .DATE
CR ." FRM "

GREEN BLUE MIX FOREGROUND INTEN.ON
STARTING.TIME "TYPE
GREEN MIX FOREGROUND
CR ." TO "
GREEN BLUE MIX FOREGROUND INTEN.ON
ENDING.TIME "TYPE

GREEN MIX FOREGROUND
CR ." BEAM NAME "
RED MIX FOREGROUND INTEN.ON
CR ." " BEAM.NAME "TYPE

GREEN MIX FOREGROUND
CR ." SAVED IN "
RED MIX FOREGROUND INTEN.ON
CR ." " DATA.FILE.NAME "TYPE
COMMON.DISH.INGREDIENTS

GREEN MIX FOREGROUND
CR ." CMNT : "
RED MIX FOREGROUND INTEN.ON
COMMENT10 "TYPE

; : SAMPLE.DISH.INGREDIENTS

GRAPHICS.DISPLAY

{SIDE.DISH}
GREEN MIX FOREGROUND
SCREEN.CLEAR

{BORDER}
GREEN BLUE MIX FOREGROUND INTEN.ON
TRANSO.-DT/T1 1 =
IF
  CR ." SMPLE.CHK -DT/T"
ELSE
  CR ." SMPLE.CHK TRANS"
THEN
GREEN MIX FOREGROUND
CR ." " .DATE
CR ." FRM "
GREEN BLUE MIX FOREGROUND INTEN.ON
STARTING.TIME "TYPE
GREEN MIX FOREGROUND
CR ." TO "
GREEN BLUE MIX FOREGROUND INTEN.ON
ENDING.TIME "TYPE

GREEN MIX FOREGROUND
CR ." SAMPLE NAME "
RED MIX FOREGROUND INTEN.ON
CR ." " SAMPLE.NAME "TYPE

GREEN MIX FOREGROUND
CR ." SAVED IN "
RED MIX FOREGROUND INTEN.ON
CR ." " DATA.FILE.NAME "TYPE
CR X.DELAY.POSITION .

GREEN MIX FOREGROUND
." pS DELAY"

COMMON.DISH.INGREDIENTS

TRANS0.-DT/T1 1 =
IF
RED MIX FOREGROUND INTEN.ON
LOCKIN1O " FRQ " SEND.CMD GET.RSP 1000. / \ READ FREQ
CR .
GREEN MIX FOREGROUND
." Hz"
CR ." TIME CONSTANT"
CR ." = "
GET.TIME.CONST
TIME.CONST [ TIME.CODE ] 1000. /
RED MIX FOREGROUND INTEN.ON
.
GREEN MIX FOREGROUND
." SEC."
THEN
GREEN MIX FOREGROUND
CR." CMNT : "
RED MIX FOREGROUND INTEN.ON
COMMENT10 "TYPE
;
: DRAW.PROFILE

HORIZONTAL LINEAR \ SINCE POSSIBLY IT IS PREVIOUSLY
\ SET TO LOGARITHMIC
LOAD.OVERLAY 3D- PLOT.SOV
2000 MSEC.DELAY
SOLID
AXIS.DEFUALTS

VU.AXON
12 LABEL.COLOR
4 COLOR
TRANS.ARRAY SUB[ 1 , Z.STEP.NUMBER ; 1 , Y.STEP.NUMBER ]
AXON.PLOT

VU.CONTOUR
AXIS.DEFUALTS

TRANSO.-DT/T1 1 =
IF
-DT/T.ARRAY SUB[ 1 , Z.STEP.NUMBER ; 1 , Y.STEP.NUMBER ]
9 CONTOUR.PLOT
ELSE
TRANS.ARRAY SUB[ 1 , Z.STEP.NUMBER ; 1 , Y.STEP.NUMBER ]

9 CONTOUR.PLOT
THEN
;

: COPY.N.SAVE1
DATA.FILE.NAME DEFER> OUT>FILE \ BEGINNING OF SAVING
BEAM.DISH.INGREDIENTS
DRAW PROFILE
SCREEN.PRINT
NORMAL.DISPLAY
TRANS.ARRAY SUB[ 1 , Z.STEP.NUMBER ; 1 , Y.STEP.NUMBER ] .
CR  CR ." =============================="  CR  CR
OUT>FILE.CLOSE \ ENDING OF SAVING
;

: COPY.N.SAVE2
DATA.FILE.NAME DEFER> OUT>FILE \ BEGINNING OF SAVING
SAMPLE.DISH.INGREDIENTS
DRAW PROFILE
SCREEN.PRINT

TRANSO.-DT/T1  1  =
IF
  O TRANSO.-DT/T1 :=
    SAMPLE.DISH.INGREDIENTS
    DRAW PROFILE
    SCREEN.PRINT
THEN
NORMAL DISPLAY
CR  CR ." TRANS.ARRAY "  CR
TRANS.ARRAY SUB[ 1 , Z.STEP.NUMBER ; 1 , Y.STEP.NUMBER ] .
TO. D1 1 =
IF
CR CR ." -DT/T.ARRAY " CR
-DT/T.ARRAY SUB[ 1 , Z.STEP.NUMBER ; 1 , Y.STEP.NUMBER ] .
THEN
CR CR ." +=+=+=+=+=+=+=+=+=+=+=+=+ " CR CR CR
OUT>FILE.CLOSE
\ ENDING OF SAVING
;

INTEGER SCALAR MEAO.MOV1
: BEAM.PROFILE
CLOSE.PREVIOUS.FILE
NORMAL.DISPLAY
0 BEAMO.SAMPLE1 :=
GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." YOU HAVE CHOSEN" 14 FOREGROUND ." BEAM.PROFILE" CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." 0 FOR THE BEAM.PROFILE MEASUREMENT," CR ." 1 FOR JUST MOVING THE ORIGIN :
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
MEAO.MOV1 :=
CR CR

MEAO.MOV1 1 =
IF
ASK.INIT.MOVE
STEPPER8 \ INITIAL
" Y.D.M" Y.INIT.MOVE 2 * NEG
"." "CAT " .G.E." "CAT \ CHANGE OF
" Z.D.M" "CAT Z.INIT.MOVE 2 *
".\" "CAT " \ .G.E." "CAT \ THE ORIGIN
GPIB.WRITE
ELSE
ASK.INFORMATIONS
"TIME \ STARTING.TIME ":=
" TO BE KNOWN" \ ENDING.TIME ":=
BEAM.DISH.INGREDIENTS
MEASURE.THE.PROFILE
"TIME \ ENDING.TIME ":=
HDCPO.WAIT1 1 =
IF
BEAM.DISH.INGREDIENTS
DRAW.PROFILE
CR
GREEN BLUE MIX FOREGROUND INTENSITY
.\" DO YOU WANT HARDCOPY? TYPE 0 FOR YES, 1 FOR NO. 
RED MIX FOREGROUND INTENSITY
CHECK.INPUT.NUMBER
HDCPO.SKIP1 :=
HDCPO.SKIP1 0 =
IF
COPY.N.SAVE1
THEN
ELSE
COPY.N.SAVE1
THEN
THEN
MAIN.DISH.INGREDIENTS
;

: SAMPLE.CHECK
CLOSE.PREVIOUS.FILE
NORMAL.DISPLAY
1 BEAMO.SAMPLE1 :=
GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." YOU HAVE CHOSEN" 14 FOREGROUND ." SAMPLE.CHECK" CR
GREEN BLUE MIX FOREGROUND INTEN.ON
CR CR ." 0 FOR THE SAMEPLE.CHECK MEASUREMENT," CR ." 1 FOR JUST MOVING THE ORIGIN : "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT NUMBER
MEAO.MOV1 := CR CR
MEAO.MOV1 1 = IF
ASK.INIT.MOVE
Y.INIT.MOVE NEG Y.INIT.MOVE :=
Z.INIT.MOVE NEG Z.INIT.MOVE :=
GPIB.WRITE
ELSE
ASK.INFORMATIONS
"TIME STARTING.TIME ":=
" TO BE KNOWN" ENDING.TIME ":=
SAMPLE.DISH.INGREDIENTS
X.DELAY.POSITION 0.04233333 / \ MOVE TO THE ASSIGNED
INTERVAL := \ POSITION
CHANGE.DELAY
INTERVAL 2.5 / MSEC.DELAY
Y.UNIT.STEP NEG Y.UNIT.STEP := \ OPPOSITE TO
Z.UNIT.STEP NEG Z.UNIT.STEP := \ BEAM PROFILE CASE
Y.INIT.MOVE NEG Y.INIT.MOVE :=
Z.INIT.MOVE NEG Z.INIT.MOVE :=
MEASURE.THE.PROFILE
Y.UNIT.STEP NEG Y.UNIT.STEP := \ RECOVER
Z.UNIT.STEP NEG Z.UNIT.STEP := \ THE SIGNS
Y.INIT.MOVE NEG Y.INIT.MOVE := \ FOR RECORD
Z.INIT.MOVE NEG Z.INIT.MOVE :=

INTERVAL NEG INTERVAL := \ RETURN TO THE ORIGINAL
CHANGE.DELAY \ POSITION

"TIME ENDING.TIME ";=

HDCPO.WAIT1 1 =
IF
SAMPLE.DISH.INGREDIENTS
DRAW.PROFILE
CR
GREEN BLUE MIX FOREGROUND INTEN.ON
." DO YOU WANT HARDCOPY? TYPE 0 FOR YES, 1 FOR NO. "
RED MIX FOREGROUND INTEN.ON
CHECK.INPUT.NUMBER
HDCPO.SKIP1 :=
HDCPO.SKIP1 0 =
IF
COPY.N.SAVE2
THEN
ELSE
COPY.N.SAVE2
THEM

THEN

MAIN.DISH.INGREDIENTS

;

\ 
\ THE COMMANDS BELOW ACTIVATES THE SPECIAL FUNCTION KEYS
\ 
: KK

MAIN.DISH.INGREDIENTS
F1 FUNCTION.KEY.DOES ROUGH.CONST.STEP
F2 FUNCTION.KEY.DOES FINE.CONST.STEP
F3 FUNCTION.KEY.DOES LINEAR.STEP
F4 FUNCTION.KEY.DOES ROUGH.EXP.STEP
F5 FUNCTION.KEY.DOES FINE.EXP.STEP
F6 FUNCTION.KEY.DOES FREE.CONST.STEP
F7 FUNCTION.KEY.DOES FREE.EXP.STEP
F8 FUNCTION.KEY.DOES BEAM.PROFILE
F9 FUNCTION.KEY.DOES SAMPLE.CHECK
INTERPRET.KEYS

;

\ 
\ MODE TO MOVE THE RETROPRISM HALF LENGTH OF
\ THE DELAY LINE FARTHER
\ 
: FF
STEPPER8 " X.D.M64000.G.E." GPIB.WRITE
;

\ 
\ MODE TO MOVE THE RETROPRISM HALF LENGTH OF
\ THE DELAY LINE NEARER
\ 

: NN
    STEPPER8 " X.D.M-64000.G.E." GPIB.WRITE
;

REAL SCALAR PS.BIAS

: ASK.BIAS

        GREEN BLUE MIX FOREGROUND INTEN.ON
        CR ." BIAS? (pS) "
        RED MIX FOREGROUND INTEN.ON
        CHECK.INPUT.NUMBER
        PS.BIAS :=
        PS.BIAS 0.04233333 /
        INTERVAL :=
;
/
: K
    ASK.BIAS
    CHANGE.DELAY
;
CR CR ." USE K TO CHANGE THE DELAY "
/
/ ACTIVATE THE SPECIAL FUNCTION KEYS
/

KK
Appendix B

List of Abbreviations

AM1 : Austin Model 1
BA : Boxcar Averager
CDD : Cavity DUmper Driver
CDH : Cavity DUmper Head
DIA : Doping-induced Absorption
EB : Emeraldine Base
ES : Emeraldine Salt
ESR : Electron Spin Resonance
F-LTPIA : Frequency-domain Long-time Photoinduced Absorption
FWHM : Full Width Half Maximum
GPIB : General Purpose Interfacing Bus
HE : High Energy
HPF : High Pass Filter
IR : Infrared
IRAV : Infrared Active Vibration
LBO : Lithium Triborate
LE : Low Energy
LEB : Leucoemeraldine Base
LESR : Light-induced Electron Spin Resonance
LIA : Lock-in Amplifier
LPF : Low Pass Filter
LTPIA : Long-time Photoinduced Absorption
ME : Middle Energy
NCPM : Non-critical Phase Matching
NDF : Neutral Density Filter
NDGS : Non-degenerate Ground State
NIR : Near Infrared
NMP : N-methyl Pyrrolidinone
NSSPIA : Near-steady-state Photoinduced Absorption
ODMR : Optically Detected Magnetic Resonance
P3AT : poly(3-alkylthienylenes)
P3BT : poly(3-butylthiophene)
P3DT : poly(3-decylthiophene)
P3HT : poly(3-hexylthiophene)
P3MT : poly(3-methylthiophene)
P30T : poly(3-octylthiophene)
PC : Personal Computer
PIA : Photoinduced Absorption
PIB : Photoinduced Bleaching
PL : Photoluminescence
PM : Photomodulation
PMT : Photomultiplier Tube
PNB : Pernigraniline Base
PPS : Polyparaphenylene Sulfide
PPV : Polyphenylenevinylene
PSPIA : Picosecond Photoinduced Absorption
PT : polythiophene
R6G : Rhodamine 6G
RRS : Resonant Raman Scattering
S9M : Styryl 9M
SDPM : Spin-dependent Photomodulation
SCE : Standard Cell Electrode
SHG : Second Harmonic Generation
SSH : Su, Schreiffer, and Heeger
T-LTPIA : Time-domain Long-time Photoinduced Absorption
TCNQ : Tetracyanoquinodimethane
TEM : Transverse Electromagnetic Modes
UV : Ultraviolet
VEH : Valence Effective Hamiltonian
YAG : Yttrium Aluminum Garnet
YLF : Yttrium Lithium Fluoride
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