OPTICAL MULTICHANNEL ANALYZER TECHNIQUES FOR HIGH RESOLUTION OPTICAL SPECTROSCOPY

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FOR HIGH RESOLUTION OPTICAL SPECTROSCOPY

James Lee Chao
(Ph.D. thesis)

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ABSTRACT

The development of optical multichannel analyzer techniques for UV/VIS spectroscopy is presented. In particular, the research focuses on the development of spectroscopic techniques for measuring high resolution spectral lineshape functions from the exciton phosphorescence in \( \text{H}_2 \cdot 1,2,4,5 \)-tetrachlorobenzene. It is found that the temperature dependent frequency shifts and widths confirm a theoretical model based on an exchange theory. The exchange of low energy phonon modes which couple with excited state exciton transitions is shown to display the proper temperature dependent behavior.

In addition to the techniques for using the optical multichannel analyzer (OMA) to perform low light level target integration, the use of the OMA for capturing spectral information in transient pulsed laser applications is discussed.

An OMA data acquisition system developed for real-time signal processing is described. Both hardware and software interfacing considerations for control and data acquisition by a microcomputer are described. The OMA detector is described in terms of the principles behind its photoelectron detection capabilities and its design is compared with other optoelectronic devices.
To my parents and my brothers, Eugene and Frank

Zwork ?? - anonymous
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... And what would I do without you Linda, for all the things you wanted interfaced to computers?

Special thanks go to Hilario, 'cause I still hope to "whup 'ya in tennis".
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My good friend Steve Marks gets special thanks for always being there when I was confused about a political issue; he made it so easy to take the "liberal" attitude.

Finally, and most importantly, I owe a great deal to my research advisor, Professor Charles Harris, who supported and encouraged me in my research activities and who offered me the very best in advice and guidance.
INTRODUCTION

There has been a great deal of interest in the dynamics of energy transfer in molecular crystals, ever since Frenkel\textsuperscript{1} first discovered that electronic excitation can be delocalized in a perfect crystal and that the propagation of the excitation can be described as a superposition of several Bloch-like wave functions. This is analogous to the propagation of lattice modes through the crystal with a group velocity determined by its phonon dispersion.

From this early work, there has been a great deal of activity in measuring and determining properties of these electronically excited states or Frenkel excitons, especially for 1-Dimensional crystal systems. Coherent energy transfer has been the subject of a great deal of controversy, even in recent years.\textsuperscript{2}

A great deal of effort has gone into experimental methods to determine pathways available for energy transfer in these molecular crystal systems. Mixed crystal systems involving isolated molecules as guests in a host lattice have been used to determine the nature of coherent exciton transport.\textsuperscript{3} These guests usually differ from the host in isotopic composition, chemical composition, or structure.

The optical lineshape function contains information about the dynamics of energy transfer. The focus of this thesis is to bring the latest in state-of-the-art instrumental techniques to obtain high-resolution measurements of exciton phosphorescence lineshape functions.
This thesis is divided into three discrete parts which contribute to the long-term research activities of our group. The first chapter is devoted to the experimental basis for the understanding of optical dephasing processes in H$_2$-1,2,4,5-tetrachlorobenzene. The work involves the measurement of the temperature dependent exciton phosphorescence lineshapes using an optical multichannel analyzer to obtain high resolution spectra. The second part describes the development of the OMA 2 Data Acquisition System for real-time control and data processing of spectra using a Digital Equipment Corporation (DEC) LSI-11 microcomputer. The final section describes the techniques and their implementation for low level light signal averaging and secondly for the detection of optical phenomenon in pulsed laser experiments.
THE BEGINNING OF THE END
CHAPTER 1

OPTICAL DEPHASING PROCESSES IN SOLIDS

I. INTRODUCTION

Since 1931 when Frenkel first published his papers on excitons in molecular solids, there has been considerable attention devoted to the understanding of energy transfer in terms of mechanisms and structures. Frenkel discovered that because of the periodic crystalline structure found in these organic solids, that an exciton picture could be used as a suitable quasi-particle description of excited state electronic migration. Since that time, excitons have been described in terms of bound electron-hole pairs which are free to migrate in a crystal based on lattice periodicity. In the Frenkel case, these pairs are tightly bound and can be described by Bloch-like wavefunctions and in the inorganic semiconductor case, are best described in terms of loosely bound Wannier states because of their rather small binding energies.

At cryogenic temperatures, perfect crystals of these organic semiconductors exhibit extremely long phosphorescence lifetimes. In the absence of chemical impurities and structural defects (dislocations, etc.), one might best describe excited state exciton dynamics in terms of the dephasing of exciton coherence. In the past decade, there has been considerable research to determine the underlying concepts for coherent exciton propagation and the role
that exciton-phonon interactions play in molecular solids. The relationship of exciton-phonon scattering to spectral lineshapes and other measurements of exciton migration dynamics provides the impetus for research in this very active area.\textsuperscript{4,5}

From experimental electron spin resonance\textsuperscript{6} and optical lineshape studies,\textsuperscript{7,8} as well as measurements of exciton dynamics, scientists have been able to compile an enormous amount of evidence for the nature of exciton coherence. It is in the area of experimental optical lineshape studies that emphasis will be placed in this manuscript.

It will become very apparent from the presentation of the theoretical basis for these studies that the development of high resolution optical multichannel analyzer techniques are of critical importance to the confirmation of these theories. The experimental work is chosen for 1-D energy transfer systems, because this makes both the theoretical and experimental studies far simpler.

In this chapter, a brief introduction to exciton states and their properties and dynamics will be presented. In the next section, a theory which we have developed that relates the optical lineshape function in absorption and emission to the dynamics of exciton transfer will be discussed. Finally, this manuscript will present the experimental results which seem to confirm the salient features of the theory.
II. EXCITON PROPERTIES AND DYNAMICS

In order to understand the nature of exciton coherence in solids, it is important that one understands the pathways available for the transfer of energy in an "isolated" molecule. See the Jablonski diagram in Figure 1. If one considers any isolated aromatic molecule, one begins with the absorption of light into the $S_1$ and higher singlet states. The creation of energy in the excited state allows for its dissipation through a number of pathways. Vibrational relaxation occurs to the first excited singlet state on a picosecond time scale. Either fluorescence or non-radiative decay back to the ground state occurs on the nanosecond to microsecond time scale. A competing process however, allows for intersystem crossing to the triplet state manifold. Relaxation occurs down to the $T_1$ state. It is this state which will be studied in terms of exciton coherence because of its extremely long lifetime of up to many hundreds of seconds. Triplet state phosphorescence (being a spin-forbidden process) is extremely long-lived and therefore it offers the possibility of transferring its excitation energy to a neighboring molecule in a crystal system. It is for this reason that the study of the time dependence of the electric transition dipole moment (through the phosphorescence lineshape function) should be intimately related to the study of the energy transfer processes themselves.

In the presence of intermolecular interactions, one has a slightly different picture, however. In a perfect crystal system, the use of the principles of solid state physics will allow us to use the periodic nature of the lattice to describe the interactions between nearest neighbors.
Figure I-1: Jablonski Diagram of Aromatic Hydrocarbons

Pathways for the absorption and relaxation of excited states are seen for a typical organic molecule.
Excitons can be formed by the absorption of photon energy, \( h\nu \), which causes the ejection of an electron from the valence band to the conduction band. In these materials, the binding of the positively charged hole formed and the negatively charged conduction electron produces the exciton. Because of the periodic nature of the crystal and its interactions, this electronic excitation can be described in terms of good quantum numbers of the crystal by delocalizing the excitation into wavefunctions of the lattice.

Figure 2 shows the coherent properties of excitons. The energy states of the "isolated" molecule are coupled by some intermolecular interaction, denoted by \( \beta \). In a linear chain crystal configuration, the nearest neighbor interaction \( \beta \) splits the degeneracy of the states of the isolated molecule into a band of states. The dispersion relationship generated from a 1-D linear chain nearest neighbor interaction with lattice spacing, \( a \), is

\[
E(k) = E_0 + 2\beta \cos k \a
\]

where \( k \) is the exciton wavevector, given for a delocalized Bloch wave function of the form

\[
|k > = N^{-k} \sum_n e^{ik\cdot r_n} |n >
\]

One should note that the band is split by an energy of \( 4\beta \), and that can be of either sign depending on whether it is an attractive or repulsive interaction. Dephasing of coherence refers to the change in wavevector or phase of the electronic Bloch wavefunction.
COHERENT PROPERTIES OF EXCITONS

1. \( \beta \) generates a rate of energy transfer between molecules: \( \nu_g(k) \).

2. Coherence lifetime, \( \tau(k) \), generates a width to the state and a mean-free path for coherent energy migration

\[
\ell(k) = \nu_g(k) \cdot \tau(k)
\]

\[
\tau(k)^{-1} = \sum_{k'} (\tau_{kk'})^{-1} = \Gamma(k)
\]

3. Distribution Function, \( D(k) \), determines the partition of energy between states of different velocities

\[
D(k)_B \sim \rho(k) \exp \left[ -\frac{E(k)}{kT} \right]
\]

Figure I-2: Summary of 1-D Excitonic Properties

The dispersion, group velocity, density of states, and distribution function in the First Brillouin Zone is shown for a one dimensional nearest neighbor interaction.
In the first Brillouin Zone, the delocalized wave packet travels with a group velocity given by \( V_g(k) \) determined from the slope of the dispersion curve.

\[
V_g(k) = \frac{1}{\hbar} \left[ \frac{\partial E(k)}{\partial k} \right]
\]  

(3)

Combining (1) and (3) one gets for a 1-D nearest neighbor interaction

\[
V_g(k) = \frac{2ga}{\hbar} \sin k a
\]

(4)

One defines a coherence lifetime for the propagation of the excitation by \( \tau(k) \). Assuming a first order stochastic Markoffian scattering process, the \( k \)-state lifetime \( \tau(k) \) yields a mean free path given by

\[
\ell(k) = V_g(k) \cdot \tau(k)
\]

(5)

The density of states function, \( \rho(E) \) is seen to pile up at the top and bottom of the band. If one weights the D.O.S. function by the Boltzmann factor, one gets a distribution function

\[
D(k) \approx \rho(k) \exp \left( \frac{-E(k)}{k_B T} \right)
\]

(6)

It should be pointed out that optical absorption or emission can occur only for \( k=0 \) and thus one really monitors only this portion of the band spectroscopically. This is a necessary consequence of the conservation of energy and momentum for the absorption of a photon to cause the creation of excited electronic states. Therefore, optical lineshape studies measure the dephasing of the \( k=0 \) electric dipole transition by the scattering of phonons.
to other band states. This has led to many exciton dynamical time
dependent techniques such as fluorescence and phosphorescence line
narrowing. There has always been considerable controversy over
whether exciton-phonon scattering necessarily results in a loss of
coherence. Furthermore, the manifestation of exciton-phonon
scattering processes in the optical lineshape function has been an
area of active research. Both of these areas will be addressed
later.
III. RELATIONSHIP OF THE OPTICAL LINESHAPE FUNCTION TO THE DYNAMICS OF ENERGY TRANSFER

We have developed a theory from which we hope to relate the optical lineshape function to the dynamics of energy transfer. The optical lineshape function contains information about the scattering of excitons with the lattice vibrations or phonons. It is through some assumptions about the nature of the coupling of excitons and phonons that we will present our exchange theory.

The zeroth order Hamiltonian for our system is shown in second quantization form.

\[ \mathcal{H}_0 = \sum_n \varepsilon_F a_n^+ a_n + \sum_m \omega (b_m^+ b_m + \frac{1}{2}) \]  

(7)

Here \( a_n \) refers to the electronic coordinates and \( b_m \) refers to the vibrational coordinates of the excitations at site N. See Figure 3. This zeroth order Hamiltonian contains just the electronic excitations of the first triplet state, \( \varepsilon_F \) and the excitations, \( \omega \) of the vibrations or optical phonons.

If one considers the linear and quadratic coupling terms of the perturbation Hamiltonian,

\[ \mathcal{H}_p = \mathcal{H}_1 + \mathcal{H}_q \]  

(8)

where \( \mathcal{H}_1 = \sum_n K a_n^+ a_n (b_n^+ b_n) \)  

(9)

and \( \mathcal{H}_q = \sum_n C a_n^+ a_n (b_n^+ b_n)^2 \)  

(10)
A SCHEMATIC REPRESENTATION OF THE ELECTRONIC AND VIBRATIONAL ENERGY LEVELS IN LOCALIZED STATES

\[ \epsilon_f + 2\omega \quad \epsilon_f + \omega \quad \epsilon_f \]

Energy \( \epsilon \)

\[ 2\omega \quad \omega \]

\( H_0 \)

**Zeroth Order Hamiltonian**

\[ H_l + H_q \]

**Perturbation Hamiltonian**

\( \mu(t) \)

**Transition Dipole Moment**

\( \mu(\omega_0) \)

\( \mu(\omega_0 + \delta\omega) \)

**Figure I-3:** The effects of the linear and quadratic coupling of electronic and vibrational states are shown and their effect on the time dependence of the transition dipole moment.
The consequence of $\mathcal{H}_1$ is that the excited states are shifted by a fixed amount. On the other hand, the quadratic coupling terms result in a non-linear shift of excited state energies. Furthermore, if one considers the exchange of vibrational energy between sites one must include an exchange Hamiltonian, $\mathcal{H}_{\text{ex}}$, given as

$$\mathcal{H}_{\text{ex}} = \sum_{n,m} J_{nm} b_n^+ b_m$$  \hspace{1cm} (11)

where the sum is over states $n \neq m$.

The two transitions, one at $\omega_0$ and one at $\omega_0 + \delta \omega$ result from different couplings between the ground and excited states. If one then considers the commutation relationships of $\mathcal{H}_{\text{ex}}$ with $\mathcal{H}_1$ and $\mathcal{H}_q$, one finds that $\mathcal{H}_q$ is the only term which does not commute. This means that the time dependence of the transition dipole moment occurs from the quadratic coupling terms of the exciton-phonon interaction. Schematically, the modulation behavior between transitions shown as $\mu(\omega_0)$ and $\mu(\omega_0 + \delta \omega)$ are introduced from $\mathcal{H}_{\text{ex}}$. What this means physically is that there is an intermolecular exchange of these low frequency modes between molecules.

If one now looks at the exchange picture of the interaction of excitons and phonons in the Brillouin Zone picture, (see Figure 4, not drawn to scale), one sees an exchange process of low frequency phonons for an exciton and phonon band. We label the states as follows, $(0,0)$ is the ground state, $(0,g)$ the optic phonon branch, $(k,0)$ the phonon-less exciton band, and $(k,g)$ the localized exciton-phonon band states. In this picture, $W$ is the absorption rate from $(00)$ to $(0g)$ and its lifetime, $\tau^{-1}$, back to the ground state is $W^-$. 
Figure I-4: The coupling of localized phonon band states to the exciton band is shown in the Brillouin Zone.

Two optical transitions, one at $\omega$ and one at $\omega + 6\omega$ are shown and the mechanism of coupling is seen through the absorption and emission of low energy phonons.
In our exchange model the absorption of a phonon does not result in a loss of exciton coherence. See Figure 5b. In most theories, it has naturally been assumed that the result of a phonon scattering process would be the evolution of an exciton of wavevector $k'$ and phonon $q'$. If, in fact, optical dephasing occurs as a phonon exchange process,

$$\begin{align*}
W_k &\xrightarrow{\text{phonon exchange}} (k,q) \\
W_k + q &\xrightarrow{\text{phonon exchange}} (k,q)
\end{align*}$$

(12)

there would be no loss of exciton coherence for this reversible process and the effects of this should manifest itself very specifically in the homogeneous optical lineshape function.

An experimental test of this would be to monitor the exchange averaging of the two optical transitions at $\omega_0$ and at $\omega_0 + \delta \omega$ by changing temperature. See Figure 6. We show three distinct cases for the absorption and emission of a phonon by the ground and exciton $(k_0,0)$ state. In the slow exchange limit ($\delta \omega_T > 1$) the two transitions are modulated very slowly (at low temperatures) and one would see two distinct transitions. In the fast exchange limit ($\delta \omega_T < 1$), the two transitions are effectively exchange averaged and a single transition is seen. However, in the intermediate exchange limit ($\delta \omega_T = 1$) the lineshape function will change markedly with temperature, thus demonstrating the degree of exchange averaging through low energy phonon absorption.

The effects of phonon exchange on the exciton absorption lineshape function can be summarized in the following way. From the exchange theory$^{11,12,13}$ formalism, the lineshape function for
OPTICAL DEPHASING ($T_2$) PROCESSES
FOR ELECTRIC DIPOLE TRANSITIONS TO $k=0$

(a) Multiple Phonon Scattering:
Loss of Exciton Coherence

(b) Phonon-Absorption:
No Loss of Exciton Coherence

Figure I-5: Dephasing processes can take one of two forms as seen in the Feynman-like diagrams. In a), scattering results in a loss of coherence to $k'+q'$. In a phonon-absorption process b.), excitonic coherence may be preserved.
PHONON EXCHANGE AVERAGING OF OPTICAL TRANSITIONS

Figure I-6: The effects of phonon exchange averaging are shown in 3 limits and their relationships to temperature dependent lineshape studies is seen. In the intermediate exchange region one expects a marked change in lineshape as a function of temperature. For slow exchange, two transitions are seen and in fast exchange a single one.
optical transitions is
\[ I(\omega) = \int_{-\infty}^{\infty} \exp(i\omega t) \langle \mu(0) \mu(t) \rangle \, dt \quad (13) \]

which says that the lineshape is given as the Fourier transform of the transition dipole moment autocorrelation function. In exchange theory, we use the quadratic coupling terms which introduce all of the time dependence into the autocorrelation function.

The autocorrelation function takes on the following form
\[ \langle \mu(0) \mu(t) \rangle = W \cdot \exp \left[ t(i\omega_0 + \Pi) \right] \quad \Pi \quad (14) \]

where \( \omega_0 = \) values of \( \omega_0(t) \)
\[ \Pi = \text{scattering rates between } \omega_0(t) \]

and \( W = \text{steady state probability distribution} \)

The result of this is that in the intermediate exchange case, the lineshape may be approximated by a Lorentzian of the form
\[ I(\omega) = (1 + (\omega_0 - \omega)^2 (T_{\text{eff}})^2)^{-1} \quad (15) \]

where \( T_{\text{eff}}^{-1} \), the linewidth of the transition is given as
\[ T_{\text{eff}}^{-1} = W_0 \left[ \frac{\delta \omega^2 \tau^2}{(1 + (\delta \omega \tau)^2)} \right] + T_1^{-1} + T_2^{-1} \quad (16) \]

and \( \omega_0 = \omega_0 + \delta \omega \left[ \frac{W_0 + \tau}{1 + (\delta \omega \tau)^2} \right] \quad (17) \)
such that \( \omega_e = \omega_0 - \Delta_{\text{eff}} \), the effective frequency shift.

The point is that

\[
W_+ \tau = \langle n(\epsilon_1) \rangle \cdot (\langle n(\epsilon_1) \rangle + 1)^{-1}
\]

(18)

for the optical phonon since it must satisfy microscopic reversibility. Since \( \langle n(\epsilon_1) \rangle \) is the Planck distribution function for the phonon mode which is taking part in this exchange mechanism, we can make some very specific predictions. At low temperatures, this just becomes the Boltzmann factor,

\[
W_+ \tau = \exp \left\{ -\epsilon_1 / k_B T \right\}
\]

(19)

The first thing that exchange theory predicts is that since \( \Delta_{\text{eff}} \) appears linearly in both the linewidth and frequency shift measurements that they will introduce a temperature dependent exponential line broadening and frequency shift. Secondly, Arrhenius plots will yield slopes which should be the same for both the homogeneous line broadening and frequency shift measurements.

Finally, if the first two conditions are met, then the dominant dephasing mechanism is through exchange of a single phonon mode whose activation energy will be characterized by the slope from the Arrhenius plots of \( T \frac{-1}{\tau} \) or \( \Delta_{\text{eff}} \) vs. \( 1/T \).

A further test of exchange theory is that we are indeed in the intermediate exchange limit which allows us to perform temperature dependent lineshape studies, i.e. \( \delta \omega_T \approx 1 \). This is measured experimentally at various temperatures since

\[
T \frac{-1}{\tau} / \Delta_{\text{eff}} = \delta \omega_T \quad \text{from (13) and (14).}
\]
IV. EXPERIMENTAL

The experimental studies were performed using $\text{H}_2$-1,2,4,5-tetrachlorobenzene (TCB). This molecular crystal was chosen because of its 1-D properties and the large amounts of experimental data available characterizing its excitonic properties.\textsuperscript{14}

The crystal geometry is seen in Figure 7. The point group symmetry is $D_{2h}(V_h')$. The space group for TCB is $P2_1/a$ at temperatures below 188 Kelvins. There are two molecules per unit cell and the transfer of energy is along the two non-equivalent stacking axes. The intermolecular spacing is 3.76 Å. Because of its geometry, a one-dimensional character along its $a$ axis is preferred.

The phosphorescence spectra of neat 1,2,4,5-tetrachlorobenzene is seen at low temperatures in Figure 8. One notes here that there is a clearly defined vibronic progression seen by the exciton and a trap state. At low temperatures (below the lambda point of He), traps are populated and account for most of the phosphorescence intensity from the crystal. However, these traps, due to impurities or to structural defects become depopulated at higher temperatures. They can be found generally from between 8-60 cm\textsuperscript{-1} below the exciton band. At 4.2 Kelvins, this particular Y-trap becomes totally depopulated.
Crystallographic Geometry of 1,2,4,5-Tetrachlorobenzene

Figure I-7: One dimensional crystallographic axis is shown. Energy migration occurs along the stacking axis by way of the aromatic $\pi$ electron ring.
Figure I-8: The phosphorescence spectrum is seen for the exciton fundamental and a Y-trap due to lattice imperfections. A vibronic progression is clearly shown. Trap depopulation occurs at 4.2 K.
A. High Resolution Using An Fe Hollow Cathode Lamp

In order to achieve extremely high resolution using an optical multichannel analyzer, one hopes to create a very high dispersion without introducing various forms of optical distortion. Instrumentally, one is ultimately limited in resolution in a grating set-up by the f-number of the monochromator, the slit width, and the grating itself. Furthermore, the f-matching of the monochromator to the light collection optics, as well as the performance of any additional lenses will affect the total resolution. Of course, high dispersion generally costs you in terms of the total amount of light which reaches the photodetector. In our system, we will discuss the methodology used to achieve a very high dispersion, and assume that the limits of the optical resolution are not yet reached.

A medium resolution spectrum (dispersion 0.75 cm\(^{-1}\)/channel) is shown in Figure 9. One should note that spatial dispersion is neither totally linear with energy or wavelength so that with a multi-element photodetector one properly describes it using an approximate average dispersion. For dispersions with which we are concerned, the differences are only a few percent. An Fe hollow cathode lamp is used because of the many emissions across the entire UV/VIS spectrum from its d-electron transitions. Table 1 lists the identifications of lines in this spectrum. Because of the many lines in this spectrum, it is advantageous to map out the entire OMA target, since the spatial dispersion of the detector optics is not precisely linear.
Medium Dispersion Iron Hollow Cathode Lamp Emissions

Figure I-9: OMA spectrum demonstrating the systematic method to obtain high resolution using Fe lines to map target area. The dispersion is 0.75 cm⁻¹/channel. Maximum number of counts is 64,244 and minimum is 455.
Fe Hollow Cathode Lamp Emissions Assignments

Table 1

<table>
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<tr>
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<td>372</td>
<td>3787.90</td>
<td>26,400</td>
</tr>
</tbody>
</table>

Dispersion = 0.75 ± 0.1 cm⁻¹/channel

* actually 2 peaks or doublet.
To obtain extremely high resolution, it is necessary to follow a systematic procedure to find the emissions of interest from the monochromator. Because high resolution is obtained in exchange for a certain degree of loss in signal intensity, and since there are very few lines with which to identify the emissions, one usually begins by using the CMA as a single channel PMT. An OMA 2 software routine performs the function of recording the data on a standard strip chart recorder while the spectrometer is slowly scanned. One must realize that in high resolution, the majority of Fe lines are very weak and cannot be seen by the CMA in real-time. Once one figures out approximately where the spectrometer is looking, then low light level target integration techniques may be used to reveal the very weak Fe lines. It should be noted that the identification of lines requires careful matching of the iron transitions reported in the literature and that relative intensities may vary considerably.

The dispersion is doubled in Figure 10 by using the spectrometer in second order. Since the grating is blazed at 5000 Å, both first and second order light intensities are about the same. Signal-to-noise is greater than 10:1.

The next step, once one knows that the exciton emission will come out on the optical axis, is to insert a 50 mm Pentax macro lens. One then puts the CMA at the focal plane of the virtual image to obtain a 5x magnification. This causes the image to become inverted from right to left so that in Figure 11, higher wavelengths occur to the left. The exciton fundamental and its Y-trap in TCB are shown with a dispersion of .144±.05 cm⁻¹/channel. The dispersion may again be doubled by going to second order and/or increasing the magnification of the macro lens.
2nd Order Dispersion- Fe Hollow Cathode Lamp

Figure I-10
High Resolution Spectrum of Exciton and Trap

Figure I-11

max = 2,246     min = -808
Figure I-10: The use of the spectrometer in second order doubles the dispersion to 0.36 cm\(^{-1}\)/channel. Peak #6 is now resolved (See Figure I-9).

Figure I-11: The use of the spectrometer in first order employing a 5x magnification macro lens gives a high resolution spectrum of the exciton (to the right) and the Y-trap. The dispersion is 0.144 cm\(^{-1}\)/channel.
B. Results

The data is compiled in Table 2 and is plotted in Figures 12 and 13. The important point to note is that the widths and shifts show the same exponential temperature dependence from the Arrhenius plots. If, in fact, a single phonon is responsible for exchange averaging in TCB, then the slopes should be the same with a value corresponding to the activation energy of the phonon mode responsible for dephasing.

The activation energy from the Arrhenius plots is 17-21 cm\(^{-1}\) which could correspond to an optic phonon branch in the TCB crystal. The literature indicates that there are lattice modes at 24, 34, and 41 cm\(^{-1}\) from an analysis of the phosphorescence spectrum in TCB. The data tabulated from this experiment makes it difficult to convincingly ascertain the nature of the phonon mode (geometrically) responsible, but it does offer a certain degree of hope that the simple exchange mechanisms discussed in this chapter may, in fact, be a very general property of 1-D exciton systems.

The linewidth data tends to have the greater difficulty agreeing with the theory, in particular for the low temperature measurements where the log of very small shifts give very large error bars. It is difficult to obtain good least squares fittings of exponential dependencies of small shifts and widths measurements. It is for this reason that a computer programmed least squares fitting routine was developed to simultaneously best fit both frequency shifts and linewidths to exchange theory.
Table 2
Temperature Dependent Frequency Shifts and Widths

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thermocouple (mV)</th>
<th>K</th>
<th>1/T</th>
<th>Channel #</th>
<th>Peak Width (channel-FWHM)</th>
<th>Relative Frequency (cm⁻¹)</th>
<th>Log Relative Frequency</th>
<th>Relative Width (cm⁻¹)</th>
<th>Log Relative Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.050</td>
<td>12.4</td>
<td>0.0806</td>
<td>27</td>
<td>13</td>
<td>0.18</td>
<td>-0.745</td>
<td>1.08</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>5.045</td>
<td>12.5</td>
<td>0.0800</td>
<td>27</td>
<td>13</td>
<td>0.18</td>
<td>-0.745</td>
<td>1.08</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>4.990</td>
<td>15.8</td>
<td>0.0633</td>
<td>27.5</td>
<td>14</td>
<td>0.36</td>
<td>-0.444</td>
<td>1.44</td>
<td>0.158</td>
<td></td>
</tr>
<tr>
<td>4.984</td>
<td>21.2</td>
<td>0.0472</td>
<td>30</td>
<td>15</td>
<td>1.26</td>
<td>0.100</td>
<td>1.00</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>4.856</td>
<td>24.6</td>
<td>0.0407</td>
<td>31</td>
<td>16</td>
<td>1.62</td>
<td>0.210</td>
<td>2.16</td>
<td>0.334</td>
<td></td>
</tr>
<tr>
<td>4.411</td>
<td>51.9</td>
<td>0.0193</td>
<td>41</td>
<td>50</td>
<td>5.22</td>
<td>0.718</td>
<td>14.40</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>4.400</td>
<td>52.0</td>
<td>0.0192</td>
<td>45</td>
<td>42</td>
<td>6.66</td>
<td>0.823</td>
<td>11.52</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>4.404</td>
<td>52.3</td>
<td>0.0191</td>
<td>41</td>
<td>41</td>
<td>6.22</td>
<td>0.718</td>
<td>11.16</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>4.378</td>
<td>53.9</td>
<td>0.0186</td>
<td>47</td>
<td>55</td>
<td>7.38</td>
<td>0.868</td>
<td>16.2</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>4.296</td>
<td>58.8</td>
<td>0.0170</td>
<td>51</td>
<td>49</td>
<td>8.62</td>
<td>0.945</td>
<td>14.04</td>
<td>1.15</td>
<td></td>
</tr>
</tbody>
</table>

*estimated.

See NOTES on next page.
NOTES:

1.) Temperature Output is ±10 mV using Chromel vs. gold at .07% iron.
2.) Reference for thermocouple corrected at ice water → 5210 mV.
3.) Spectral dispersion = 0.36 cm⁻¹/channel.
4.) Shift is to lower frequency for increasing temperature.
5.) Linewidth is to greater widths with increasing temperature.
6.) Extrapolating to T=0 Kelvin, peak channel # is 26.5.
7.) Extrapolating to T=0 Kelvin, inhomogeneous (non-temp. dependent) width contribution is 10 channels.
8.) Error bars based on ± 0.5 channel resolution for relative frequency and ± 1 channel for FWHM.
ARRHENIUS PLOT
$H_2-1,2,4,5$ TETRACHLOROBENZENE
$S_0 \rightarrow T_1$

Slope = 17 cm$^{-1}$

Figure I-12
ARRHENIUS PLOT
H₂⁻-1,2,4,5 TETRACHLOROBENZENE

S₀ → T₁

Slope = 21.3 cm⁻¹

Figure I-13
XBL805-5185
V. CONCLUSION

The interpretation of optical lineshape functions is an important area of study which requires a great deal of experimental and theoretical work, as well as intuition. From the studies of TCB, we have developed the ground work for many more experimental studies to elucidate the nature of exciton-phonon dephasing processes. Exchange theory, in general, presents a mechanism by which two transitions in close proximity (hot bands) may become coupled through fluctuations in the thermal (phonon) bath. This theory has been applied successfully for vibrational relaxation in crystalline durene\textsuperscript{11} and seems to display the proper trends for optical dephasing processes\textsuperscript{5}, as well. In any case, we have demonstrated that optical multichannel analyzer techniques may be used successfully for high resolution lineshape measurements.

There is one more aspect of an optical lineshape function which in general does not receive much attention. Besides the frequency shift and change in linewidth, one may also gather information about the relative intensity or peak height as a function of temperature. If one assumes a Lorentzian lineshape, of course, then this is not truly an additional source of information which is independent of the linewidth. However, because the OMA has such a uniform and linear response to the detection of photoelectrons, it lends itself particularly well to the quantification of peak heights. Appendix A addresses the question of how more information might be obtained from the experimental data by using it as an additional parameter for least squares fitting of exchange theory data. Thus, careful analyses of lineshape data promises to reveal a great deal of information as to the nature of exciton migration in solids.
CHAPTER TWO

LSI-11 MICROCOMPUTER-BASED DATA ACQUISITION SYSTEM
FOR AN OPTICAL MULTICHANNEL ANALYZER

I. INTRODUCTION

The emergence of the optical multichannel analyzer as an instrument for two dimensional electronic imaging has allowed for extremely high-speed signal processing capabilities as well as to provide a means of detection of optical signals in instances where no other practical means is possible.\textsuperscript{15,16,17} Based primarily on the existing television vidicon technology, the programmable optical multichannel analyzer has been enhanced to provide both extremely broad spectral sensitivity (200-800 nm) as well as excellent quantum efficiency (Q.E.=2-10\%). The ability of the optical multichannel analyzer to record spectral information has given atomic and molecular spectroscopists an advantage in speed and accuracy of data collection, especially when one considers the recent advances made in the peripheral area of high-speed digital signal processing capabilities.

In this chapter I would like to describe the use of a dedicated LSI-11 to provide real time data acquisition from the OMA 2 optical multichannel analyzer. The software is packaged to be sufficiently simple, yet comprehensive, and is applicable to anyone with access to any one of the many PDP-11 family computers, in particular for LSI-11 microprocessors operating under the Digital Equipment Corporation (DEC) RT-11 disk operating system.

\textsuperscript{15,16,17} OMA is a registered trademark of Princeton Applied Research Corporation.
While the interfacing of digital instrumentation to computers for control and data acquisition is generally straightforward, this particular interface of the OMA to an LSI-11 requires some rather special considerations. Because of rather rigid constraints related to high-speed image processing, the timing requirements for the I/O can be rather intricate. Through the efficient coupling of both hardware and software, the LSI-11 can be made to perform successive buffer additions within the time limits, without the need to build special hardware adders.

Since it is written in standard FORTRAN IV and in MACRO-11 assembly language, it can also be made to run in any other PDP-11 operating system (RSX-11, RSTS, etc.) with no modifications with the possible exception of necessary software address changes to reflect particular system configuration device handlers and specific file management CALL subroutines.

The optical multichannel analyzer system consists of three parts: 1.) the Princeton Applied Research Corporation (PARC) 1254 SIT detector 2.) the PARC 1216 Detector Controller and 3.) DEC LSI-11 computer. This data acquisition system replaces the PARC 1215 OMA 2 Console, which uses a software package written in the FORTH language.\textsuperscript{18,19} The software for this operating system is totally written in the high-level language FORTRAN IV, except for several FORTRAN-callable, assembly-level I/O routines.

There are several advantages for development of this OMA 2 Data Acquisition System\textsuperscript{20,21} in our laboratory. The most important consideration is compatibility with an existing (and much more powerful and expandable) DEC RT-11 based system with its advanced software capabilities. Our RT-11 disk operating system, not only supports an LSI-11 based network system (REMOTE-11), but numerous
peripherals, including graphics with hardcopy.

Furthermore, since this operating system is built on any PDP-11 general purpose computer, one has the ability to efficiently use the computer for many other laboratory functions, as well as for programming needs of data reduction and analyses. Furthermore, custom modifications by users for specific applications are far simpler, since FORTRAN is a much more universally accepted programming language than is FORTH.
II. DATA ACQUISITION SYSTEM CAPABILITIES

Use of the optical multichannel analyzer in conjunction with a dispersive monochromator allows one, in effect, to digitally process an entire lineshape function simultaneously. This not only relieves one of the necessity to scan the frequency region of interest, but also makes lineshape studies easily accessible for transient optical signals.

The user of the optical multichannel analyzer interactively runs a series of routines from a Tektronix graphics terminal connected to an ISI-11 microcomputer. The ISI-11 computer is configured to operate under DEC's RT-11 V3B operating system which also supports a hardcopy terminal, a hardcopy graphics plotter, as well as two digital-to-analog converters (DAC).

In the first part of the program, the user selects the scan parameters for a particular scanning routine, which are then translated into instructions for the 1216 Multichannel Detector Controller. These scan parameters include the region(s) of the target to be scanned, the dwell time in any particular channel, and the total number of scans to be accumulated in memory.

A 14-bit analog-to-digital converter presents the data synchronously to a 16-bit TTL bus which is then added into memory by the computer. A single-ended handshake was built into the interface to improve system integrity.

The user also collects a background scan, in order to subtract out any effects of concomitant dark current. At this point, the data may be viewed directly, plotted on the graphics screen or hardcopy terminal, or stored in a data file on a floppy diskette. One can also look at a previously collected data file, repeat the
experiment, or perform a different scanning routine.

Low light level signals may be detected by using extended delay target integration methods. Since dark current may be a substantial fraction of the signal detected by the OMA under certain conditions, one can reduce the dark current by as much as $10^8$, by cooling of the detector to $-60^\circ C$ by means of a liquid ethanol bath. Light is allowed to integrate on the target for a pre-determined amount of time and is then read off with a much higher signal-to-noise ratio. Operations in extended delay require the LSI-11 computer to interactively program the 1216 Multichannel Detector Controller so as to prepare the target for optimal reading efficiency.

This operating system has been developed so as to offer the user the ability to easily implement other scanning features as special applications might require. Such features which we have implemented include multiple tracks data collection and time resolved electronic shuttering of the OMA detector\textsuperscript{22,23,24}, which then allow us to electronically record more than one aspect of a transient optical experiment simultaneously.
III. OPTICAL MULTICHANNEL ANALYZER DATA ACQUISITION SYSTEM
IMPLEMENTATION

A. Interface Considerations

The interface for the PARC Model 1216 Multichannel Detector Controller is provided through a 16-bit DEC DRV11 parallel interface board by means of processor control. This interface provides both scan instructions to the 1216, as well as real time data acquisition from the detector controller. The digitized data from the OMA Controller is collected and summed in real time through a 16-bit parallel interface at up to 25 K words/second.

Since the data must then be stored in real time, the computer must acquire the data during the data valid period of the channel dwell time. The user may choose dwell times/channel of between 20-140 µsec. The timing sequence is shown in Figure 1. The worst case data valid period is 9 µsec for dwell times of 20 µsec. Unfortunately, the LSI-11/2 CPU cannot handle the necessary instruction executions within these time constraints. Thus for operation of the OMA 2 in this system, 40 microseconds/channel is the minimum dwell time allowable. In almost all applications, this represents a very minor limitation.
OMA 2 Timing Sequence for Interface

Figure II-1: TTL compatible 16-bit parallel interface handshaking lines are seen for DEC LSI-11 DRV11 parallel interface card and OMA 2 Multichannel Detector Controller.
During the data valid time interval, the software logic must:

1.) Check for DATA VALID
2.) Check for LAST CHANNEL flag
3.) Double precision add 14 bits of data to buffer
4.) Clear DATA VALID flag,
as well as periodically input new scan parameters during data acquisition operations, such as in extended delay target integration and electronic detector gating. Reliability is tested for at the end of each scan routine. One should note here that the 1216 presents the data synchronously and that the handshake is really only a single-ended one. Furthermore, interrupts are not generated, nor is DMA required; instead, the processor polls the device status address for a DATA REQUEST signal.
B. Hardware

The hardware for the data acquisition system is seen in Figure 2. The optical multichannel analyzer (OMA 2) is interfaced to the LSI-11 microcomputer through a 16-bit parallel I/O card. Any suitable video monitor or CRT display is used to provide a real 2-D display of the target. The PARC 1216 Multichannel Detector Controller stores the op codes for the scanning routines and also provides a 14-bit dynamic range A/D converter which presents the digitized signal intensity in real time synchronously to the LSI-11 computer.

The detector used in our laboratory is the Model 1254 silicon intensified target (SIT) tube with a UV scintillator coating to extend its S-20 response into the UV. The target is a 500x500 channel silicon diode array with approximate dimensions of 1.5x1.5 cm. To reduce dark current, the detector can be optionally enclosed in a dry ice cooled housing, which we have modified into a closed system liquid ethanol refrigeration unit. Peripherals for the data acquisition system include a Tektronix console graphics terminal and hardcopy plotter, an ADAC Corporation 12-bit multiplexed A/D and DAC, a DECrewriter, and the system device is a dual floppy disk unit from Data Systems Design. An oscilloscope is used to obtain a real time spectrum display.

A typical LSI-11 backplane configured in our laboratory contains the following microcomputer module components. An LSI-11/2 CPU card and 32 K memory card (Monolithic Memories) occupy the first two slots in the Q-bus. A DEC DRV11, used to provide parallel I/O to the 1216 Multichannel Detector Controller, is given a high priority daisy chain bus position. The backplane includes a floppy disk interface card as well as DEC DLV11 serial I/O cards to
LSI-II BASED OPTICAL MULTICHANNEL ANALYZER DATA ACQUISITION SYSTEM

Figure II-2: Components of OMA 2 Data Acquisition System for spectroscopic applications in a laboratory environment.
the Tektronix console terminal as well as a DECwriter hardcopy terminal. An ADAC 600 LSI11 card containing 16 multiplexed A/D channels with two programmable gain digital-to-analog converters is included to provide system monitoring and other laboratory digital voltage measurements.
C. Software

The software is comprehensive and requires 24 K of memory. It may be shortened depending on whether the user requires all of the features of the system. Also, one can expand it easily with the use of overlays.

It is written in FORTRAN IV except for some input/output routines written in the MACRO-11 assembly language. Users can change the FORTRAN software with little trouble as their specific applications might require, since the software is written in a rather modular fashion.

Figure 3 shows the interface registers and their functionality on the DRV11 parallel input/output board. Bits 15 an 07 are used to test for the DATA VALID and LAST CHANNEL flags, respectively. INTERRUPT ENABLES A and B are set at 0 to inhibit vector interrupt generation. CSR1 is used for the EXTERNAL EVENT FLAG which can be used for applications requiring EXPERIMENT START triggers, or for tagging data events.

DROUTBUFF is a read/write buffer area for input to the 1216 controller. These bits effectively override the front panel toggle switches on the 1216. DRINBUFF is a read only buffer containing the synchronous data from each channel as the OMA scans. All of the controls for the input buffer DRINBUFF and status register DRCSR are written in MACRO-11 for speed and simplicity.

In the OMA 2 Data Acquisition System, the user interacts at the terminal console. A flow chart for the data acquisition software is seen in Figure 4.
INTERFACE REGISTERS FOR DRVII PARALLEL PORT I/O TO OMA 2 1216 MULTICHLANL DETERMINAL CONTROLLER

Figure II-3

INT ENB A

15
REQUEST B
REQUEST A
INT ENB B
CSRI
CSRΦ

FUNCTION: Data Valid
Lost Channel
Ext Event Flag

DRCSR

DROUTBUF
(Input to 1216)

(Read/Write)

(Read Only)

DRINBUF
(Output from 1216)

Address

DRCSR 167760 Status Register
DROUTBUF 167762 Data Out Buffer
DRINBUF 167764 Data In Buffer

Vector Address-314 (unused)

XBL 803-4805
Figure II-4: A generalized block diagram is seen for the OMA 2, Version 2 system developed in our laboratory. Features are very modular and may be easily modified in standard FORTRAN IV.
The program is loaded from a floppy diskette upon which time several questions are asked about the user's system configuration. After the initialization process is completed, the user has the opportunity to avoid the data acquisition portion of the software and may proceed directly to the LOOK subroutine in order to view and perform data massage of a previously collected data file.

In normal operation, a directory is presented to the user, allowing him to change scan regions of the target, dwell times, and number of scans to signal average, as well as many other options. When the user has determined a set of mutually compatible scan instructions, he is allowed to proceed to data collection. A background collection of the associated dark current is collected and stored in a background buffer area. Signal collection proceeds after which time the user is given the opportunity to subtract out the background and replace his signal data buffer with the signal-only normalized data.

At this point, the user can perform any of the following routines. He may REPEAT the scan routine with or without first zeroing the data buffer; he may SAVE the data and its scan parameters, as well as comments about the experiment on a floppy diskette, or he can LOOK at previously collected data stored in a data file.

The user can also LIST or PLOT the data. Plotting includes the ability to smooth the data and display the spectra on the graphics terminal as histograms, line spectra, or point spectra. Figure 5 shows a typical spectrum generated by the hardcopy plotter. The software used is an assembly level condensed version of a Tektronix PLOT-10 software package. Finally, the user has the option to QUIT the program and return to the RT-11 monitor.
OMA (Optical multichannel analyzer) Spectrum

Figure II-5: Spectrum as generated by OMA 2 Data Acquisition System hardcopy plotter.
III. ALTERNATIVE APPLICATIONS OF OPTICAL MULTICHANNEL ANALYZERS

It is becoming increasingly clear that electronic imaging technology will play an important role in many scientific as well as commercial industries. For example, in the medical instrumentation area, the development of the X-ray CAT scanner for high-speed medical diagnosis has proven to be an invaluable tool. Secondly, the development of economic, yet powerful, microprocessors to perform data acquisitions, pattern recognition, and data storage is equally impressive. Thus, the combination of both the state-of-the-art in optoelectronic imaging as well as in high-speed signal processing are necessary for the highest overall performance in commercial instrument systems.

In industry, the implementation of optical multichannel analyzers, reticon arrays, and CCD array packages, has begun to see use for the control monitoring of many clinical and manufacturing processes. Finally, we hope that this report provides sufficient evidence that rather low-cost, dedicated microcomputers can be made to perform quite favorably in many imaging applications.
CHAPTER THREE

APPLICATIONS OF THE OPTICAL MULTICHANNEL ANALYZER FOR
1.) LOW LIGHT LEVEL SIGNAL AVERAGING AND
2.) 2-D MODE DETECTION OF PICOSECOND LASER GENERATED RAMAN SPECTRA

I. INTRODUCTION

The use of the optical multichannel analyzer (OMA) is a powerful instrument for high-speed photodetection in atomic and molecular spectroscopy. The many diverse applications of this instrument which have received considerable attention include the areas of electron and mass spectroscopy, laser diagnostics, pulsed X-ray crystallography, biomedical instrumentation, LEED, and also time-resolved streak cameras and other gating techniques. This report directs its attention towards the use of the OMA as a spectroscopic instrument for scientists. We would like to address two very specific areas dealing with signal-limited applications, namely the use of the OMA as an instrument for the signal averaging of very weak light emissions and secondly for its use to capture spectral information in transient pulse experiments.

The optical multichannel analyzer (OMA 2) from PARC represents a second generation instrument which is fully programmable and may be interfaced to any of a number of 16-bit computers. The use of a Digital Equipment Corporation (DEC) LSI-11 microcomputer through a 16-bit parallel interface to the OMA for processor-controlled high-speed signal averaging has been demonstrated. While a wide variety of detectors are available,
in most spectroscopic applications, the 500x500 diode array SIT (silicon intensified target) or ISIT (intensified silicon intensifier target) tubes are recommended. Besides being fully programmable, the improved CMA 2 provides for a very large A/D dynamic range (10,000 counts) as well as a much better charge-sensitive preamplifier section which greatly reduces electronic readout noise. The flexibility gained from computer programmability, for example, can be quite substantial since the ability to optimize detector scan and readout parameters is an absolute requirement for obtaining good S/N measurements from low level light signals. In addition, the ability of the computer to perform image enhancement, baseline renormalization, and statistical treatment of the data completes the signal processing capabilities of these detectors.

In this chapter, I would like to present techniques developed in our laboratory for performing optical spectroscopy in two signal-limited areas. The first area that should be addressed is low light level CW optical emissions where extended delay target integration techniques are required. The second area is that of capturing spectral information in a pulsed optical transient experiment, particularly in a picosecond Nd:glass laser experiment. The statistical treatment in these two cases is based on the consideration of the limitations of the signal rather than that of the detector.

In order to present the salient features of this article, I will first begin with a brief introduction into the theory of the SIT & ISIT detectors and a description of the principles behind their operation. Since the characteristics and specifications for CMA vidicon detectors are readily obtainable, this paper
will emphasize only those comparisons which are of special interest. After presenting the details of the two signal-limited areas, and examples of spectra collected using these methods, I would like to conclude with other potential uses for these instruments. Finally I would like to present some information about other imaging technologies and discuss suitable applications for those solid state devices.
II. THEORY OF SIT AND ISIT DETECTORS

The silicon intensified target (SIT) detector is based primarily on the existing television vidicon technology. The detectors available include UV/VIS response as well as some which have extended IR sensitivity. By the addition of one or two image intensifier stages, as in the SIT & ISIT detectors, respectively, their sensitivity and response is greatly enhanced.

A. Vidicon Section

The vidicon section uses a standard electron beam which is focussed from an electron beam cathode filament and which is programmed to scan the silicon target. The scan routine is provided by the PARC 1216 Multichannel Detector Controller which is programmed by our custom interfaced LSI-11 to scan a particular pattern.

The silicon target is made up of a microscopic array of photodiodes. The distance between photodiodes is about eight microns. The scanning electron beam uniformly charges the surface of the diode array target, thus creating a depletion region between the p- and n-type silicon. Because the silicon target stores optical signals with excellent linearity, the scanning electron beam can read the signal from the target at a later time. Signal is stored on the target by the formation of electron-hole pairs referred to as target pairs. These target pairs may be created either by direct electron bombardment or by absorption of photons. Electron-hole pair are generated as in all solid state devices by the excitation of an electron from the valence band into the conduction band. Once formed in the target diodes, the positively
charged holes and the negatively charged electrons migrate to the appropriate regions of the diode. When the electron-hole pairs recombine, they deplete the surface charge on the target. The QMA preamplifier measures the amount of charge required to refresh the target. The current required to refresh the target due to charge depletion is integrated for one channel period and thus converts the current measurement back to charge for the QMA electronics. This charge sensitive preamplifier circuit is then connected to an analog-to-digital converter which sends the signal for each channel in real-time to the computer through a 16-bit parallel interface.

B. SIT Intensification

Figure 1 shows the response of the SIT and ISIT detectors. The response is roughly 2-10% quantum efficiency for SIT detectors. The ISIT has a much better red and near IR response. The addition of a UV scintillator coating on the fiber optic faceplate serves to extend the UV response of the detectors.

Figure 2a shows the electrostatic SIT detector in cross section. As in photomultiplier tubes (PMT), photons are image on an S-20 photocathode. The detection of photoelectrons that are formed is the essential consideration in intensifier design. The image intensification stage in this detector yields approximately 2000x amplification in target pair generation. This is accomplished by the acceleration of photoelectrons generated at the photocathode through approximately a 10 KV potential. However, because of other losses associated with the intensifier design, the net improvement of the detector sensitivity is only about 200x. Direct electron bombardment results in useful signal amplification through the gain in kinetic energy provided by the
Figure III-1: The S-20 response of the 1254 SIT w/ and w/o UV scintillator is seen. Two ERMA (extended red multi-alkali) detector response curves of the ISIT design are shown.
Cross-section of SIT (silicon intensified target)

Figure III-2a
Cross-section of ISIT Detector

Figure III-2b
Figure III-2a: The detection of photoelectrons generated at the photocathode is the primary concern of intensifier design. The image intensifier section provides electron acceleration to produce a linear response of target pairs generated at the silicon target. A slow scanning electron beam reads off the resulting charge loss stored on the target.

Figure III-2b: A doubly intensified ISIT results in a statistical response of 1 count/photoelectron. A P-20 phosphor is used after the first electrostatically intensified section of the detector.
high voltage acceleration.

The SIT intensifier design also allows one to gate the high voltage to the photocathode. The PARC Model 1211 High Voltage Pulse Generator is capable of gating the high voltage with 1 nsec accuracy. This allows one, in effect, to electronically shutter the OMA from between 40 nsec to several hundred milliseconds. Furthermore, the delay and pulse duration may be pre-programmed by our LSI-11 computer. The shuttering ratio for this detector can be as high as $10^8$ and may be improved in pulsed laser applications with the use of a Pockel Cell (electro-optic) switch.

C. ISIT Intensification

The ISIT (intensified silicon intensifier) target detector employs a two stage photoelectron amplification design, seen in Figure 2b. It should be pointed out that the comparison of opto-electronic devices should be made in terms of photoelectron detection sensitivity. In the SIT, statistically, two photoelectrons generated from the S-20 photocathode are required to yield a single detector count. In the ISIT, this is improved so that statistically each photoelectron produces a single detector count. In addition, the ISIT uses an ERMA (extended red multi-alkali) photocathode which improves the red and near-IR response of the detector. See Figure 1.

Photoelectrons may be detected quite effectively in photomultiplier tubes used as photon counters without worry about amplifier noise, since such detection schemes apply the time profile of the photoelectron detections as a necessary criterion for the generation of a detected count. However, photomultipliers
must operate in real-time, whereas vidicon targets allow one to store the data for later readout. This advantage is exploited in cooled detector extended delay target integration techniques.

To detect photoelectrons, a single electron is amplified in energy by electric field acceleration. This extra energy, in the SIT produces a very large gain in the number of target pairs on the target, which are then measured in terms of local charge depletion. However, the ISIT (as seen in Figure 2b) differs from the SIT in that a P-20 phosphor acts to provide photon multiplication to the S-20 photocathode of the SIT stage. This serves to produce suitable gain such that single photoelectrons may be counted.

There are several disadvantages associated with ISIT detectors, however. Besides the added expense associated with these two stage intensifiers, they are not easily cooled for long term target integration. The ISIT does not handle cooling very well because of the problem of the very long persistence of the P-20 phosphor at low temperatures.

D. Other Intensifier Designs

The inverting electrostatic intensifier (SIT) is widely used because of its stability against stray electric and magnetic fields, as well as low cost. However, because of the curvature of the photocathode, a certain amount of distortion is introduced. Furthermore, the use of the glass fiber optic faceplate cuts off its UV and IR sensitivity.

The magnetic intensifier employs both electric and magnetic fields to image the photoelectrons directly onto a phosphor screen without image inversion. However, this design does requires very
stable electric and magnetic fields and therefore, costly power supplies.

Another intensifier utilizes extremely large electric fields to focus the electrons for very short distances. This intensifier is of a very simple design and is referred to as the proximity focus intensifier. It also requires very stable power supplies.

The detection of a single photoelectron generated at the photocathode can be done in other ways besides electron acceleration to form greater numbers of target pairs. One may also design intensifiers to provide electron multiplication, much in the same way that a dynode cascade architecture is designed in photomultiplier tubes.

An important intensifier technology which employs electron multiplication is the microchannel plate intensifier. The honeycomb design allows electrons to propagate down these narrow channels. Successive collisions allow for a great deal of electron gain. Although these devices provide significant gain, they do introduce some loss in resolution because of their physical dimensions and they tend to be very susceptible to amplification of noise. Furthermore, because of the high gain associated with electron multiplication, attachments of microchannel plate intensifiers on devices such as reticons, result in high susceptibility to heavy wear and damage. Consequently, frequent replacement of large diode arrays can be very expensive. Microchannel plate intensifiers, because of their freedom from lag, do however, result in excellent performance in single shot and gated experiments.
III. LOW LIGHT LEVEL SIGNAL INTEGRATION

One would like to compare the performance of cooled vidicon (SIT) detectors with other kinds of photodetectors, in particular single-photon counting schemes. In this domain, I would like to consider photon fluxes of less than about 1 photon/sec-channel.

We would like to evaluate the performance of the optical multichannel analyzer in terms of sensitivity and compare it with conventional photon counting schemes. Photon counting employs the use of a single channel photodetector which effectively applies the light pulse time profile to the electronic detection. This ultimate system results in the rejection of non-photon correlation functions and therefore such systems do not suffer from amplifier noise. This system however is somewhat limited to single channel detection and thus does not offer the parallelism versatility of an optical multichannel analyzer. We will investigate the sensitivity of the CMA vidicon under optimal conditions by comparing it with other photon counting systems. We would like to point out that such comparisons of the detector sensitivity depend on a number of factors and are still a topic of considerable controversy, in particular with respect to other diode array scanners, reticon devices, and CCD array packages. It is particularly dangerous to utilize these values for specification purposes for vidicon technology, since the user is given quite a bit of freedom with which to optimize the readout efficiency of his detector for specific applications. Furthermore, the emphasis here is on techniques rather than on absolute values which may not be routinely achievable under all possible applications.
A. Target Integration

For very low light levels, it is advantageous to allow the signal to acquire on the target before electronic readout because of the amplifier noise generated for each scan. Therefore, instead of reading it out continuously and averaging in computer memory, one allows the signal to integrate on the target. A charge sensitive preamplifier circuit measures the amount of current required to recharge the SIT target as the electron beam scans each pixel area or channel. Because this is essentially an analog measurement, this preamplifier circuit suffers from amplifier noise. The amplifier noise is roughly one count rms/scan.

The total amount of photoelectron generated noise goes as the square root of the number of photoelectrons detected. The total noise (in counts) is given as:

\[ N_t = (N_q^2 + N_s^2)^{1/2} \]

where \( N_q \) is the noise contribution associated with the electronic readout and \( N_s \) is the noise due to the signal.

It is easy to see that since the contribution due to readout can be a large fraction of the total noise for extremely low level light signals, it is advantageous to reduce the actual number of readout scans such that the photoelectron statistics will dominate the S/N performance.

It is for this reason that the technique of extended delay target integration was developed. Improvements in the S/N are made by allowing the signal to acquire on the target so as to reduce the total number of readout scans and to bring the signal well above
the detection limit threshold.

Electron-hole pairs generated on the target migrate to the appropriately charged area of the target. At room temperature, the charge stored on the target has a lifetime of several hundred milliseconds after which time capacitive leakage of the charge occurs. Normally, since the vidicon scanning beam reads out the signal within 70 msec for single track scanning, this does not result in significant signal losses due to this charge leakage. However, when one performs extended delay target integration for much longer periods of time, one encounters severe data loss.

By cooling of the detector to dry ice temperatures (-60 °C), one increases the time to as much as several hours for which the signal remains. This allows one to collect signal on the target for extremely long periods of time and to read it off after significant signal has been acquired on the target. It is found that we achieve S/N ratios greater than 5:1 only after target integration for times such that the electronics detect at least 300 counts/channel-scan.

B. Dark Current

For extremely low light signals, one has to consider the problem associated with thermal dark current. Dark current arises from the Boltzmann distribution of electronic energy states about the Si band gap. These thermally generated electron-hole pairs then manifest themselves macroscopically as charge leakage from the target surface. For example, in intrinsic silicon the band gap is about 1.1 eV. If one looks at the Boltzmann distribution at various temperatures, one finds that the cooling of the detector
from room temperature to \(-60^\circ C\) can yield an attenuation in excess of \(10^8\). Since the dark current is an intrinsic property of the detector, it is sometimes difficult to assess the absolute number of thermally generated detector counts, apart from other possible sources of A/D counts.

In Figure 3, we show the dark current thermal profile across the detector from channels 0-500 before and after background subtraction is seen for the detector at room temperature and when it is cooled. One should note that the baseline is not flat \(^{41}\); this may be attributed to the actual thermal fall off at the edges. At \(-50^\circ C\), one would estimate that the dark current is less than 2 counts/sec based on Figure 3d, since the # counts rms/channel after subtraction is approximately 10.

One should note here that provided the temperature of the SIT detector is constant and that suitable target preparation techniques are used, a background collection of the detector (including dark current) can be stored in digital form in the computer memory and will not change substantially during the course of an experiment. It is for this reason that the actual dark current does not hurt too badly, since it is normally subtracted out. However, for extremely low level light signal, dark current can potentially hurt you in the following way. Since it is, in fact, a real signal source, it also has a noise associated with it which goes as the square root of the number of thermally generated counts. By lowering the dark current through cooling, one hopes that thermally generated counts will be substantially less than the photoelectron counts so that the noise associated with the dark current will have a much smaller effect.
Room Temperature Thermal Profile of SIT Detector

Figure III-3a

max = 31,251

min = 25,035
Room Temperature Noise After Background Subtraction

Figure III-3b

Maximum # counts = 358
SIT Detector Thermal Profile at -60° C

Figure III-3c
SIT Detector Noise After Background Subtraction at -60 °C

Figure III-3d
Figure III-3 Captions

a.) Room Temperature Thermal Profile of SIT Detector
b.) Room Temperature Noise After Background Subtraction
c.) SIT Detector Thermal Profile at -60 °C
d.) SIT Detector Noise After Background Subtraction

From a.) and b.) one can estimate the dark current contribution by taking the r.m.s. # background counts (~200 counts/channel). By squaring this figure one gets approximately 4.0 x 10^4 counts. Since this was collected over 50 msec, we get roughly 8 x 10^5 thermally generated counts/sec at room temperature.

Similarly, for cooled detector target integration one sees that roughly the number of rms counts is 10 counts/channel. This means that 100 real thermal counts are generated for the 45 seconds target integration time. This means that one can estimate the dark current at about 2 counts/sec at -60 °C, which represents an attenuation of about 10^5. This is just an order of magnitude calculation and ignores other sources of noise or stray light.
The normal way that one acquires good spectra is to repetitively signal average until a reasonable S/N ratio is obtained. Since the signal goes up linearly with collection time and the noise goes up only as the square root, one hopes to eventually reach a suitable S/N ratio. However, there are practical limits to signal averaging and target integration capabilities of the SIT detector. For fluxes of about 0.3 photoelectrons/second-channel, we have been able to achieve S/N ratios from extended delay target integration of 10:1 by cooling the detector to -60 °C and integrating signal for approximately 3 hours.

Figure 4 shows the general specifications to be expected upon cooling of the detector. Depending on the time for which signal integration takes place, one can effectively improve their S/N ratio. It should be pointed out that cooling to eliminate dark current has a lower limit, since the manufacturer warns against the possibility of tube damage from differential contraction for temperatures much below that of liquid nitrogen.

Cooling of the detector was achieved by converting the PARC 1212 Dry Ice Cooled Housing for the OMA to a closed system liquid ethanol refrigeration unit. A freon based two stage cooling tip from F.T.S. Corp. was built into the dry ice reservoir. Two liters of ethanol was used in the cooling reservoir for the SIT detector and equilibration was generally achieved after about a five hour waiting period. The refrigeration unit was preferable to the dry ice system since it was difficult to replenish the dry ice reservoir without disturbing the optical alignment. It should be noted that during signal integration, the liquid cooler was turned off since the compressor tended to introduce vibrations into the
Signal-to-Noise Ratios for Various Photon Fluxes and Extended Delay Target Integration Times

Figure III-4: Cooling allows one to go to extremely long signal integration times to achieve high S/N ratios.
detector. A nitrogen purge, as well as a dessicant, were used to prevent condensation on the detector, in particular on the diode array target.

C. Target Preparation and Readout Optimization

In the OMA 2 system, the Multichannel Detector Controller is fully programmable. This allows one to scan the region(s) of interest at various dwell speeds, as well as to optimize the detector readout capability. For extended delay target integration, the user interacts with the OMA from the keyboard console. Besides the usual scan parameters specifying a scan program, the user is queried as to the length of time for which he wishes to allow the light to integrate on the target, the number of readout scans, and the number of times he would like to repeat the target integration.

Vidicon detectors suffer from a phenomenon known as lag. Because of lag, silicon target pairs cannot be read off completely in a single reading scan. At low temperatures, this electronic time constant can be quite long. One must therefore judiciously choose the number of readout scans such that most of the signal is read off without introducing too much noise from the amplifier circuitry. At low temperatures, we have found that from 10-50 scans are optimal for extremely weak signals.

Since the signal is stored on the target for a finite time, one often would like to repeat the target integration process several times to get the averaging effect one obtains from continuous scanning. This also allows the computer to completely run the experiment for very long periods.
For extended delay target integration, the target is first illuminated by flashing an LED to uniformly discharge the detector target for optimal reading efficiency. Fifteen preparatory frames are used to read off the saturated target from the LED flash.

At this point, the target is allowed to integrate the light. The filament to the scanning electron beam is turned off in order to reduce the possibility of it being a source of stray light to the vidicon target. It is then turned back on approximately 20 seconds before readout.

The detector target is then scanned at a higher cathode voltage (+0.5 V), in order to improve the readout efficiency and to therefore reduce the effects of lag. The programmed op codes are sent in real-time for target preparation and are double latched so that the scanning process changes are assuredly frame synchronized. The LSI-11 computer thus provides the timing for the experiment as well as performs a number of housekeeping chores, besides providing the real-time data acquisition and data manipulation routines.

D. Experimental: High Resolution UV/VIS Spectroscopy

The use of the OMA for high resolution UV/VIS spectroscopy was the primary aim of the development of extended delay target integration methods. The measurement of temperature dependent triplet state exciton lineshapes in 1,2,4,5-tetrachlorobenzene (TCB) was the goal of our research. Since the phosphorescence linewidths are very narrow (3-10 cm⁻¹ FWHM), it was critical that the detection of very small frequency shifts and widths as a function of temperature be measured with very high resolution. Because of the reproducibility problems in the scanning of the
spectrometer in a conventional single channel PMT experiment, the use of a multichannel detector was very attractive. With an OMA, one would be able to collect the spectroscopic lineshapes without the necessity to mechanically scan the frequency region of interest. To acquire the necessary dispersion (0.05 cm\(^{-1}\)/channel) required the use of a 2 meter Jarrel-Ash spectrometer in second order, in addition to using a 5x magnification macro camera lens at the exit port.

The experimental set-up is seen in Figure 5. A single crystal of 1,2,4,5-TCB is immersed in a liquid helium cryostat between 4.2-50 Kelvins. A 75 watt high pressure Hg arc lamp is used as an excitation source in the UV region. Triplet state phosphorescence at 3750 Å is then focussed into the spectrometer and the lineshape is imaged onto the SIT detector with a macro lens. Since the amount of phosphorescence intensity is very low, alignment is aided with a He-Ne laser and/or an Fe hollow cathode lamp used for calibration purposes. In this particular set-up, a dedicated LSI-11 satellite is used for data collection and is networked (REMOTE-11) into an LSI-11 host computer. A multichannel analyzer (MCA)\(^{44}\) is used optionally for real-time spectrum integration viewing. Temperatures can be controlled by the host computer through a calibrated Carbon resistance thermometer connected to a precision digital multimeter \(^{45}\), which is interfaced to the host computer.

Figure 6 shows the exciton fundamental in TCB using extended delay techniques with target integration for six minutes. The first plot shows the signal collected with the concommitant dark current while the second shows the spectrum after digital background subtraction. One should note in Figure 6a that the dark
High Resolution Phosphorescence Emission Experimental Set-up

Figure III-5: The OMA is part of the experimental set-up which includes cryogenic handling equipment. Computers automate the experimentation providing feedback as well as data acquisition for long target integration times.
Figure III-6: 1,2,4,5-Tetrachlorobenzene Exciton Phosphorescence a.) Before and b.) After Background Subtraction Using Extended Delay Target Integration Techniques.

Thermal background features are removed using background subtraction.
current/background is considerably greater than the signal itself, i.e. the signal sits on a very large DC offset. One quantitatively performs background subtraction and baseline renormalization to restore the AC features of the spectrum. The photoelectron flux corresponds to less than 40 counts/sec-channel. One should also note that features of the thermal background profile are most pronounced near the edges. After background subtraction, these features are removed. See Figure 6b. The rising and falling tails of the lineshape are very important in our theoretical models and are not artifacts of the signal integration process.

Finally, I would like to emphasize the importance of detector temperature stability for cooling. Before reaching steady-state, background subtraction and renormalization are almost useless. Also, I would like to point out the advantages of this kind of extended delay techniques over the use of photographic plates. Besides the ability to collect the data quickly without photographic processing, the signal processing capabilities of a computer are quite significant. In addition, the QMA has an extremely linear response to photons which results in extremely good lineshape data. On the other hand, silver halide photographic response is logarithmic and therefore requires careful calibration procedures.
IV. TRANSIENT PULSE SIGNAL CAPTURE

The CMA is ideally suited for transient pulse signal capture because of its multiple channel storage capabilities. This is considerably more advantageous than fast multiplexing electronics (> several hundred nsec) since one effectively stores the data for later readout.

Earlier, I described the mechanisms by which photoelectrons may be formed to create images which may then be digitized for computer data processing. These mechanisms still apply in transient systems; however, the techniques involved for optimizing signal processing are necessarily different because of the pulsed nature of the signal.

There has been a great deal of interest in the possibilities of gating the detector for time-resolved spectroscopic applications, but these in general are more relevant to the observation of kinetic phenomenon with microsecond decay life times.

I would like to present techniques which have been successful for the data capture of subnanosecond transient phenomenon generated from a pulsed ND:glass picosecond laser. In addition, I will show an example where we use the 2-D nature of the photodetector for multiple tracks data acquisition.

A. Pulse Synchronization- EXPERIMENTAL TRIGGER START

In a transient pulse experiment, it is necessary to synchronize the vidicon readout with the light pulse for greatest
readout efficiency. The advantage of reading out the detector only when there is signal present is obvious. In a low light level CW experiment, target pairs must build up on the SIT detector, whereas in the case of a pulsed experiment, peak light power is very great, but its duration is quite short.

In a synchronous experiment, the computer generates a trigger which gates both the laser as well as prompting the OMA to begin readout scanning. Depending on the experimental trigger delay requirements, a number of different alternatives are available for synchronizing the OMA readout electronics.

In the experiment, the computer prepares the OMA target, after which time the 1216 Multichannel Detector Controller sends a +5V EXPERIMENT START pulse to the laser. Since the laser propagation time is well below 100 microseconds (actually 50-200 nsec), the laser flashes before readout occurs on any of the central 500 channels of the target. The vidicon detector then performs about 10-15 readout scans to efficiently collect all the stored signal.

If the propagation delay time for the trigger was not performed through hardware at high speeds (> 100 microseconds, i.e. such as manually), one might expect that the light pulse hits the target during the middle of a readout frame. Because of surface charge leakage and other effects, one may find that this may cause a non-uniform spectrum to occur on the left and right of the channel in question. Successive readouts tend to reduce this effect, which seems to be a more serious problem with the OMA 1.

One should also make sure that the pulse repetition rate does not exceed the readout time for the detector. For example, for a 500 channel frame at 60 microseconds/channel using 10 readout
frames requires 300 msec. This means that approximately 3 Hz would be the highest repetition rate possible under these conditions.

There are many alternative ways to obtain pulse synchronization. The 1216 Multichannel Detector Controller also provides for programmable TRIGGER 1 and TRIGGER 2 outputs, as well as an EXTERNAL EVENT input (also connected to interface bus (read/write)). These alternatives can be programmed and controlled by our LSI-11 directly.

B. Signal Capture and Readout

The stored charge on the silicon target has an image latency of several hundred milliseconds at room temperature. Because the detector suffers from lag, the SIT Detector requires more than a single scan to effectively read off the total charge. One must be reassured, however, that provided that the readout is optimized to read off the charge completely that the signal response will be linear (±2%). The dynamic range is well over 1x10⁴. For optimal results, one should attenuate the light if necessary by using neutral density filters.

Generally ten to fifteen scans is optimal at room temperature. However, there has always been some question as to whether cooling of the detector will improve the S/N in a pulsed application. My belief is that in general for spectroscopic applications that it is not likely to help at all, even though the dark current will be reduced. Since our light pulse is so intense, the thermally generated dark current is a negligible fraction of the total signal, especially since the readout is tailored to less than a few milliseconds.
However, for two dimensional imaging where one uses 500 tracks, the total readout time is multiplied by 500. The effect of this is that the readout times for a single frame scan far exceeds the storage retention time of the silicon detector at room temperature. By cooling, one reduces the dark current, but more importantly, one allows the storage of the charge image until it can be completely read off. I would like to point out that a 500x500 scan program requires over 240 K words of memory in single precision and furthermore takes many seconds to read it off just once.

C. Experimental: 2-D Mode Detection of Picosecond Laser Generated Raman Spectra

This research effort is aimed at understanding the nature of energy transfer in condensed phases using picosecond laser spectroscopy. A mode locked Nd:glass laser (pulse width \( \sim 5 \) psec) is used to study excited state vibrational relaxation by measuring lineshapes from the Stokes Stimulated Raman Scattering process.

The laser pulse repetition rate is once every 45 seconds and the experiment is almost completely automated with control to our microprocessors. Once it is set up, the user interacts with the data acquisition system only to save the data on mass storage or to discontinue the experiment. In this experiment, a single TEM 00 pulse at 10,600 Å is picked from a mode-locked pulse train using a Pockel cell. See Figure 7.

The laser pulse is frequency doubled using a KDP crystal and is then beam split into two different optical paths. In a classic excite and probe technique, the liquid in a 10 cm. Raman cell is
Figure III-7: Laser set-up shows Pockel Cell switch for extracting a single picosecond (~5 psec FWHM) pulse from a mode-locked train.
illuminated. See Figure 8. The Stokes Stimulated Raman emissions are labelled in the following ways. First, they are delayed in time with respect to one another through the use of a nanosecond optical delay line. Secondly, they are tagged with different polarizations. It is this difference in polarization which is used to spatially resolve the excitation from the probe stokes lines. The pulses are resolved spatially through Glan-Thompson polarizers which image the light into either the top or bottom halves of the entrance slit to the monochromator.

With the use of the 2-D OMA one is able to collect the spectra by subdividing the vertical channel elements into two sections and programming for two tracks. Figure 9 shows the result from a single picosecond laser shot which is displayed on the users graphics console. It is by measuring the differences in the lineshapes that one obtains information about the dynamics of the vibrational relaxation processes.

The user is presented with the spectrum immediately after signal processing is completed and is given the opportunity to write to the disk, save the data in buffer memory, or to stop the laser data acquisition and manipulate the data.

With this system, our research group has been able to study many different liquids and to make some predictions about vibrational dephasing times and their relationships to other macroscopic properties of these solvents.
Figure III-8: Orthogonal polarizations are used to measure lineshapes from an excite and probe Stokes Stimulated Raman experiment.
Two-Track Picosecond Laser Generated Raman Spectra

WRITE TO DISK, SAVE BUFFER, MANIPULATE DATA?

Figure III-9: Upper spectrum shows the probe Stokes emission while lower one shows the excitation Stokes emission.
D. General Comments

It is clear that if one understand the physics behind the CMA as a detector that one would best be able to use it to the greatest advantage. Furthermore, the use of 2-D mode for multiple tracks allows one, in effect, to monitor more than one optical process in an experiment. This represents a great advantage over similar 1-D array detectors which offer far less programmability and therefore versatility.

In many cases, the use of the CMA as a 2-D imaging device represents a low cost means of image processing by using the techniques described in this paper.

The CMA 2 can also be used in random mode as well to signal average single pixels or regions of the target. This would be a great application for LEED intensity analysis. It is clear that the CMA properly used can be implemented in a wide variety of experimental situations.
V. CONCLUSION

It is clear that the direction for applications of these 2-D vidicon detectors of this type will be in the area of 1) time-resolved spectroscopy or time-domain imaging and 2) full 2-D imaging for low-light level signals. In the area of time-resolved spectroscopy, the use of a HV pulse generator unit\(^{47}\), optionally in conjunction with a Pockel cell switch in high power pulsed laser applications\(^{24}\), will be an extremely important tool for electronic shuttering from about 40 nanoseconds to several milliseconds.

The use of the CMA or similar 2-D imaging device will play an important role in high-speed monitoring of manufacturing processes in a number of diverse industries. In this area, considerable attention has been given also towards the use of these devices with appropriate spectral converters to image X-rays. Finally, as progress in electronic imaging becomes more and more advanced, the degree of sophistication in data processing will undoubtedly grow. Developments in the areas of image enhancement and pattern recognition will further the use of these two dimensional imaging systems. Certainly, in the medical area, the use of CAT scanners to provide X-ray sectioning to reconstruct 3-D images has proven to be a very valuable medical diagnostic tool.
REFERENCES AND FOOTNOTES


20. J. L. Chao & C. B. Harris, OMA 2 DATA ACQUISITION USERS MANUAL, Lawrence Berkeley Laboratory, University of California, PUB #3008, 1980.

21. Helpful discussions were provided by Dr. Jonathon Weber & Paul Roehrenbeck of Princeton Applied Research Corporation.

22. Time resolved optical spectroscopy is accomplished by gating the HV to the vidicon intensifier which yields a shuttering ratio of as much as 10,000. With the PARC 1211 High Voltage Pulse Generator, shuttering can be as fast as 50 nsec with 1 nsec accuracy.


25. Tektronix Graphics terminal model 4006-1 or 4010 series with 4662 Hardcopy Plotter, Tektronix Corporation, Beaverton, Oregon 97005.


36. Photoelectron losses can occur at a number of places in the intensifier stage. The fiber optic faceplate and UV scintillator coating introduce losses. Spurious reflections may occur; this often leads to a phenomenon known as halation.

37. See Application Notes, for example from Princeton Applied Research Corporation, Princeton, N.J., or Pacific Precision Instruments (PC-1), Concord, CA.

38. For example from Tracor Northern, DARSS, Middleton, WI.

39. For example from Reticon, subsidiary of E G&G Company, Sunnyvale, CA.

40. For example, Fairchild Semiconductor, Mountain View, California.

41. The detector is actually a 512x512 array. However, because of edge distortions of the target by virtue of the curvature of the photocathode in the design of the electrostatic intensifier, only 500x500 is actually used. In addition, freedom from distortion, i.e. uniformity is achieved principally in the central region of the target so that normal spectroscopic lineshape information is obtained by using 500 channels and using a central channel height of 250 channels.

42. F.T.S. Model LC-80 Liquid Cooler, Stoneridge, N.Y.


44. Tracor Northern, Model NS-575 Signal Averager.

45. Data Precision Model #DM 3500, Wakefield, Mass.


47. PARC Model 1211 High Voltage Pulse Generator, Princeton, N.J.
The delay and pulse duration are programmable through the OMA 2 1216 Multichannel Detector Controller.
APPENDIX A

In our exchange theory we have explicitly shown the relationship of the temperature dependence of the optical lineshape function in terms of the frequency shift and linewidth broadening.

We begin with a Lorentzian approximation of

\[ I(\omega) = (1 + (\omega - \omega_0)^2 (T_{\text{eff}})^2)^{-1} \]  \hspace{1cm} (1)

where \( \omega_e = \omega_0 + \delta \omega \left( \frac{W+ \tau}{1 + (\delta \omega T)^2} \right) \), \( \omega_e = \omega_0 - \Delta_{\text{eff}} \) \hspace{1cm} (2)

and \( T_{\text{eff}}^{-1} = W \left[ \frac{\delta \omega^2 \tau^2}{(1 + (\delta \omega T)^2)} \right] \) \hspace{1cm} (3)

such that \( W+ \tau = <n(\varepsilon_1)>(<n(\varepsilon_1) > + 1)^{-1} \) satisfies microscopic reversibility,

\[ = <n(\varepsilon_1)> \]  \hspace{1cm} (4)

at low temperatures.

Recall that \( <n(\varepsilon_1)> \) is the Planck Distribution given as:

\[ <n(\varepsilon_1)> = \frac{\exp(\varepsilon_1/kT) - 1}{\exp(\varepsilon_1/kT)} \]  \hspace{1cm} (5)

Furthermore, \( \delta \omega T \) may be taken from the plots of

\[ \frac{T_{\text{eff}}^{-1}}{\Delta_{\text{eff}}} = \delta \omega T \]  \hspace{1cm} i.e. the ratio of the effective relaxation time to the effective frequency shift.
Substituting (2), (3), and (4) into (1) yields

\[
I(\omega) = \left[ 1 + \left\{ \omega - \omega_* - \left( \frac{\delta \omega T}{1 + (\delta \omega T)^2} \right) \frac{n(\varepsilon_1)}{T} \right\}^2 \left\{ \frac{1 + (\delta \omega T)^2}{(\delta \omega T)^2} \frac{n(\varepsilon_1)}{T} \right\} \right]^{-1}
\]  

(6)

Letting \( C = \delta \omega T \) and using equation (5)

\[
= \left[ 1 + \left\{ \omega - \omega_* - \left( \frac{C}{1 + C^2} \right) \frac{e^{\varepsilon_1/kT - 1}}{\tau} \right\}^2 \left\{ \frac{(1 + C^2)(e^{\varepsilon_1/kT - 1})}{C\delta \omega} \right\} \right]^{-1}
\]  

(7)

Letting \( Q = \frac{C}{1 + C^2} \) and \( P = \omega - \omega_* \)

\[
= \left[ 1 + \left\{ P - \frac{Q}{\tau} \frac{1}{e^{\varepsilon_1/kT - 1}} \right\} \frac{1}{Q\delta \omega} \left( e^{\varepsilon_1/kT - 1} \right)^2 \right]^{-1}
\]  

(8)

Simplifying...

\[
I(\omega) = \left[ 1 + \left\{ \frac{P}{Q\delta \omega} \left( e^{\varepsilon_1/kT - 1} \right) - \frac{1}{C} \right\} \right]^{-1}
\]  

(9)

It seems perfectly reasonable that the change in absolute intensity would be important to the characterization of the temperature dependence of the lineshape function instead of merely characterizing the optical lineshape by just widths and shifts. A good way to include this dependence would be to
incorporate the change in intensity as a function of temperature change or $\frac{dI(\omega)}{dT}$.

Differentiation of equation (9) yields

$$
\frac{dI(\omega)}{dT} = \frac{2\varepsilon}{kT^2} \left[ \frac{(\omega - \omega_p)(1+C^2)}{\delta_\omega} \right] e^{\varepsilon_1/kT} (I(\omega))^2 \times \left[ \frac{P}{Q\delta_\omega} \left\{ e^{\varepsilon_1/kT} - 1 \right\} - \frac{1}{C} \right]
$$

Experimentally, the change in peak height may be used as an additional variable with which to get a least square best fit for $\delta_\omega$, $\tau$, etc. Conversely, we can use this as a test of our exchange theory fits (obtained by computer). In this way, one can test the theory in terms of its intensity as well.

To test the exchange theory, a plot of this equation vs. temperature performed digitally on the computer is made, using the parameters found from the best fit frequency shift and linewidth data. The next step is to identify the temperature where the function goes to zero. This represents the temperature for which the lineshape peak is maximum. This is guaranteed, since for both $T \to 0$ and $T \to \infty$, $I(\omega) \to 0$. One may then check back through the original data to see if this is, in fact, true. This is a relatively simple exercise, and its significance as a critical test of exchange theory should be carefully considered, particularly because of the additional constraints applied to the data. Since we use an OMA to collect the lineshape data, it is both ideal and appropriate that we include these intensity studies, especially since its sensitivity is linear within $\pm 2\%$.

The computer program is listed next and includes the code for the plotting of $dI(\omega)/dT$ from parameters determined from the exchange theory fitting program.
Program for the theoretical determination of the variance of intensity vs. temperature for phonon absorption processes based on mechanism II.

**Specification Statements**

```plaintext
REAL*8 C, D, W, W0, AA, E, Q, I(400), DV(400), T, P, ENERGY
REAL*8 QIMAX, QIMIN, DQIMAX, DQIMIN
INTEGER NON(3), NOFF(3)
INTEGER*4 ANS
```

**Initialization of Parameters**

```plaintext
TEMP(JJJ) = TEMMIN + TINCR * FLOAT(JJJ - 1)
ENERGY = 17.0
WRITE (5, 111)
```

111 FORMAT ('/' Parameters to be read in: '/4X,'C',8X,'D',17X,'W',8X,'W0')

READ (5, 1) C, D, W, W0
WRITE (5, 7)

7 FORMAT (' Read in temp. min, max and the number of points to be plotted')

READ (5, 3) TEMMIN, TEMMAX, NPTS

3 FORMAT (2F10.4, 13)

TINCR = (TEMMAX - TEMMIN) / FLOAT(NPTS - 1)
WRITE (5, 220)

220 FORMAT (' C=',F10.4,' D=',F10.4,' W=',F10.4,' W0=',F10.4,'
1/ Would you like a listing of the points? '/' Read (5, 229) ANS
WRITE (5, 222)

222 FORMAT (' Value is ',I10)

239 FORMAT (A3)

DO 20 J = 1, NPTS

T = TEMP(J)
E = ENERGY / (.69558 * T)
AA = DEXP(E)
OI(J) = 1.0D0 + (P*(AA-1.0D0) / (Q*DW)) - (1.0D0/C)**2
DV(J) = (E**P*AA*(OI(J)**2))**((P**AA-P)/(Q*DW)-1.0D0) / (T**Q*DW)

20 IF (ANSWER.EQ.17753) WRITE (5, 2) T, QI(J), DV(J)

2 FORMAT (3X,'TEMP.',F10.2,2X,2(3X,D20.13))

**Plotting Section**

```

QIMAX = QI(1)
DQIMAX = DV(1)
QIMIN = QI(1)
DQIMIN = DV(1)
```

DO 22 J = 2, NPTS

C EXTRACTS LARGEST INTENSITY VALUE
IF (QIMAX - QI(J)) 150, 151, 151

150 QIMAX = QI(J)

C EXTRACTS POINT OF GREATEST CHANGE IN INTENSITY
IF (DQIMAX - DV(J)) 152, 153, 153

152 DQIMAX = DV(J)

C EXTRACTS SMALLEST 1) CHANGE OF INTENSITY 2) INTENSITY
IF (DV(J) - DQIMIN) 154, 154, 155

154 DQIMIN = DV(J)

C CONTINUE
C GIVES TEMPERATURE FOR MAXIMA MINIMA
WRITE (5,1223) QMIN, QMAX, DQMIN, DQMAX, RR, QQ, PP
QIMAX<INTENSITY<QIMIN
TMIN<TEMPERATURE<TMAX

PLOTING ROUTINES
11 WRITE (5,238)
238 FORMAT ('Would you like a hardcopy?')
READ (5, 239) ANSWER
CALL INITT(120)
IF (ANSWER.EQ.14533) GO TO 535
C 34533 HAS TO BE CHANGED AT A LATER TIME, OKAY?
IF (ANSWER.EQ.17753) CALL TOIST(3, NON) PUT IN PARAMETERS FOR MECHANISM II LATER PUT ALSO IN INTENSITY, DINTENSITY, AND TEMP. (KELVIN)
PLOT AXES CALL MOVABS(50, 65)
CALL DRWABS(925, 65)
CALL MOVABS(75, 700)
CALL MOVABS(50, 340)
CALL DRWABS(925, 340)
C LOOP TO PUT IN MARKERS ALONG X-AXES DO 50 JJ=55, 200, 20
DO 50 J=160, 250, 5
CALL MOVABS(J, JJ)
50 CALL DRWREL(0, 20)
C DEFINING USER VIRTUAL AND SCREEN WINDOW CALL DWINDO(TMIN, TMAX, DQMIN, DQMAX)
CALL SWINDO(75, 925, 850, 230)
PLOT OF CHANGE OF INTENSITIES CALL MOVEA(TMIN, 0.)
CALL DRWREL(-11, 0)
CALL DASHA(TMAX, 0., 3)
CALL MOVEA(TMIN, DV(1))
DO 53 J=2, NPTS
53 CALL DRAWA(TMP(J), DV(J))
C LABELLING OF MAXIMA MINIMA CALL MOVEA(TMP(NP), DV(NP)) PUT AN X IN CALL MOVEA(TMP(NQ), DV(NQ)) PUT IN AN X PUT IN A P WRITE P = DEG. KELVIN CALL MOVEA(TMP(NQ), DV(NQ)) PUT IN AN X PUT IN A Q WRITE Q = DEG KELVIN PLOT OF INTENSITY REDEFINE VIRTUAL AND SCREEN WINDOWS IF (QIMAX.LT.1.7) QIMAX=1.0 CALL DWINDO(TMIN, TMAX, QIMIN, QIMAX)
CALL SWINDO(75, 925, 375, 595)
PLOT IN ZERO INTENSITY REFERENCE CALL MOVEA(0., 0.)
CALL DRWREL(-11, 0, 3)
CALL DASHA(TMAX, 0., 3)
C STILL NEEDS TO PUT IN ZERO IF (QIMAX.LT.1.7) GO TO 218 ROUTINE TO PUT IN MAXIMUM (1) INTENSITY REFERENCE CALL MOVEA(0., 1.)
CALL DRWREL(-11,0,3)
C
SHOWS WHERE MAXIMUM INTENSITY OCCURS
218 CALL MOVEA(TEMP(NR),0.)
CALL DASHA(TEMP(NR),1.)
C
PLOTTING OF INTENSITY
CALL MOVEA(TEMPMIN,QI(1))
DO 54 J=2,NPTS
54 CALL DRAWA(TEMP(J),QI(J))
CALL MOVABS(0,767)
CALL ALFND
IF (ANSWER.NE.17753) GO TO 11
CALL TOUIST(3,NOFF)
535 STOP
END