AN ABSTRACT OF THE THESIS OF

Robin L. Zagone for the degree of Doctor of Philosophy in Physics presented on August 30, 1995. Title:

Linear and Nonlinear Optical Investigation of Films:
I. Formalism for Time Resolved Multi-Photon Processes
II. Detection of Solid Water Phase Transitions on Si-SiO₂
III. Waveguided CARS Spectroscopy

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William M. Hetherington III

Nonlinear optical processes can be described as multiphoton scattering events in terms of high order perturbation theory. The standard procedure for quantitative calculation of high order terms is to impose a steady state condition on the perturbative radiation fields. In the present work, this condition will be lifted, and explicit time dependencies in terms of pulsed radiation will be examined at length.

Enhanced Linear and nonlinear scattering of laser radiation from a cryogenic Si-SiO₂ surface in the presence of H₂O vapor reveals the influence of the irreversible structural phase changes of solid water on and within the oxide layer of Silicon.

Coherent Anti-Stokes Raman Scattering (CARS) is a four-photon process which, when conducted within the boundary conditions of a waveguiding medium, can serve as an enhanced surface and bulk probe.
Linear and Nonlinear Optical Investigation of Films:
I. Formalism for Time Resolved Multiphoton Processes
II. Detection of Solid Water Phase Transitions on Si-SiO$_2$
III. Wave Guided CARS Spectroscopy

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Robin L. Zagone

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Robin L. Zagone, Author
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C. Y. Ju worked significantly on the collection and interpretation of the cryogenic Silicon work. A. Shultz assisted in data collection in the Silicon experiment and performed all of the Atomic Force Microscopy imaging which appears in this text. J. Griffiths contributed to the programming of the Lyot filter simulation code. W. Jang performed the Quartz dispersion fitting for the Lyot filter. In addition, he created the original design of the optical leg of the one meter monochromator. W. H. Li worked extensively on the acquisition of the Raman signal in the optical wave guide. W. M. Hetherington III and D. Cebula recorded the off-axis scattering images.
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This work describes three projects undertaken with the goal of using linear and nonlinear optics to study surface-adsorbate interactions.

The first section contains the analytical development of a microscopic susceptibility tensor for a high order nonlinear scattering event. The expression derived is original and unique in that the effects of pulse width and delay are introduced and emphasized. The utility of such a theoretical expression comes into play for the pursuit of nonlinear optical spectroscopy in a truly time resolved fashion. The importance of the analytical rather than numerical solution to a high order interaction cross section should not be overlooked.

The next section describes the serendipitous observation of a hitherto unreported interaction between the surface oxide layers of Silicon and adsorbed solid water. The phase changes in the latter express themselves in a dramatic fashion through changes in the linear and nonlinear optical properties of the solid water/Si-SiO₂ system. At the very least, these observation stand as a new, inexpensive and highly sensitive method for study of the transitions between the various crystal structures of ice, and perhaps other materials as well. But more important, the apparent strain induced changes in the dielectric function of Si-SiO₂ brought about by the presence of ice points to an avenue of further study of the
material properties of this technologically important film in particular, and surface oxides in general.

The final section describes an implementation of a Coherent Anti-Stokes Raman Scattering spectrometer for application to guided wave spectroscopy. With the technological importance of nonlinear optical waveguides as optical switches, signal couplers, etc. in mind, the ability to spectroscopically characterize waveguide materials becomes valuable. Further, as a means of creating a highly surface sensitive means of surface-adsorbate interaction observation, perfection the waveguided CARS technique finds importance. The system built is described in detail and an experiment in the spectroscopic characterization of a fabricated planar optical waveguide is presented.
Chapter 2

Formalism for Time Resolved Multi-Photon Interactions

Nonlinear optical processes can be described as multi-photon scattering events in the language of high order perturbation theory. The standard procedure for quantitative calculation of high order terms is to impose a steady state condition on the perturbative radiation fields. However, with the continued improvement in the development of femtosecond-scale pulsed lasers, a need to abandon the steady state condition becomes important. Presently, this condition will be lifted, and the explicit time dependencies of pulsed radiation will be included in the interaction cross section. The goal, then, will be to produce a generalized and analytic expression for a time dependent microscopic nonlinear susceptibility.

As Wynne points out, ultrashort time resolved expressions are important because (1) physical relaxation and dephasing can be apprehended directly without appeal to Fourier transforms spectroscopy, (2) liquid and solid state relaxation phenomena occur on femtosecond time scales and (3) extraction of relaxation parameters from experimental data requires very careful understanding of the coherence characteristics of the fields[1]. However, Wynne proceeds to attack the problem not in terms of pulsed coherent radiation, but with a formalism based on the short coherence times of unpulsed, incoherent light. Thus, the need for an expression explicit in time remains, and the following will set out to answer it.
2.1 Time Dependent Perturbation Theory Approach

The macroscopic susceptibilities of a given material, $\chi^{(n)}$ (see Section 4.1), which characterize experimental effects such as Parametric Oscillation and Amplification, Sum and Difference Frequency Generation (SFG, DFG), Second and Third Harmonic Generation (SHG, THG), etc. stem from spatial ensemble averages over the quantum microscopic susceptibilities, $\beta^{(n)}$. The quantum transition probability is proportional to the microscopic susceptibility $\beta$ contracted with the driving fields. Determination, then, of the appropriate quantum transition probability is tantamount to expression of $\beta$.

The matrix element representing the transition amplitude between physical states $a$ and $b$ mediated by an interaction potential $U_v$ is expressed[2]

$$\langle b|U_v|a\rangle = \delta_{ab}$$

$$+ \left(\frac{-i}{\hbar}\right)^1 \int_0^t dt_1 \langle b|V_H(t')|a\rangle$$

$$+ \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} \langle b|V_H(t')V_H(t'')|a\rangle$$

$$+ \left(\frac{-i}{\hbar}\right)^3 \int_0^t dt' \int_0^{t'} \int_0^{t''} \langle b|V_H(t')V_H(t'')V_H(t''')|a\rangle$$

$$+ \left(\frac{-i}{\hbar}\right)^4 \int_0^t dt' \int_0^{t'} \int_0^{t''} \int_0^{t'''} \langle b|V_H(t')V_H(t'')V_H(t''')V_H(t''')|a\rangle$$

$$+ \cdots$$

where each successive term in the expansion represents a higher order multi-photon event.

Focusing on just the third order term in this expansion (which corresponds to the subset of nonlinear phenomena such as SFG, DFG and SHG), the interaction matrix element can
be expanded by insertion suitable projection operators of the form $\sum \rho \langle \rho |$ between each interaction potential.

$$
\langle b | U_a | a \rangle_{3\rightarrow d} = + \left( \frac{-i}{\hbar} \right)^3 \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} \langle b | V_H(t') V_H(t'') V_H(t''') | a \rangle
$$

$$
= \left( \frac{-i}{\hbar} \right)^3 \sum_c \sum_d \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} \langle b | V_H(t') | d \rangle \langle d | V_H(t'') | c \rangle \langle c | V_H(t''') | a \rangle
$$

(2.2)

The remainder of this chapter will focus on variations of this transition matrix element.

### 2.2 2 Photon Absorption 1 Photon Emission

One subset of possible three photon events is two photon absorption with single photon emission. In the case of degenerate absorbed photons, this process corresponds to Second Harmonic Generation (SHG). Without that constraint of frequency degeneracy, the more general Sum Frequency Generation (SFG) is the corresponding optical phenomena described by this formalism.

Three of the six possible time orderings are pictured in generalized energy level schematics in Figure 2.1. Henceforth, the following level definitions will apply:

- State $b$ will have $n - 1$ photons.
- State $d$ will have $n - 2$ photons.
- State $c$ will have $n - 1$ photons.
- State $a$ will have $n$ photons.

The integrals will look like this:

$$
\langle b, n - 1 | V(t') | d, n - 2 \rangle \langle d, n - 2 | V(t'') | c, n - 1 \rangle \langle c, n - 1 | V(t''') | a, n \rangle
$$

Using the above number populations, the following substitutions are made:
Figure 2.1: Energy level representation of some of the possible time orderings for 2 $\gamma$ absorption 1 $\gamma$ emission. States c and d are virtual states, states a and b are physical states.

$$n_3 \equiv n - 1 \quad n_2 \equiv n - 1 \quad n_1 \equiv n$$

yielding

$$\langle b, n_3|V(t')|d, n_3 - 1\rangle\langle d, n_2 - 1|V(t'')|c, n_2\rangle\langle c, n_1 - 1|V(t''')|a, n_1\rangle$$

with six time orderings:

(i) $\psi_1 \downarrow \psi_2 \downarrow \psi_3 \downarrow a \rightarrow c \rightarrow d \rightarrow b$

(ii) $\psi_2 \downarrow \psi_1 \downarrow \psi_3 \downarrow a \rightarrow c \rightarrow d \rightarrow b$

(iii) $\psi_3 \downarrow \psi_1 \downarrow \psi_2 \downarrow a \rightarrow c \rightarrow d \rightarrow b$

(iv) $\psi_2 \downarrow \psi_3 \downarrow \psi_1 \downarrow a \rightarrow c \rightarrow d \rightarrow b$

(v) $\psi_1 \downarrow \psi_3 \downarrow \psi_2 \downarrow a \rightarrow c \rightarrow d \rightarrow b$

(vi) $\psi_2 \downarrow \psi_1 \downarrow \psi_3 \downarrow a \rightarrow c \rightarrow d \rightarrow b$

which gives
Figure 2.2: Feynman representation of the six permutations of photon ordering.

\[ \langle b|U_v|a \rangle \mid_{3\rightarrow d} = \left( \frac{-i}{\hbar} \right)^3 \sum_c \sum_d \int_0^t \int_0^{t'} \int_0^{t''} e^{iE_0 t'/\hbar} e^{iE_0 t''/\hbar} e^{iE_{\text{ext}} t''/\hbar} \]

\[ \times \{ \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \} \]

\[ + \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \} \]

\[ + \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \} \]

\[ + \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \} \]

\[ + \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \} \]

\[ + \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \} \]

The potential V is, in the absence of the electric dipole approximation,
\[ V(t) = \sum_i \frac{e}{mc} \vec{A}(\vec{r}_i, t) \cdot \vec{p}_i \]  

(2.11)

and the full vector potential becomes, for all three photons:

\[ \vec{A}(\vec{r}_i, t) = c \sqrt{\frac{\hbar}{\nu}} \left\{ \frac{1}{\sqrt{2\omega_1}} a_{k_1\alpha_1} \vec{e}_{\alpha_1} e^{i(\vec{k}_1 \cdot \vec{r}_i - \omega_1 t)} + \frac{1}{\sqrt{2\omega_2}} a_{k_2\alpha_2}^\dagger \vec{e}_{\alpha_2} e^{-i(\vec{k}_2 \cdot \vec{r}_i - \omega_2 t)} \right. \\
+ \frac{1}{\sqrt{2\omega_3}} a_{k_3\alpha_3}^\dagger \vec{e}_{\alpha_3} e^{-i(\vec{k}_3 \cdot \vec{r}_i - \omega_3 t)} \left. \right\} \]  

(2.12)

For \( \omega_3 \) emitted with \( \omega_1 \) and \( \omega_1 \) absorbed, the vector potential reduces to:

\[ \vec{A}(\vec{r}_i, t) = c \sqrt{\frac{\hbar}{\nu}} \left\{ \frac{1}{\sqrt{2\omega_1}} a_{k_1\alpha_1} \vec{e}_{\alpha_1} e^{i(\vec{k}_1 \cdot \vec{r}_i - \omega_1 t)} \right. \\
+ \frac{1}{\sqrt{2\omega_2}} a_{k_2\alpha_2} \vec{e}_{\alpha_2} e^{i(\vec{k}_2 \cdot \vec{r}_i - \omega_2 t)} \right. \\
+ \frac{1}{\sqrt{2\omega_3}} a_{k_3\alpha_3}^\dagger \vec{e}_{\alpha_3} e^{-i(\vec{k}_3 \cdot \vec{r}_i - \omega_3 t)} \left. \right\} \]  

(2.13)

If one wanted to include the pulse shape one would multiply each field component by a distribution amplitude envelope in time, \( f(t) \).

\[ \vec{A}(\vec{r}_i, t) = c \sqrt{\frac{\hbar}{\nu}} \left\{ \frac{1}{\sqrt{2\omega_1}} a_{k_1\alpha_1} \vec{e}_{\alpha_1} e^{i(\vec{k}_1 \cdot \vec{r}_i - \omega_1 t)} f_1(t) \right. \\
+ \frac{1}{\sqrt{2\omega_2}} a_{k_2\alpha_2} \vec{e}_{\alpha_2} e^{i(\vec{k}_2 \cdot \vec{r}_i - \omega_2 t)} f_2(t) \right. \\
+ \frac{1}{\sqrt{2\omega_3}} a_{k_3\alpha_3}^\dagger \vec{e}_{\alpha_3} e^{-i(\vec{k}_3 \cdot \vec{r}_i - \omega_3 t)} f_3(t) \left. \right\} \]  

(2.14)

and
\[ V(t) = -\frac{e}{m} \sqrt{\frac{\hbar}{v}} \sum_i \left\{ \frac{1}{\sqrt{2}\omega_1} a_{k_1\alpha_1} \vec{e}_{\alpha_1} \cdot \vec{F}_1 e^{i(k_1 \cdot \vec{r}_1 - \omega_1 t)} f_1(t) \right. \]
\[ \quad + \frac{1}{\sqrt{2}\omega_2} a_{k_2\alpha_2} \vec{e}_{\alpha_2} \cdot \vec{F}_2 e^{i(k_2 \cdot \vec{r}_2 - \omega_2 t)} f_2(t) \]
\[ \quad + \frac{1}{\sqrt{2}\omega_3} a_{k_3\alpha_3} \vec{e}_{\alpha_3} \cdot \vec{F}_3 e^{-i(k_3 \cdot \vec{r}_3 - \omega_3 t)} f_3(t) \} \]  

(2.15)

So the matrix element is expressed

\[ \langle b|U_v|a \rangle_{3rd} = \sum_{c,d} \left( \frac{-i}{\hbar} \right)^3 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{iE_{bd}t/\hbar} e^{iE_{dc}t''/\hbar} e^{iE_{ce}t'''/\hbar} \]
\[ \times \{(i) + (ii) + (iii) + (iv) + (v) + (vi)\} \]

2.3 (i) Term Integration

Examining only the (i) term,

\[ \sum_{c,d} \left( \frac{-i}{\hbar} \right)^3 \int t \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{iE_{bd}t/\hbar} e^{iE_{dc}t''/\hbar} e^{iE_{ce}t'''/\hbar} \]
\[ \times \langle b, n_3|V(t')|d, n_3 - 1 \rangle \langle d, n_2 - 1|V(t'')|c, n_2 \rangle \langle c, n_1 - 1|V(t''')|a, n_1 \rangle = \]

(2.16)
Substitution of 2.15 into the above expression yields:

\[
\sum_{c,d,i,j,k} \left( \frac{-ie}{m\sqrt{\hbar v}} \right)^3 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{iE_{bd}t'/\hbar} e^{iE_{ed}t''/\hbar} e^{iE_{ca}t'''/\hbar} \\
\times \langle b, n_3 \rangle \{ \frac{1}{\sqrt{2}\omega_1} a_{k_1a_1} \cdot \bar{P}_1 e^{i(k_1 \cdot \vec{r}_1 - \omega_1 t_1)} f_1(t_1) \\
+ \frac{1}{\sqrt{2}\omega_2} a_{k_2a_2} \cdot \bar{P}_2 e^{i(k_2 \cdot \vec{r}_2 - \omega_2 t_2)} f_2(t_2) \\
+ \frac{1}{\sqrt{2}\omega_3} a_{k_3a_3} \cdot \bar{P}_3 e^{i(k_3 \cdot \vec{r}_3 - \omega_3 t_3)} f_3(t_3) \} |d, n_3 - 1\rangle
\]

\[
\times \langle d, n_2 - 1 \rangle \{ \frac{1}{\sqrt{2}\omega_1} a_{k_1a_1} \cdot \bar{P}_1 e^{i(k_1 \cdot \vec{r}_j - \omega_1 t_2)} f_1(t_2) \\
+ \frac{1}{\sqrt{2}\omega_2} a_{k_2a_2} \cdot \bar{P}_2 e^{i(k_2 \cdot \vec{r}_j - \omega_2 t_2)} f_2(t_2) \\
+ \frac{1}{\sqrt{2}\omega_3} a_{k_3a_3} \cdot \bar{P}_3 e^{-i(k_3 \cdot \vec{r}_j - \omega_3 t_2)} f_3(t_2) \} |c, n_2\rangle
\]

\[
\times \langle c, n_1 - 1 \rangle \{ \frac{1}{\sqrt{2}\omega_1} a_{k_1a_1} \cdot \bar{P}_1 e^{i(k_1 \cdot \vec{r}_k - \omega_1 t_3)} f_1(t_3) \\
+ \frac{1}{\sqrt{2}\omega_2} a_{k_2a_2} \cdot \bar{P}_2 e^{i(k_2 \cdot \vec{r}_k - \omega_2 t_3)} f_2(t_3) \\
+ \frac{1}{\sqrt{2}\omega_3} a_{k_3a_3} \cdot \bar{P}_3 e^{-i(k_3 \cdot \vec{r}_k - \omega_3 t_3)} f_3(t_3) \} |a, n_1\rangle
\]

(2.17)

Allowing each creation/annihilation operator to work on the kets simplifies the expression, as two thirds of the transformed field number state vectors will be orthogonal to their associated bras. Carrying out this number space integration yields:

\[
\sum_{c,d,i,j,k} \left( \frac{-ie}{m\sqrt{\hbar v}} \right)^3 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{iE_{bd}t'/\hbar} e^{iE_{ed}t''/\hbar} e^{iE_{ca}t'''/\hbar} \\
\times \sqrt{\frac{n_3}{2\omega_3}} \langle b|\vec{c}_3 \cdot \bar{P}_1 e^{-i(k_3 \cdot \vec{r}_1 - \omega_3 t_3)} f_3(t_3)|d\rangle \\
\times \sqrt{\frac{n_2}{2\omega_2}} \langle d|\vec{c}_2 \cdot \bar{P}_2 e^{-i(k_2 \cdot \vec{r}_2 - \omega_2 t_2)} f_3(t_2)|c\rangle \\
\times \sqrt{\frac{n_1}{2\omega_1}} \langle c|\vec{c}_1 \cdot \bar{P}_3 e^{-i(k_1 \cdot \vec{r}_k - \omega_1 t_3)} f_3(t_3)|a\rangle
\]

(2.18)
Finally, the entire expression can be factored, culling out the time dependent from time independent integrals.

\[
\left( \frac{-ie}{m \sqrt{\hbar v}} \right)^3 \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b | \tilde{e}_3 \cdot \tilde{P}_1 e^{-i \tilde{k}_1 \cdot \tilde{r}_i} | d \rangle \langle d | \tilde{e}_2 \cdot \tilde{P}_2 e^{-i \tilde{k}_2 \cdot \tilde{r}_j} | c \rangle \langle c | \tilde{e}_1 \cdot \tilde{P}_k e^{-i \tilde{k}_3 \cdot \tilde{r}_k} | a \rangle
\]

\[
\times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{i(E_{bd}/\hbar - \omega_1) t'} f_3(t') e^{i(E_{de}/\hbar - \omega_2) t''} f_2(t'') e^{i(E_{ca}/\hbar - \omega_3) t'''} f_1(t''')
\]

\[
= \text{(constant) (three spatial integrals)(three temporal integrals)} \quad (2.19)
\]

2.4 The (ii)--(vi) Terms

Permutation of the association of each transition's photon label gives the form of the remaining five time ordered terms, yielding:

term (ii):

\[
\left( \frac{-ie}{m \sqrt{\hbar v}} \right)^3 \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b | \tilde{e}_3 \cdot \tilde{P}_1 e^{-i \tilde{k}_1 \cdot \tilde{r}_i} | d \rangle \langle d | \tilde{e}_2 \cdot \tilde{P}_2 e^{-i \tilde{k}_2 \cdot \tilde{r}_j} | c \rangle \langle c | \tilde{e}_1 \cdot \tilde{P}_k e^{-i \tilde{k}_3 \cdot \tilde{r}_k} | a \rangle
\]

\[
\times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{i(E_{bd}/\hbar - \omega_1) t'} f_3(t') e^{i(E_{de}/\hbar - \omega_2) t''} f_2(t'') e^{i(E_{ca}/\hbar + \omega_3) t'''} f_1(t''')
\]

\[
(2.20)
\]
term (ii):
\[
\frac{(-ie)^3}{m^2 \hbar^2} \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b| \tilde{e}_2 \cdot \vec{P}_1 e^{-i \vec{k}_2 \cdot \vec{r}_1} |d \rangle \langle d| \tilde{e}_3 \cdot \vec{P}_2 e^{-i \vec{k}_3 \cdot \vec{r}_1} |c \rangle \langle c| \tilde{e}_1 \cdot \vec{P}_k e^{-i \vec{k}_1 \cdot \vec{r}_k} |a \rangle \\
\times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{i(\omega_1/k - \omega_2)} f_2(t') e^{i(\omega_2/k + \omega_3)} f_3(t'') f_1(t''')
\]
(2.21)

term (iii):
\[
\frac{(-ie)^3}{m^2 \hbar^2} \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b| \tilde{e}_3 \cdot \vec{P}_2 e^{-i \vec{k}_3 \cdot \vec{r}_1} |d \rangle \langle d| \tilde{e}_1 \cdot \vec{P}_3 e^{-i \vec{k}_1 \cdot \vec{r}_3} |c \rangle \langle c| \tilde{e}_2 \cdot \vec{P}_k e^{-i \vec{k}_2 \cdot \vec{r}_k} |a \rangle \\
\times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{i(\omega_1/k - \omega_2)} f_2(t') e^{i(\omega_2/k + \omega_3)} f_1(t'') f_3(t''')
\]
(2.22)

term (iv):
\[
\frac{(-ie)^3}{m^2 \hbar^2} \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b| \tilde{e}_3 \cdot \vec{P}_1 e^{-i \vec{k}_3 \cdot \vec{r}_1} |d \rangle \langle d| \tilde{e}_2 \cdot \vec{P}_3 e^{-i \vec{k}_2 \cdot \vec{r}_2} |c \rangle \langle c| \tilde{e}_1 \cdot \vec{P}_k e^{-i \vec{k}_1 \cdot \vec{r}_k} |a \rangle \\
\times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{i(\omega_1/k + \omega_3)} f_3(t') e^{i(\omega_2/k + \omega_3)} f_1(t'') f_2(t''')
\]
(2.23)

term (v):
\[
\frac{(-ie)^3}{m^2 \hbar^2} \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b| \tilde{e}_3 \cdot \vec{P}_1 e^{-i \vec{k}_3 \cdot \vec{r}_1} |d \rangle \langle d| \tilde{e}_2 \cdot \vec{P}_2 e^{-i \vec{k}_2 \cdot \vec{r}_2} |c \rangle \langle c| \tilde{e}_1 \cdot \vec{P}_k e^{-i \vec{k}_1 \cdot \vec{r}_k} |a \rangle \\
\times \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 e^{i(\omega_1/k + \omega_2)} f_3(t') e^{i(\omega_2/k + \omega_3)} f_2(t'') f_1(t''')
\]
(2.24)
term (vi):

$$
(-ie \frac{1}{m \sqrt{h \nu}})^3 \sqrt{\frac{n_1 n_2 n_3}{8 \omega_1 \omega_2 \omega_3}} \sum_{c,d,i,j,k} \langle b| \bar{e}_1 \cdot \bar{P}_1 e^{-i \bar{r}_1 \cdot \bar{r}_1} |d\rangle \langle d| \bar{e}_3 \cdot \bar{P}_2 e^{-i \bar{r}_3 \cdot \bar{r}_3} |c\rangle \langle c| \bar{e}_2 \cdot \bar{P}_k e^{-i \bar{r}_k \cdot \bar{r}_k} |a\rangle
$$

\[
\times \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t_2} dt_2 \int_{-\infty}^{t'} dt_3 e^{i(E_{bd}/h - \omega_1)t'} f_1(t') e^{i(E_{de}/h + \omega_3)t''} f_3(t'') e^{i(E_{ca}/h - \omega_2)t'''} f_2(t''')
\]

(2.25)

2.5 Temporal Integration

From this point on the focus shall be placed upon the temporal integration and with different forms of the pulse envelope \( f(t) \).

2.5.1 \( f(t) = 1 \)

Of course the simplest temporal pulse shape would be no pulse at all, that is, a steady state of radiation for each field, \( f(t) = 1 \). In this case, the temporal portion of term
(i) shown in expression 2.19 becomes

\[
\int_0^t dt_1 e^{i(E_{bd}/h + \omega_3) t_1} \int_0^{t_1} dt_2 e^{i(E_{dc}/h - \omega_2) t_2} \int_0^{t_2} dt_3 e^{i(E_{ca}/h - \omega_1) t_3} \\
= \int_0^t dt_1 e^{i(E_{bd}/h - \omega_3) t_1} \int_0^{t_1} dt_2 e^{i(E_{dc}/h - \omega_2) t_2} \left( \frac{e^{i(E_{ca}/h - \omega_1) t_3} - 1}{i(E_{ca}/h - \omega_1)} \right) \\
= \int_0^t dt_1 e^{i(E_{bd}/h + \omega_3) t_1} \int_0^{t_1} dt_2 \left( \frac{e^{i((E_{ca}+E_{dc})/h - \omega_1 - \omega_2) t_2} - e^{i(E_{dc}/h - \omega_2) t_2}}{i(E_{ca}/h + \omega_1)} \right) \\
= \int_0^t dt_1 e^{i(E_{bd}/h + \omega_3) t_1} \left\{ \frac{e^{i((E_{ca}+E_{dc})/h - \omega_1 - \omega_2) t'} - 1}{i^2(E_{ca}/h - \omega_1)((E_{dc}+E_{ca})/h - \omega_1 - \omega_2)} \right. \\
\left. - \frac{e^{i(E_{dc}/h - \omega_2) t'} - 1}{i^2(E_{dc}/h + \omega_2)(E_{ca}/h - \omega_1)} \right\} \\
= \int_0^t dt_1 \left\{ \frac{e^{i((E_{ca}+E_{dc}+E_{bd})/h - \omega_1 - \omega_2 + \omega_3) t'}}{i^3(E_{ca}/h - \omega_1)((E_{dc}+E_{ca})/h - \omega_1 - \omega_2) ((E_{ca}+E_{dc}+E_{bd})/h - \omega_1 - \omega_2 + \omega_3)} \\
- \frac{e^{i(E_{bd}/h + \omega_3) t_1}}{i^3(E_{ca}/h - \omega_1)((E_{dc}+E_{ca})/h - \omega_1 - \omega_2)(E_{bd}/h + \omega_3)} \\
+ \frac{e^{i(E_{dc}/h + \omega_2)(E_{ca}/h - \omega_1)(E_{bd}/h + \omega_3)}}{i^3(E_{dc}/h + \omega_2)(E_{ca}/h - \omega_1)((E_{dc}+E_{bd})/h - \omega_2 + \omega_3)} \\
- \frac{e^{i((E_{dc}+E_{bd})/h - \omega_2 + \omega_3) t'}}{i^3(E_{dc}/h + \omega_2)(E_{ca}/h - \omega_1)(E_{dc}+E_{bd})/h - \omega_2 + \omega_3)} \right\} \Bigg|_0^t
\]
\[
\left\{ \begin{array}{l}
\frac{\exp\left(\frac{i((E_{ca} + E_{dc} + E_{bd})/h - \omega_1 - \omega_2 + \omega_3)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
- \frac{\exp\left(\frac{i(E_{bd}/h + \omega_3)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
+ \frac{\exp\left(\frac{i(E_{dc}/h + \omega_2)(E_{ca}/h - \omega_1)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
- \frac{\exp\left(\frac{i((E_{dc} + E_{bd})/h - \omega_1)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
\end{array} \right\}
\]

(2.26)

Imposing an energy conservation constraint \((E_{ca} + E_{dc} + E_{bd})/h - \omega_1 - \omega_2 + \omega_3) = 0\) will simplify the above slightly by through the resultant elimination of the first term in the sum, yielding:

\[
\left\{ \begin{array}{l}
\frac{\exp\left(\frac{i(E_{bd}/h + \omega_3)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
- \frac{\exp\left(\frac{i(E_{dc}/h + \omega_2)(E_{ca}/h - \omega_1)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
+ \frac{\exp\left(\frac{i((E_{dc} + E_{bd})/h - \omega_1)}{\omega_1 - \omega_2 + \omega_3}\right)}{i^3(\omega_1 - \omega_2 + \omega_3)}
\end{array} \right\}
\]

(2.27)

Permutation of indices and signs yields similar expressions for the remaining five terms (ii)–(vi).
2.5.2 $f(t) = \cos^2(t)$

Since the Gaussian pulse is mathematically intractable, a qualitatively similar but integratable pulse profile can be found in the $\cos^2$ envelope. The $\cos^2$ function will be gated with Heavyside step functions to eliminate the periodicity of the trigonometric function. The square gate will have width $2\gamma$.

$$f(t) = \cos^2((t - t^0)\frac{\pi}{2\gamma})\Theta(t - (t^0 - \gamma))\Theta(t^0 + \gamma - t)$$ (2.28)

The first temporal integral becomes:

$$\int_{-\infty}^{t''} e^{iQ t'''} f(t''') dt''' = \int_{t_1^0 - \gamma_1}^{X} \cos^2[(t''' - t_1^0)\frac{\pi}{2\gamma_1}] e^{iQ t'''} f(t''') dt'''$$

$$X = \begin{cases} 
  t'' & t'' < t_1^0 + \gamma \\
  t_1^0 + \gamma & t'' > t_1^0 + \gamma 
\end{cases}$$ (2.29)

For these finite limit integrals, a single integration yields an Error Function, which, although well characterized, is not the kind of analytic function desired for repeated integration through the nested integrals in this development.
Henceforth, in order to compact the notation, \( Q \) will denote the quantity \( E_{ca}/\hbar - \omega_1 \), \( R \) will represent \( E_{dc}/\hbar - \omega_2 \) and \( S \) will be used in place of \( E_{bd}/\hbar + \omega_3 \).

Noting that
\[
\cos^2(x) = \frac{1}{2}(\cos(2x) + 1) = \frac{1}{2} \left( \frac{e^{i2x} + e^{-i2x}}{2} + 1 \right)
\]

\[
\int_{-\infty}^{t''} e^{iQt''} f(t'') dt''
\]

\[
= \frac{1}{2} \int_{t_0 - \gamma_1}^{X} \left\{ \frac{e^{i(Q+\pi/\gamma_1)t''-t_0^0 \pi/\gamma_1}}{2} + \frac{e^{i(Q-\pi/\gamma_1)t''+t_0^0 \pi/\gamma_1}}{2} + e^{iQt''} \right\} dt''
\]

\[
= \left\{ \frac{e^{i(Q+\pi/\gamma_1)t''} e^{-t_0^0 \pi/\gamma_1}}{4i(Q + \pi/\gamma_1)} + \frac{e^{i(Q-\pi/\gamma_1)t''} e^{t_0^0 \pi/\gamma_1}}{4i(Q - \pi/\gamma_1)} + \frac{e^{iQt''}}{2iQ} \right\} \bigg|_{t_0^0 - \gamma_1}^{X}
\]

\[
= \frac{e^{-t_0^0 \pi/\gamma_1} (e^{i(Q+\pi/\gamma_1)X} - e^{i(Q+\pi/\gamma_1)(t_0^0 \pi/\gamma_1))}}{4i(Q + \pi/\gamma_1)}
\]

\[
+ \frac{e^{t_0^0 \pi/\gamma_1} (e^{i(Q-\pi/\gamma_1)X} - e^{i(Q-\pi/\gamma_1)(t_0^0 \pi/\gamma_1))}}{4i(Q - \pi/\gamma_1)}
\]

\[
+ \frac{e^{iQX} - e^{iQ(t_0^0 - \gamma_1)}}{2iQ}
\]

(2.30)

At this point, a brief inspection of the exponent \((Q + \pi/\gamma)(t^0 - \gamma)\) is warranted.

\[
(Q + \pi/\gamma)(t^0 - \gamma) = Qt^0 - Q\gamma + \pi t^0/\gamma - \pi
\]

Multiplying the leading exponential \(e^{-t^0 \pi/\gamma}\) will add another term to the exponent yielding:

\[
Qt^0 - Q\gamma + \pi t^0/\gamma - \pi - t^0 \pi/\gamma = Qt^0 - Q\gamma - \pi
\]
The trailing $-\pi$ represents a phase factor which merely changes the sign of the coefficient of the exponential, so the simplified form of the first temporal integration becomes:

$$\int_{-\infty}^{t''} e^{iQ t''} f(t'') dt''$$

$$= e^{-\frac{\pi}{\gamma_1} e^{i(Q+\pi/\gamma_1)X} + e^{iQ(t''_1)}}$$

$$+ \frac{4i(Q+\pi/\gamma_1)}{e^{i\pi/\gamma_1} e^{i(Q-\pi/\gamma_1)X + e^{iQ(\text{naught1-)}}}}$$

$$+ \frac{e^{iQX} - e^{iQ(\text{naught1-)}}}{2iQ}$$

(2.31)

The next level of temporal integration is:

$$\int_{-\infty}^{t'} \left[ \text{eq.2.31} \right] f_2(t'') e^{iR t''} dt''$$

where $R \equiv E_{cd}/h - \omega_2$.

$$\int_{-\infty}^{t'} \left[ \text{eq.2.31} \right] \frac{1}{2} \left( e^{i(R+\pi/\gamma_2)t'' - \pi t''_2} + e^{i(R-\pi/\gamma_2)t'' + i\pi t''_2} + e^{iR t''} \right) dt''$$

$$= \int_{-\infty}^{t'} \left[ \text{eq.2.31} \right] \frac{e^{i(R+\pi/\gamma_2)t''} e^{-i\pi t''_2/\gamma_2}}{4} dt''$$

(2.32a)

$$+ \int_{-\infty}^{t'} \left[ \text{eq.2.31} \right] \frac{e^{i(R-\pi/\gamma_2)t''} e^{i\pi t''_2/\gamma_2}}{4} dt''$$

(2.32b)

$$+ \int_{-\infty}^{t'} \left[ \text{eq.2.31} \right] \frac{e^{iR t''}}{2} dt''$$

(2.32c)

Examination of term 2.32a will follow, with the following notation:

$$Q^\pm \equiv Q \pm \frac{\pi}{\gamma_1} \quad R^\pm \equiv R \pm \frac{\pi}{\gamma_1} \quad S^\pm \equiv S \pm \frac{\pi}{\gamma_1}$$
\[ [2.32a] = \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \int_{-\infty}^{t'} \frac{e^{iR+t''}}{iQ^+} dt'' \]

\[ = \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \int_{t_2}^{Y} \frac{e^{-i\pi t_1^0/\gamma_1} e^{iQ+} x e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}{4iQ^+} dt'' \]  
\[ + \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \int_{t_2}^{Y} \frac{e^{i\pi t_1^0/\gamma_1} e^{iQ-} x e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}{4iQ^-} dt'' \]  
\[ + \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \int_{t_2}^{Y} \frac{e^{iQ} x e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}{2iQ} dt'' \]  
(2.33a)  
(2.33b)  
(2.33c)

where

\[ Y = \begin{cases} 
  t' & t' < t_2^0 + \gamma_2 \\
  t_2^0 + \gamma_2 & t' > t_2^0 + \gamma_2 
\end{cases} \quad \text{and} \quad X = \begin{cases} 
  t'' & t'' < t_1^0 + \gamma_1 \\
  t_1^0 + \gamma_1 & t'' > t_1^0 + \gamma_1 
\end{cases} \]

Examination of only term 2.33a shows:

\[ [2.33a] = \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \int_{t_2}^{t_1^0+\gamma_1} \left( \frac{e^{-i\frac{\pi t_1^0}{\gamma_1} e^{iQ+} X e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}}{4iQ^+} \right) dt'' \]
\[ + \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \int_{t_2}^{Y} \left( \frac{e^{-i\frac{\pi t_1^0}{\gamma_1} e^{iQ-} X e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}}{4iQ^-} \right) dt'' \]
\[ + \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \left\{ \frac{e^{-i\frac{\pi t_1^0}{\gamma_1} e^{i(Q^+ + R^+)} x e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}}{i2Q^+ (Q^+ + R^+)} + \frac{e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}{i2Q^+ + R^+} \right\} \bigg|_{t''=t_1^0+\gamma_1}^{t''=t_2-\gamma_2} \]
\[ + \frac{1}{4} e^{-i\frac{\pi t_2}{\gamma_2}} \left\{ \frac{e^{-i\frac{\pi t_1^0}{\gamma_1} e^{i(Q^+ + R^+)} x e^{iR+t''} + e^{i(t_1^0-\gamma_1)Q} e^{iR+t''}}}{iR^+} \right\} \bigg|_{t''=t_1^0+\gamma_1}^{t''=t_2-\gamma_2} \]
[2.33a] = \frac{1}{4} e^{-it^2 \pi/\gamma} \left\{ \frac{e^{-it^2 \pi/\gamma} \left( e^{i(Q^+ + R^+)(t^2 + \gamma)} - e^{i(Q^+ + R^+)(t^2 - \gamma)} \right)}{i^2 4Q^+(Q^+ + R^+)} \right. \\
+ \frac{e^{i(t^2 - \gamma)Q} \left( e^{iR^+(t^2 + \gamma)} - e^{iR^+(t^2 - \gamma)} \right)}{i^2 \tau Q^+ + R^+} \\
+ \left( \frac{e^{-it^2 \pi/\gamma} e^{i(Q^+ + R^+)(t^2 + \gamma)} + e^{i(t^2 - \gamma)Q}}{4iQ^+} \right) \frac{e^{iR^+Y} - e^{iR^+(t^2 + \gamma)}}{iR^+} \right\}

Again, the leading factor $e^{-it_2^2 \pi/\gamma}$ will be absorbed by using the definition $R^+ = R + \pi/\gamma$ thus:

$-e^{-it^2 \pi/\gamma} e^{R^+(t^2 - \gamma)^2} = -e^{-it^2 \pi/\gamma} e^{R(t^2 - \gamma^2) + \frac{\pi}{\gamma} (t^2 - \gamma^2)}
+ e^{(Q^+ + R)(t^2 - \gamma)}

[2.33a] = \frac{e^{-it^2 \pi/\gamma} \left( e^{-it^2 \pi/\gamma} e^{i(Q^+ + R^+)(t^2 + \gamma)} + e^{i(Q^+ + R)(t^2 - \gamma)} \right)}{i^2 16Q^+(Q^+ + R^+)} \\
+ \frac{e^{i(t^2 - \gamma)Q} \left( e^{iR^+(t^2 + \gamma)} + e^{iR^+(t^2 - \gamma)} \right)}{i^2 16Q^+ + R^+} \\
+ \frac{e^{-it^2 \pi/\gamma} \left( e^{-it^2 \pi/\gamma} e^{i(Q^+(t^2 + \gamma)} + e^{i(t^2 - \gamma)Q} \right) \left( e^{iR^+Y} - e^{iR^+(t^2 + \gamma)} \right)}{i^2 16Q^+ + R^+}

[2.33b] is exactly the same as [2.33a] with the following transformations:

e^{-it^2 \pi/\gamma} \to e^{it^2 \pi/\gamma}, \quad Q^+ \to Q^-

[2.33b] = \frac{e^{it^2 \pi/\gamma} \left( e^{-it^2 \pi/\gamma} e^{i(Q^- + R^+)(t^2 + \gamma)} + e^{i(Q^+ + R)(t^2 - \gamma)} \right)}{i^2 16Q^- (Q^- + R^+)} \\
+ \frac{e^{i(t^2 - \gamma)Q} \left( e^{iR^+(t^2 + \gamma)} + e^{iR^+(t^2 - \gamma)} \right)}{i^2 16Q^- + R^+} \\
+ \frac{e^{-it^2 \pi/\gamma} \left( e^{it^2 \pi/\gamma} e^{i(Q^-(t^2 + \gamma)} + e^{i(t^2 - \gamma)Q} \right) \left( e^{iR^+Y} - e^{iR^+(t^2 + \gamma)} \right)}{i^2 16Q^- + R^+}
Similarly, the final term of 2.32a, term 2.33c, becomes, when integrated:

\[
[2.33c] = \frac{e^{-it_0^2 \pi / \gamma} e^{i(Q^+ + R^+)(t_0^2 + \gamma)} + e^{i(Q + R)(t_2 - T)}}{i^2 8 Q (Q + R^+)} \\
\frac{e^{-it_0^2 \pi / \gamma} e^{Q(t_0^2 + \gamma)} \left( e^{iR^+ Y} - e^{iR^+(t_2 + \gamma)} \right)}{i^2 8 R^+ Q} \\
\frac{e^{iQ(t_2 - \gamma)} \left( e^{-it_2^2 \pi / \gamma} e^{iR^+ Y} + e^{iR(t_2 - T)} \right)}{i^2 8 Q (Q + R^+)}
\]

(2.34)

\[
[2.33c] = \frac{e^{-it_0^2 \pi / \gamma} e^{i(Q + R^+)(t_0^2 + \gamma)} + e^{i(Q + R)(t_2 - T)}}{i^2 8 Q (Q + R^+)} \\
\frac{e^{-it_0^2 \pi / \gamma} e^{Q(t_0^2 + \gamma)} \left( e^{iR^+ Y} - e^{iR^+(t_2 + \gamma)} \right)}{i^2 8 R^+ Q} \\
\frac{e^{iQ(t_2 - \gamma)} \left( e^{-it_2^2 \pi / \gamma} e^{iR^+ Y} + e^{iR(t_2 - T)} \right)}{i^2 8 Q (Q + R^+)}
\]

and this completes term 2.32a = 2.33a + 2.33b + 2.33c.

\[
[2.32a] = \frac{e^{-it_0^2 \pi / \gamma} \left( e^{-it_0^2 \pi / \gamma} e^{i(Q^+ + R^+)(t_0^2 + \gamma)} + e^{i(Q^+ + R)(t_2 - T)} \right)}{i^2 16 Q^+(Q^+ + R^+)} \\
\frac{e^{i(t_0^2 - \gamma) Q} \left( e^{iR^+(t_0^2 + \gamma)} + e^{iR(t_2 - T)} \right)}{i^2 16 Q^+ R^+} \\
\frac{e^{-it_0^2 \pi / \gamma} \left( e^{-it_0^2 \pi / \gamma} e^{i(Q^+ + R^+)(t_0^2 + \gamma)} + e^{i(Q^+ + R)(t_2 - T)} \right)}{i^2 16 Q^+ R^+} \\
\frac{e^{i(t_0^2 - \gamma) Q} \left( e^{iR^+(t_0^2 + \gamma)} + e^{iR(t_2 - T)} \right)}{i^2 16 Q^+ R^+} \\
\frac{e^{-it_0^2 \pi / \gamma} \left( e^{-it_0^2 \pi / \gamma} e^{i(Q^- + R^+)(t_0^2 + \gamma)} + e^{i(Q^- + R)(t_2 - T)} \right)}{i^2 16 Q^- (Q^- + R^+)} \\
\frac{e^{i(t_0^2 - \gamma) Q} \left( e^{iR^+(t_0^2 + \gamma)} + e^{iR(t_2 - T)} \right)}{i^2 16 Q^- R^+} \\
\frac{e^{-it_0^2 \pi / \gamma} \left( e^{i(t_0^2 - \gamma) Q} \left( e^{iR^+(t_0^2 + \gamma)} + e^{iR(t_2 - T)} \right) \right)}{i^2 16 Q^- R^+} \\
\frac{e^{-it_0^2 \pi / \gamma} e^{i(Q^+ + R^+)(t_0^2 + \gamma)} + e^{i(Q + R)(t_2 - T)}}{i^2 8 Q (Q + R^+)} \\
\frac{e^{-it_2^2 \pi / \gamma} e^{Q(t_2^2 + \gamma)} \left( e^{iR^+ Y} - e^{iR^+(t_2 + \gamma)} \right)}{i^2 8 R^+ Q} \\
\frac{e^{iQ(t_2 - \gamma)} \left( e^{-it_2^2 \pi / \gamma} e^{iR^+ Y} + e^{iR(t_2 - T)} \right)}{i^2 8 Q (Q + R^+)}
\]
Next comes evaluation of term 2.32b:

\[
[2.32b] = \int_{-\infty}^{t'} \left[ \text{term 2.31} \right] \frac{e^{i(R-\pi/\gamma_2)t''} e^{+it_2^0 \pi/\gamma_2}}{4} dt''
\]

which is identical to expression 2.5.2, providing these transforms are made:

\[
R^+ \rightarrow R^- \quad e^{-it_2^0 \pi/\gamma_2} \rightarrow e^{+it_2^0 \pi/\gamma_2}
\]

\[
[2.32b] = \frac{e^{-it_2^0 \pi/\gamma_2} \left( e^{+it_2^0 \pi/\gamma_2} e^{i(Q^+ + R^-)(t_2^0 + \gamma_1)} + e^{i(Q^+ + R)(t_2^0 - \gamma_2)} \right)}{i^2 16 Q^+(Q^+ + R^-)}
\]

\[
+ \frac{e^{i(t_2^0 - \gamma_1)Q} \left( e^{R^-(t_2^0 + \gamma_1)} + e^{iR(t_2^0 - \gamma_2)} \right)}{i^2 16 Q^+ R^-}
\]

\[
+ \frac{e^{-it_2^0 \pi/\gamma_2} \left( e^{+it_2^0 \pi/\gamma_2} e^{i(Q^- + R^-)(t_2^0 + \gamma_1)} + e^{i(Q^- + R)(t_2^0 - \gamma_2)} \right)}{i^2 16 Q^- R^-}
\]

\[
+ \frac{e^{i(t_2^0 - \gamma_1)Q} \left( e^{R^-Y} - e^{iR^-(t_2^0 + \gamma_1)} \right)}{i^2 16 Q^+ R^-}
\]

\[
+ \frac{e^{-it_2^0 \pi/\gamma_2} \left( e^{+it_2^0 \pi/\gamma_2} e^{i(Q^+ + R^-)(t_2^0 + \gamma_1)} + e^{i(Q^+ + R)(t_2^0 - \gamma_2)} \right)}{i^2 8 Q(Q + R^-)}
\]

\[
+ \frac{e^{iR^-Y} - e^{iR^-(t_2^0 + \gamma_1)}}{i^2 8 R^- Q}
\]

\[
+ \frac{e^{iR^-Y} + e^{iR(t_2^0 - \gamma_2)}}{i^2 8 Q(Q + R^-)}
\]

The final portion of this time integral is term [2.32c] which is similar to term [2.32a] with

\[
R \rightarrow R^-, \quad R^+ \rightarrow R
\]

and an overall phase factor of \(2e^{+it_2^0 \pi/\gamma_2}\) multiplied on all terms.
\[ [2.32c] = 2e^{+it_2^2 \pi/\gamma_2} \left\{ \frac{e^{-it_2^2 \pi/\gamma_2} (e^{-it_2^2 \pi/\gamma_2} e^{i(Q^+ + R)(t_2^2 + \gamma_2) + e^{i(Q^+ + R)(t_2^2 - \gamma_2)})}{i^2 16Q^+ (Q^+ + R)} \right. \\
+ \frac{e^{i(t_2^2 - \gamma_2) Q} (e^{iR(t_2^2 + \gamma_2)} + e^{iR^-(t_2^2 - \gamma_2)})}{i^2 16Q^+ R} \\
+ \frac{e^{-it_2^2 \pi/\gamma_2} (e^{-it_2^2 \pi/\gamma_2} e^{i(Q^+ + R)(t_2^2 + \gamma_2) + e^{i(Q^+ + R)(t_2^2 - \gamma_2)})}{i^2 16Q^- (Q^- + R)} \right. \\
+ \frac{e^{i(t_2^2 - \gamma_2) Q} (e^{iR(t_2^2 + \gamma_2)} + e^{iR^-(t_2^2 - \gamma_2)})}{i^2 16Q^- R} \\
+ \frac{e^{-it_2^2 \pi/\gamma_2} (e^{i(Q^- + R)(t_2^2 + \gamma_2) + e^{i(Q^- + R)(t_2^2 - \gamma_2)})}{i^2 16Q^- R} \\
+ \frac{e^{-it_2^2 \pi/\gamma_2} e^{i(Q^+ + R)(t_2^2 + \gamma_2) + e^{i(Q^+ + R^-(t_2^2 - \gamma_2)}}}{i^2 8Q (Q + R)} \\
+ \frac{e^{-it_2^2 \pi/\gamma_2} e^{iQ(t_2^2 + \gamma_2) + e^{iR(t_2^2 - \gamma_2)}}}{i^2 8RQ} \\
- \frac{e^{iQ(t_2^2 - \gamma_2) (e^{-it_2^2 \pi/\gamma_2} e^{iR(t_2^2 - \gamma_2)})}{i^2 8Q (Q + R)} \right\} \\
\]

And this completes the second layer of temporal integration. Adding all these terms gives:
\[
\int_{-\infty}^{t'} \left[ f_2(t''') e^{iR''} dt'' \right] = [2.5.2] + [2.35] = \\
\frac{e^{-it_2^0 \pi / \gamma_1} \left( e^{-it_2^0 \pi / \gamma_2} e^{i(Q^+ + R^+)(\ell_i^0 + \gamma_1)} + e^{i(Q^+ + R^+)(\ell_i^0 - \gamma_2)} \right)}{i^2 16Q^+ (Q^+ + R^+)} \\
+ \frac{e^{i(t_i^0 - \gamma_1)Q} \left( e^{iR^+ (\ell_i^0 + \gamma_1)} + e^{iR^+ (\ell_i^0 - \gamma_2)} \right)}{i^2 16Q^+ R^+} \\
+ \frac{e^{-it_2^0 \pi / \gamma_2} \left( e^{-it_2^0 \pi / \gamma_1} e^{i(Q^- + R^+)(\ell_i^0 + \gamma_1)} + e^{i(Q^- + R^+)(\ell_i^0 - \gamma_2)} \right)}{i^2 16Q^- (Q^- + R^+)} \\
+ \frac{e^{i(t_i^0 - \gamma_1)Q} \left( e^{iR^+ (\ell_i^0 + \gamma_1)} + e^{iR^+ (\ell_i^0 - \gamma_2)} \right)}{i^2 16Q^- R^+} \\
+ \frac{e^{-it_2^0 \pi / \gamma_2} e^{i(Q^- R^+)(\ell_i^0 + \gamma_1)} + e^{i(Q^- R^+)(\ell_i^0 - \gamma_2)}}{i^2 16Q^- (Q^- + R^+)} \\
+ \frac{e^{i(t_i^0 - \gamma_1)Q} \left( e^{iR^+ (\ell_i^0 + \gamma_1)} + e^{iR^+ (\ell_i^0 - \gamma_2)} \right)}{i^2 16Q^- R^+} \\
+ \frac{e^{-it_2^0 \pi / \gamma_2} e^{i(Q+ R^+)(\ell_i^0 + \gamma_1)} + e^{i(Q+ R^+)(\ell_i^0 - \gamma_2)}}{i^2 8Q(Q + R^+)} 
\]
\[
\frac{e^{-it_1^0\pi/\gamma_1}e^{Q(t_0^1+\eta_1)}}{i^28R^+Q} \left( e^{iR^+Y} - e^{iR^+(t_0^1+\eta_1)} \right) \\
+ \frac{e^{iQ(t_0^1-\eta_1)}\left( e^{-it_1^0\pi/\gamma_2}e^{iR^+Y} + e^{iR(t_0^2-\eta_2)} \right)}{i^28Q(Q + R^+)} \\
+ \frac{e^{-it_1^0\pi/\gamma_1} \left( e^{+it_2^0\pi/\gamma_2}e^{i(Q^+-R^-)(t_0^1+\eta_1)} + e^{i(Q^+-R^+)(t_0^2-\eta_2)} \right)}{i^216Q^+(Q^+ + R^-)} \\
+ \frac{e^{i(t_0^1-\eta_1)Q} \left( e^{iR^-(t_0^1+\eta_1)} + e^{iR(t_0^2-\eta_2)} \right)}{i^216Q^-R^-} \\
+ \frac{e^{+it_2^0\pi/\gamma_2} \left( e^{-it_1^0\pi/\gamma_1}e^{iQ^+(t_0^1+\eta_1)} + e^{i(t_0^2-\eta_2)Q} \right) \left( e^{iR^-Y} - e^{iR^-(t_0^2+\eta_2)} \right)}{i^216Q^+R^-} \\
+ \frac{e^{+it_1^0\pi/\gamma_1} \left( e^{-it_2^0\pi/\gamma_2}e^{iQ^+(t_0^1+\eta_1)} + e^{iQ^+(t_0^2-\eta_2)} \right) \left( e^{iR^-Y} - e^{iR^-(t_0^2+\eta_2)} \right)}{i^216Q^+R^-} \\
+ \frac{e^{+it_2^0\pi/\gamma_2} \left( e^{-it_1^0\pi/\gamma_1}e^{iQ^-(t_0^1+\eta_1)} + e^{iQ^-(t_0^2-\eta_2)} \right) \left( e^{iR^-Y} - e^{iR^-Y(t_0^1+\eta_1)} \right)}{i^216Q^-R^-} \\
+ \frac{e^{+it_1^0\pi/\gamma_1}e^{i(Q^+-R^-)(t_0^1+\eta_1)} + e^{i(Q^+R)(t_0^2-\eta_2)}}{i^28Q(Q + R^-)}
\]
\[
\begin{align*}
&\quad + \frac{e^{+it_2^Q/R} e^{Q(t_1^Q + \gamma_1)} \left( e^{iR^-Y} - e^{iR^-(t_2^Q + \gamma_2)} \right)}{i^2 8R^-Q} \\
&- \frac{e^{iQ(t_1^Q - \gamma_1)} \left( e^{+it_2^Q/R} e^{iR^-Y} + e^{iR^-(t_2^Q - \gamma_2)} \right)}{i^2 8Q(Q + R^-)} \\
&\quad - \frac{e^{-it_2^Q/R} \left( e^{i(Q^+ + R)(t_1^Q + \gamma_1)} + e^{i(Q^- + R^-)(t_2^Q - \gamma_2)} e^{+it_2^Q/R} \right)}{i^2 8Q^+(Q^+ + R)} \\
&\quad + \frac{e^{i(Q^+ R)(t_1^Q + \gamma_1)} \left( e^{iR^-(t_2^Q - \gamma_2)} \right)}{i^2 8Q^+(Q^- + R)} \\
&\quad + \frac{e^{-it_2^Q/R} \left( e^{-it_2^Q/R} e^{i(Q^- + R)(t_1^Q + \gamma_1)} + e^{i(Q^- + R^-)(t_2^Q - \gamma_2)} \right)}{i^2 8Q^+(Q^- + R)} \\
&\quad - \frac{e^{i(Q^- R)(t_1^Q + \gamma_1)} \left( e^{iR^-Y} - e^{iR^-(t_2^Q + \gamma_2)} \right)}{i^2 4R QA} \\
&\quad + \frac{e^{i(Q^- R)(t_1^Q + \gamma_1)} \left( e^{iR^-Y} - e^{iR^-(t_2^Q + \gamma_2)} \right)}{i^2 4RQA} \\
&\quad + \frac{e^{i(Q^- R)(t_1^Q - \gamma_1)} \left( e^{-it_2^Q/R} e^{iR^-Y} + e^{iR^-(-(t_2^Q - \gamma_2)} \right)}{i^2 4Q(Q + R)}
\end{align*}
\]
The third and final temporal integration remains:

\[
\int_{-\infty}^{T} \left( [2.5.2] + [2.5.2] + [2.35] f_3(t') e^{iS't'} dt' \right)
= \int_{-\infty}^{T} [2.5.2] f_3(t') e^{iS't'} dt' + \int_{-\infty}^{T} [2.5.2] f_3(t') e^{iS't'} dt' + \int_{-\infty}^{T} [2.35] f_3(t') e^{iS't'} dt' \quad (2.36)
\]

Starting with the A integration,

\[
A = \int_{t_3^g - \gamma_3}^{Z} \frac{1}{2} \left( \frac{e^{iS't'} e^{-it_3^g \pi/\gamma_3} - }{2} + \frac{e^{iS't'} e^{+it_3^g \pi/\gamma_3}}{2} + e^{iS't'} \right) dt'
\]

Looking for the moment only at the Ac term,

\[
Ac = \int_{t_3^g - \gamma_3}^{t} [2.33a] e^{iS't'} dt'
\]

\[
= \int_{t_3^g - \gamma_3}^{t} [2.33a] e^{iS't'} dt' + \int_{t_3^g - \gamma_3}^{t} [2.33b] e^{iS't'} dt' + \int_{t_3^g - \gamma_3}^{t} [2.33c] e^{iS't'} dt'
\]

\[
Ac_1 = \int_{t_3^g - \gamma_3}^{t} \frac{e^{+it_3^g \pi/\gamma_3} \left( e^{iR^- (t_3^g + \gamma_3)} + e^{i(Q^- + R^-) (t_3^g + \gamma_3)} \right)}{i^{3}16Q^- (Q^- + R^-)}
+ \frac{e^{iR^- (t_3^g - \gamma_3)} \left( e^{iR^- (t_3^g + \gamma_3)} + e^{iR^- (t_3^g - \gamma_3)} \right)}{i^{3}16Q^- R^-}
+ \frac{e^{+it_3^g \pi/\gamma_3} \left( e^{iQ^- (t_3^g + \gamma_3)} + e^{iQ^- (t_3^g - \gamma_3)} \right) \left( e^{iR^- Y} - e^{iR^- (t_3^g + \gamma_3)} \right)}{i^{3}16Q^- R^-} \right) e^{iS't'} dt'
\]
\[ Ac1 = \int_{t_2 - \gamma_2}^{t} \left[ \frac{e^{-i\theta_2 \pi / \gamma_2} e^{-i\theta_2 \pi / \gamma_2} e^{i(Q^+ + R^+)(t_2^0 + \gamma_2)} + e^{i(Q^+ + R)(t_2^0 - \gamma_2)} e^{-i\theta_2 \pi / \gamma_2}}{i^3 16 Q^+ (Q^+ + R^+)} \right. \\
+ \frac{e^{iQ(t_2^0 - \gamma_2)} \left( e^{iR^+(t_2^0 + \gamma_2)} e^{-i\theta_2 \pi / \gamma_2} + e^{iR(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+} \\
- \frac{e^{iR^+(t_2^0 + \gamma_2)} e^{-i\theta_2 \pi / \gamma_2} \left( e^{-i\theta_2 \pi / \gamma_2} e^{iQ(t_2^0 + \gamma_2)} + e^{iQ(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+} \\
\left. \right] e^{iS't'} dt' \]
\\
+ \int_{t_2 - \gamma_2}^{t} \frac{e^{-i\theta_2 \pi / \gamma_2} \left( e^{iQ(t_2^0 + \gamma_2)} + e^{iQ(t_2^0 - \gamma_2)} \right) e^{i(R^+ + S)t'}}{i^3 16 Q^+ R^+} dt'
\\
+ \int_{t_2 - \gamma_2}^{t} \frac{e^{-i\theta_2 \pi / \gamma_2} \left( e^{-i\theta_2 \pi / \gamma_2} e^{iQ(t_2^0 + \gamma_2)} + e^{iQ(t_2^0 - \gamma_2)} \right) e^{iR^+(t_2^0 - \gamma_2)} e^{iSt'}}{i^3 16 Q^+ R^+} dt'

\[ Ac_1 = \left[ \frac{e^{-i\theta_2 \pi / \gamma_2} e^{-i\theta_2 \pi / \gamma_2} e^{i(Q^+ + R^+)(t_2^0 + \gamma_2)} + e^{i(Q^+ + R)(t_2^0 - \gamma_2)} e^{-i\theta_2 \pi / \gamma_2}}{i^3 16 Q^+ (Q^+ + R^+)} S \right. \\
+ \frac{e^{iQ(t_2^0 - \gamma_2)} \left( e^{iR^+(t_2^0 + \gamma_2)} e^{-i\theta_2 \pi / \gamma_2} + e^{iR(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+ S} \\
- \frac{e^{iR^+(t_2^0 + \gamma_2)} e^{-i\theta_2 \pi / \gamma_2} \left( e^{-i\theta_2 \pi / \gamma_2} e^{iQ(t_2^0 + \gamma_2)} + e^{iQ(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+ S} \left( e^{iSt} - e^{i(t_2^0 - \gamma_2)} \right) \right. \\
\left. \right. \\
+ \frac{e^{-i\theta_2 \pi / \gamma_2} \left( e^{-i\theta_2 \pi / \gamma_2} e^{iQ(t_2^0 + \gamma_2)} + e^{iQ(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+ S} \\
\left. \right. \\
\left. \times \frac{\left( e^{i(R^+ + S)(t_2^0 + \gamma_2)} - e^{i(R^+ + S)(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+ S} \right. \\
\left. \right. \\
+ \frac{e^{-i\theta_2 \pi / \gamma_2} \left( e^{-i\theta_2 \pi / \gamma_2} e^{iQ(t_2^0 + \gamma_2)} + e^{iQ(t_2^0 - \gamma_2)} \right)}{i^3 16 Q^+ R^+ S} \\
\left. \right. \\
\left. \times \frac{\left( e^{iSt} - e^{iS(t_2^0 + \gamma_2)} \right)}{i^3 16 Q^+ R^+ S} \right. \\

\[ Ac_2 \text{ can be had by making the following transformations:} \]
\\
e^{-i\theta_2 \pi / \gamma_2} \rightarrow e^{+i\theta_2 \pi / \gamma_2} \quad Q^+ \rightarrow Q^- \quad Q \rightarrow Q
\[
A_{c2} = \left[ \frac{e^{i\frac{\theta}{\gamma}} e^{-i\frac{\varphi}{\gamma}} e^{i(Q^+ + R^+)(t_1^2 + \gamma_1)} + e^{i(Q^+ + R)(t_2^2 - \gamma_2)} e^{i\frac{\theta}{\gamma}}}{i^3 16 Q - (Q^+ + R^+) S} + \frac{e^{iQ(t_1^2 - \gamma)} \left( e^{iR^+(t_2^2 + \gamma_1)} e^{-i\frac{\varphi}{\gamma}} + e^{iR(t_2^2 - \gamma_2)} \right)}{i^3 16 Q - R^+ S} - \frac{e^{iR^+(t_1^2 + \gamma_1)} e^{-i\frac{\varphi}{\gamma}} \left( e^{i\frac{\theta}{\gamma}} e^{iQ^-(t_2^2 + \gamma_2)} + e^{iQ(t_2^2 - \gamma_2)} \right)}{i^3 16 Q - R^+ S} \right] \left( e^{i S t} - e^{i(t_2^2 - \gamma_2)} \right)
\]

\[
e^{-i\frac{\theta}{\gamma}} \left( e^{i\frac{\theta}{\gamma}} e^{iQ^-(t_1^2 + \gamma_1)} + e^{iQ(t_2^2 - \gamma_2)} \right) + \frac{e^{-i\frac{\varphi}{\gamma}} \left( e^{i\frac{\theta}{\gamma}} e^{iQ^-(t_2^2 + \gamma_2)} + e^{iQ(t_2^2 - \gamma_2)} \right)}{i^3 16 Q - R^+ S} \times \frac{e^{iQ^+(t_1^2 + \gamma_1)} \left( e^{iS t} - e^{iS(t_2^2 + \gamma_2)} \right)}{i^3 16 Q - R^+ S}
\]

The final portion of \(A_c\) becomes, when integrated:

\[
A_{c3} = \left[ \frac{e^{-i\frac{\theta}{\gamma}} e^{iQ^+(t_1^2 + \gamma_1)} + e^{iQ^+(R^+)(t_2^2 - \gamma_2)} - e^{iQ(t_2^2 - \gamma_2)} e^{iR(t_2^2 - \gamma_2)}}{8i^3 Q (Q + R^+) S} - \frac{e^{-i\frac{\varphi}{\gamma}} e^{iQ^+(R^+)(t_1^2 + \gamma_1)}}{8i^3 R^+ Q S} \left( e^{iS t} - e^{iS(t_2^2 - \gamma_2)} \right) \right]
\]

\[
+ \left[ \frac{e^{-i\frac{\theta}{\gamma}} e^{iQ^+(t_2^2 - \gamma_2)} - e^{iQ(t_2^2 - \gamma_2)} e^{-i\frac{\varphi}{\gamma}}}{8i^2 R^+ Q} - \frac{e^{-i\frac{\varphi}{\gamma}} e^{iQ^+(t_2^2 - \gamma_2)} e^{-i\frac{\varphi}{\gamma}}}{8i^2 Q (Q + R^+)} \right] \times \left\{ \frac{e^{i(R^+ + S)(t_2^2 + \gamma_2)} - e^{iQ(t_2^2 + \gamma_1)} \left( e^{iS t} e^{iR(t_2^2 + \gamma_2)} \right)}{i(R^+ + S) + \frac{-e^{i(R^+ + S)(t_2^2 + \gamma_2)} + e^{iS t} e^{iR(t_2^2 + \gamma_2)}}{iS} \right\}
\]

And \(A_c = A_{c1} + A_{c2} + A_{c3}\) is complete. The analogous term \(A_{b} = A_{b1} + A_{b2} + A_{b3}\) can be
had by multiplying the concomitant portions of $Ac$ by $\frac{1}{4}e^{+it^2_3\pi/\gamma_3}$ and transforming $S \rightarrow S^\prime$.

$$Ab_1 = \frac{1}{4}e^{+it^2_3\pi/\gamma_3} \left[ \frac{-e^{-it_3^2/\gamma_3} e^{-it^2_3/\gamma_3} e^{i(Q^+ + R^+)(t_3^2 + \gamma_3)} + e^{i(Q^+ + R^+)(t_3^2 - \gamma_3)} e^{-it_3^2/\gamma_3}}{i^316Q^+(Q^+ + R^+)S^-}ight. $$

$$+ \frac{e^{iQ(t_3^- - \gamma)} \left( e^{iR^+(t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} + e^{iR(t_3^2 - \gamma_3)} \right)}{i^316Q^+R^+S^-}$$

$$- \frac{e^{iR^+(t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} \left( e^{-it^2_3/\gamma_3} e^{iQ(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)}{i^316Q^+R^+S^-}$$

$$\left( e^{iS^2 - t} - e^{i(t_3^2 - \gamma_3)} \right)$$

$$+ \frac{1}{4}e^{+it^2_3/\gamma_3} e^{-it^2_3/\gamma_3} \left( e^{-it^2_3/\gamma_3} e^{iQ^+(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)$$

$$+ \frac{e^{iR^+ t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} \left( e^{-it^2_3/\gamma_3} e^{iQ(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)$$

$$\times \frac{e^{iS^2 - t} - e^{iS^2 - (t_3^2 + \gamma_3)}}{i^316Q^+R^+S^-}$$

$$Ab_2 = \frac{1}{4}e^{+it^2_3\pi/\gamma_3} \left[ \frac{e^{iQ(t_3^2 - \gamma)} \left( e^{iR^+(t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} + e^{iR(t_3^2 - \gamma_3)} \right)}{i^316Q^-(Q^- + R^+)S^-}$$

$$+ \frac{e^{iQ(t_3^2 - \gamma)} \left( e^{iR^+(t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} + e^{iR(t_3^2 - \gamma_3)} \right)}{i^316Q^-R^+S^-}$$

$$- \frac{e^{iR^+(t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} \left( e^{-it^2_3/\gamma_3} e^{iQ(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)}{i^316Q^-R^+S^-}$$

$$\left( e^{iS^2 - t} - e^{i(t_3^2 - \gamma_3)} \right)$$

$$+ \frac{1}{4}e^{+it^2_3/\gamma_3} e^{-it^2_3/\gamma_3} \left( e^{+it^2_3\pi/\gamma_3} e^{iQ^-(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)$$

$$+ \frac{e^{iQ(t_3^-)} \left( e^{iR^+ t_3^- + \gamma_3)} e^{-it^2_3/\gamma_3} \right.}{i^316Q^-R^+S^-}$$

$$\times \frac{e^{iQ(t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} \left( e^{-it^2_3/\gamma_3} e^{iQ(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)}{i^316Q^-R^+S^-}$$

$$+ \frac{1}{4}e^{+it^2_3/\gamma_3} e^{-it^2_3/\gamma_3} \left( e^{+it^2_3\pi/\gamma_3} e^{iQ^-(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)$$

$$+ \frac{e^{iR^+ (t_3^2 + \gamma_3)} e^{-it^2_3/\gamma_3} \left( e^{-it^2_3/\gamma_3} e^{iQ(t_3^2 + \gamma_3)} + e^{iQ(t_3^2 - \gamma_3)} \right)}{i^316Q^-R^+S^-}$$

$$\times \frac{e^{iS^2 - t} - e^{iS^2 - (t_3^2 + \gamma_3)}}{i^316Q^-R^+S^-}$$
8i^3 Q (Q + R^+) S
- \frac{e^{-it_0^2 \pi / \gamma_2} e^{i(Q + R^+) (t_0^2 + \gamma_2)} + e^{i(Q + R)(t_0^2 - \gamma_2)} - e^{i Q(t_0^2 - \gamma_2)} e^{i R(t_0^2 - \gamma_2)}}{8i^3 Q (Q + R^+) S}
+ \frac{1}{4} e^{i S^- t} - e^{i S^- (t_0^2 - \gamma_2)}
+ \left\{ \frac{e^{i (R^+ + S^-) (t_0^2 + \gamma_2)} - e^{i Q(t_0^2 + \gamma_2)}}{i (R^+ + S^-)} + \frac{-e^{i (R^+ + S^-) (t_0^2 + \gamma_2)} + e^{i S^- t} e^{i R(t_0^2 + \gamma_2)}}{i S^-} \right\}

Likewise, the $Aa$ term can be represented as the three $Ac$ terms with $S \rightarrow S^+$ and a phase factor of $\frac{1}{4} e^{-it_0^2 \pi / \gamma_2}$.

$Aa1 = \frac{1}{4} e^{-it_0^2 \pi / \gamma_2} \left[ \frac{e^{-it_0^2 \pi / \gamma_2} e^{i Q(t_0^2 + \gamma_2)} e^{i (Q^+ + R^+) (t_0^2 + \gamma_2)} + e^{i (Q^+ + R)(t_0^2 - \gamma_2)} e^{-it_0^2 \pi / \gamma_2}}{i 316 Q^+ (Q^+ + R^+) S^+} \right.$

\[ \frac{e^{i Q(t_0^2 - \gamma_2)}}{i 316 Q^+ (Q^+ + R^+) S^+} \left( e^{i R^+ (t_0^2 + \gamma_2)} - e^{-it_0^2 \pi / \gamma_2} \left( e^{-it_0^2 \pi / \gamma_2} e^{i Q^+(t_0^2 + \gamma_2)} + e^{i Q(t_0^2 - \gamma_2)} \right) \right) \]

\[ \frac{1}{4} e^{-it_0^2 \pi / \gamma_2} e^{-it_0^2 \pi / \gamma_2} \left( e^{-it_0^2 \pi / \gamma_2} e^{i Q^+(t_0^2 + \gamma_2)} + e^{i Q(t_0^2 - \gamma_2)} \right) \]

\[ \times \frac{e^{i R^+ (t_0^2 + \gamma_2)} \left( e^{i S^+ t} - e^{i S^+ (t_0^2 - \gamma_2)} \right)}{i 316 Q^+ (Q^+ + R^+) S^+} \]
\[ Aa2 = \frac{1}{4} e^{-it^2_{\gamma}/\gamma_3} \left[ e^{+it^0_{\gamma}/\gamma_2} e^{-it^2_{\gamma}/\gamma_2} e^{i(Q^{-}+R^{+})(t^0_{\gamma}+\gamma_1)} + e^{i(Q^{-}+R^{+})(t^0_{\gamma}-\gamma_2)} e^{+it^0_{\gamma}/\gamma_3} ight. \\
\quad \quad + \left. \frac{e^{iQ(t^0_{\gamma}-\gamma_2)} \left( e^{iR^+(t^0_{\gamma}+\gamma_1)} e^{-it^2_{\gamma}/\gamma_2} + e^{iR(t^2_{\gamma}-\gamma_2)} \right)}{i^316Q^{-}(Q^{-} + R^{+})S^+} \right] \\
\quad \quad + \frac{e^{iR^+(t^0_{\gamma}+\gamma_1)} e^{-it^2_{\gamma}/\gamma_2} \left( e^{+it^0_{\gamma}/\gamma_1} e^{Q^{-}(t^0_{\gamma}+\gamma_1)} + e^{iQ(t^0_{\gamma}-\gamma_2)} \right)}{i^316Q^{-}R^{+}S^+} \right] \left( e^{iS^+} - e^{i(t^2_{\gamma}-\gamma_2)} \right) \\
\quad \quad + \frac{\frac{1}{4} e^{-it^2_{\gamma}/\gamma_3} e^{-it^2_{\gamma}/\gamma_2} \left( e^{+it^0_{\gamma}/\gamma_2} e^{Q^{-}(t^0_{\gamma}+\gamma_1)} + e^{iQ(t^0_{\gamma}-\gamma_2)} \right)}{i^316Q^{-}R^{+}S^+} \\
\quad \quad \times \left( e^{i(R^++S^+)(t^0_{\gamma}+\gamma_2)} - e^{i(R^++S^+)(t^0_{\gamma}-\gamma_2)} \right) \\
\quad \quad + \frac{\frac{1}{4} e^{-it^0_{\gamma}/\gamma_3} e^{-it^2_{\gamma}/\gamma_2} \left( e^{+it^0_{\gamma}/\gamma_1} e^{Q^{-}(t^0_{\gamma}+\gamma_1)} + e^{iQ(t^0_{\gamma}-\gamma_2)} \right)}{i^316Q^{-}R^{+}S^+} \\
\quad \quad \times \left( e^{R^+(t^2_{\gamma}+\gamma_2)} \left( e^{iS^+} - e^{iS^+(t^2_{\gamma}+\gamma_2)} \right) \right) \\
\quad \quad \times \frac{i^316Q^{-}R^{+}S^+}{i^316Q^{-}R^{+}S^+} \\
\quad \quad \right] \\
\quad \quad + \frac{1}{4} e^{-it^0_{\gamma}/\gamma_2} e^{Q^+(t^0_{\gamma}+\gamma_1)} - e^{iQ(t^0_{\gamma}-\gamma_2)} e^{iR(t^2_{\gamma}-\gamma_2)} \\
\quad \quad \times \frac{ei^3Q(Q + R^+)S + e^{-it^2_{\gamma}/\gamma_2} e^{iQ(t^0_{\gamma}+\gamma_1)}}{8i^2R^+Q S^+} - \frac{1}{4} e^{-it^0_{\gamma}/\gamma_3} e^{iQ(t^0_{\gamma}-\gamma_2)} e^{-it^2_{\gamma}/\gamma_2} \\
\quad \quad \times \left\{ \frac{e^{i(R^++S^+)(t^2_{\gamma}+\gamma_2)} - e^{iQ(t^0_{\gamma}+\gamma_1)}}{i(R^++S^+)} + \frac{-e^{i(R^++S^+)(t^2_{\gamma}+\gamma_2)} + e^{iS^+} e^{iR(t^2_{\gamma}+\gamma_2)}}{iS^+} \right\} \\
\]

With the entire A integral thus solved, note that the B integral can be built by
altering the A solution so that \( R^+ \to R^- \) and \( e^{-it^2_{\gamma}/\gamma_2} \to e^{+it^2_{\gamma}/\gamma_2} \). Likewise, term C is a
modified form of A with \( R \to R^- \), \( R^+ \to R \) and an extra phase factor of \( 2e^{+it^2_{\gamma}/\gamma_2} \). What
follows, then, is the final solution for the three photon process, with all terms intact.
\[
+ \frac{1}{4} e^{-it_0^3 \pi / \gamma_0} \left[ e^{-it_0^3 \pi / \gamma_0} e^{-it_2^3 \pi / \gamma_2} e^{i(Q^+ + R^+)(t_0^3 + \gamma_0)} + e^{i(Q^+ + R)(t_0^2 - \gamma_2)} e^{-it_0^3 \pi / \gamma_0} \right] \frac{i^3 16 Q^+ (Q^+ + R^+) S^+}{i^3 16 Q^+ (Q^+ + R^+) S^+}
+ \frac{e^{iQ(t_0^3 - \gamma_0)} \left( e^{iR^+(t_0^3 + \gamma_0)} e^{-it_2^3 \pi / \gamma_2} + e^{iR(t_0^2 - \gamma_2)} \right)}{i^3 16 Q^+ R^+ S^+}
+ \frac{e^{iR^+(t_0^3 + \gamma_0)} e^{-it^3_0^3 \pi / \gamma_2} (e^{-it^3_0^3 \pi / \gamma_1} e^{Q^+(t_0^3 + \gamma_0)} + e^{iQ(t_0^3 - \gamma_1)})}{i^3 16 Q^+ R^+ S^+}
\]
\[
\begin{align*}
+ \frac{e^{-it_2^0 \pi / \gamma_2} e^{i(Q+R^+)(t_0^0 + \gamma_2)} + e^{i(Q+R)(t_0^0 - \gamma_2)} - e^{iQ(t_0^0 - \gamma_1)} e^{iR(t_0^0 - \gamma_2)}}{8i^3 Q(Q + R^+) S} \\
- \frac{e^{-it_2^0 \pi / \gamma_2} e^{i(Q^+ + R^+)(t_0^0 + \gamma_1)} - e^{iQ(t_0^0 - \gamma_1)}}{8i^3 R^+ Q S^+} \left( \frac{1}{4} e^{-it_2^0 \pi / \gamma_3} \right) \left( e^{iS^+ t} - e^{iS^-(t_0^0 - \gamma_3)} \right)
\end{align*}
\]

\[
+ \frac{e^{-it_2^0 \pi / \gamma_2} e^{iQ(t_0^0 + \gamma_1)}}{8i^2 R^+ Q} - \frac{e^{-it_2^0 \pi / \gamma_2}}{8i^2 Q(Q + R^+)} \left( \frac{1}{4} e^{-it_2^0 \pi / \gamma_3} \right) \left( e^{i(R^+ + S^+)(t_0^0 + \gamma_1)} - e^{iQ(t_0^0 + \gamma_1)} \right)
\times \left\{ \frac{e^{i(R^+ + S^+)(t_0^0 + \gamma_1)} - e^{iQ(t_0^0 + \gamma_1)}}{i(R^+ + S^+)} + \frac{-e^{i(R^+ + S^+)(t_0^0 + \gamma_1)} + e^{iS^+ t}}{iS^+} \right\}
\]

\[
\frac{1}{4} e^{+it_2^0 \pi / \gamma_2} \left[ \frac{e^{-it_2^0 \pi / \gamma_2} e^{-it_2^0 \pi / \gamma_2} e^{i(Q^+ + R^+)(t_0^0 + \gamma_1)} + e^{i(Q^+ + R)(t_0^0 - \gamma_2)} e^{-it_2^0 \pi / \gamma_2}}{i^3 16 Q^+(Q^+ + R^+)^S^-} e^{iQ(t_0^0 - \gamma_1)} \left( e^{iR^+(t_0^0 + \gamma_1)} e^{-it_2^0 \pi / \gamma_2} + e^{iR(t_0^0 - \gamma_2)} \right)
\right.
\]

\[
+ \frac{i^3 16 Q^+ R^+ S^-}{e^{i(R^+ + S^-)(t_0^0 + \gamma_1)} - e^{i(R^+ + S^-)(t_0^0 - \gamma_2)}} \left( e^{i(R^+ + S^+)(t_0^0 + \gamma_1)} - e^{iQ(t_0^0 + \gamma_1)} \right)
\times \frac{i^3 16 Q^+ R^+ S^-}{i^3 16 Q^+ R^+ S^-} \left( e^{iS^+ t} - e^{iS^-(t_0^0 - \gamma_3)} \right)
\]

\[
+ \frac{1}{4} e^{+it_2^0 \pi / \gamma_2} e^{-it_2^0 \pi / \gamma_2} \left( e^{-it_2^0 \pi / \gamma_2} e^{iQ^+(t_0^0 + \gamma_1)} + e^{iQ(t_0^0 - \gamma_2)} \right)
\times \frac{i^3 16 Q^+ R^+ S^-}{i^3 16 Q^+ R^+ S^-} \left( e^{iS^+ t} - e^{iS^-(t_0^0 - \gamma_2)} \right)
\]
\[
\begin{align*}
&+ \frac{1}{4} e^{+i\theta_2^0 \pi/\gamma_3} \left[ e^{+it_1^0 \pi/\gamma_1} e^{-it_2^0 \pi/\gamma_2} e^{i(Q^++R^+)(t_1^0+\eta_1)} + e^{i(Q^-+R^-)(t_2^0-\eta_2)} e^{+it_1^0 \pi/\gamma_1} \right] \\
&\times \frac{i^3 16Q^- (Q^- + R^+)^S^-}{i^3 16Q^- (Q^- + R^+)S^-} \\
&\times \left( e^{iR^+(t_1^0+\eta_1)} e^{-it_2^0 \pi/\gamma_2} + e^{iR^-(t_2^0-\eta_2)} \right) \\
&\times \left( e^{iS^-t} - e^{i(t_2^0-\eta_2)} \right) \\
&+ \frac{1}{4} e^{+i\theta_2^0 \pi/\gamma_3} e^{-it_2^0 \pi/\gamma_2} \left( e^{+it_1^0 \pi/\gamma_1} e^{Q^- (t_1^0+\eta_1)} + e^{iQ^-(t_1^0-\eta_1)} \right) \\
&\times \left( e^{i(R^+-S^-)(t_2^0+\eta_2)} - e^{i(R^++S^-)(t_2^0-\eta_2)} \right) \\
&\times \left( e^{iR^+(t_1^0+\eta_1)} e^{-it_2^0 \pi/\gamma_2} + e^{iQ^-(t_1^0-\eta_1)} \right) \\
&\times \frac{i^3 16Q^- (Q^- + R^+)^S^-}{i^3 16Q^- (Q^- + R^+)S^-} \\
&\times \left( e^{iS^-t} - e^{iS^-(t_2^0-\eta_2)} \right) \\
&+ \left[ e^{-it_2^0 \pi/\gamma_2} e^{i(Q^++R^+)(t_1^0+\eta_1)} + e^{i(Q^++R^-)(t_2^0-\eta_2)} - e^{iQ^-(t_2^0-\eta_2)} e^{iR^+(t_2^0-\eta_2)} \right] \\
&\times \frac{8i^3 Q(Q^++R^+)S^-}{8i^3 Q^+(Q^++R^+)S^-} \\
&- \frac{e^{-it_2^0 \pi/\gamma_2} e^{i(Q^++R^+)(t_1^0+\eta_1)} e^{iQ^-(t_2^0-\eta_2)} e^{-it_2^0 \pi/\gamma_2}}{8i^3 Q^+(Q^++R^+)S^-} \left( e^{iS^-t} - e^{iS^-(t_2^0-\eta_2)} \right) \\
&\times \frac{1}{4} e^{+it_2^0 \pi/\gamma_3} \\
&+ \left[ e^{-it_2^0 \pi/\gamma_2} e^{iQ^-(t_2^0-\eta_2)} e^{-it_2^0 \pi/\gamma_2} \right] \frac{8i^2 R^+ Q}{8i^2 Q^+(Q^++R^+)} \left( e^{i(R^+-S^-)(t_2^0+\eta_2)} - e^{iQ^-(t_2^0-\eta_2)} e^{-it_2^0 \pi/\gamma_2} \right) \left( e^{i(R^++S^-)(t_2^0+\eta_2)} + e^{iS^-t} e^{iR^+(t_2^0+\eta_2)} \right) \\
&\times \frac{1}{4} e^{+it_2^0 \pi/\gamma_3} \\
&\times \left\{ e^{i(R^++S^-)(t_2^0+\eta_2)} - e^{iQ^-(t_2^0-\eta_2)} e^{iS^-t} e^{iR^+(t_2^0+\eta_2)} \right\} \\
&\times \frac{i(R^++S^-)}{iS^-} \\
&\times \left\{ e^{i(R^+-S^-)(t_2^0+\eta_2)} - e^{iQ^-(t_2^0-\eta_2)} e^{iS^-t} e^{iR^+(t_2^0+\eta_2)} \right\} \\
&\times \left\{ e^{i(R^++S^-)(t_2^0+\eta_2)} - e^{iQ^-(t_2^0-\eta_2)} e^{iS^-t} e^{iR^+(t_2^0+\eta_2)} \right\}
\end{align*}
\]
\[
\begin{align*}
&+ \left[ e^{-i\frac{\varphi}{\gamma}} e^{-i\frac{\varphi}{\gamma}} e^{i(Q^+ + R^+)(t_1^+ + \gamma)} + e^{i(Q^+ + R^+)(t_2^- - \gamma)} e^{-i\frac{\varphi}{\gamma}} \right] \\
&+ \frac{i^3 16Q^+ (Q^+ + R^+) S}{i^3 16Q^+ R^+ S} \\
&+ \frac{e^{i R^+ (t_1^+ + \gamma)} e^{-i\frac{\varphi}{\gamma}} e^{i R^+ (t_2^- - \gamma)}}{i^3 16Q^+ R^+ S} \\
&- \frac{e^{i R^+ (t_1^+ + \gamma)} e^{-i\frac{\varphi}{\gamma}} \left( e^{-i\frac{\varphi}{\gamma}} e^{i Q^- (t_1^+ + \gamma)} + e^{i Q^- (t_2^- - \gamma)} \right)}{i^3 16Q^+ R^+ S} \\
&\times \left( e^{i Q^+ (t_1^+ + \gamma)} e^{i Q^+ (t_2^- - \gamma)} + e^{i Q^- (t_1^+ + \gamma)} \right) \\
&+ \left[ e^{+i\frac{\varphi}{\gamma}} e^{-i\frac{\varphi}{\gamma}} e^{i(Q^- + R^-)(t_1^+ + \gamma)} + e^{i(Q^- + R^-)(t_2^- - \gamma)} e^{+i\frac{\varphi}{\gamma}} \right] \\
&+ \frac{i^3 16Q^- (Q^- + R^-) S}{i^3 16Q^- R^+ S} \\
&+ \frac{e^{i R^+ (t_1^+ + \gamma)} e^{-i\frac{\varphi}{\gamma}} e^{i R^+ (t_2^- - \gamma)}}{i^3 16Q^- R^+ S} \\
&- \frac{e^{i R^+ (t_1^+ + \gamma)} e^{-i\frac{\varphi}{\gamma}} \left( e^{+i\frac{\varphi}{\gamma}} e^{i Q^- (t_1^+ + \gamma)} + e^{i Q^- (t_2^- - \gamma)} \right)}{i^3 16Q^- R^+ S} \\
&\times \left( e^{i Q^+ (t_1^+ + \gamma)} e^{i Q^- (t_2^- - \gamma)} + e^{i Q^- (t_1^+ + \gamma)} \right) \\
&+ \left[ e^{-i\frac{\varphi}{\gamma}} e^{+i\frac{\varphi}{\gamma}} e^{i(Q^- - R^-)(t_1^+ + \gamma)} + e^{i(Q^- - R^-)(t_2^- - \gamma)} e^{-i\frac{\varphi}{\gamma}} \right] \\
&+ \frac{i^3 16Q^- R^+ S}{i^3 16Q^- R^+ S} \\
&+ \frac{e^{i R^+ (t_1^+ + \gamma)} e^{-i\frac{\varphi}{\gamma}} e^{i R^+ (t_2^- - \gamma)}}{i^3 16Q^- R^+ S} \\
&- \frac{e^{i R^+ (t_1^+ + \gamma)} e^{-i\frac{\varphi}{\gamma}} \left( e^{+i\frac{\varphi}{\gamma}} e^{i Q^- (t_1^+ + \gamma)} + e^{i Q^- (t_2^- - \gamma)} \right)}{i^3 16Q^- R^+ S} \\
&\times \left( e^{i Q^+ (t_1^+ + \gamma)} e^{i Q^- (t_2^- - \gamma)} + e^{i Q^- (t_1^+ + \gamma)} \right)
\end{align*}
\]
\[
\begin{align*}
&+ \left[ \frac{e^{-it_2^2/\gamma} e^{i(Q+R^+)(t_1^2+\gamma)} + e^{i(Q+R)(t_2^2-\gamma)} - e^{iQ}(t_1^2-\gamma) e^{iR}(t_2^2-\gamma)}{8iQ(Q + R^+)S} \\
&\quad - \frac{e^{-it_2^2/\gamma} e^{i(Q^++R^+)(t_1^2+\gamma)}}{8i^2 R^+ QS} \right] \left( e^{iS_t - e^{iS}(t_2^2-\gamma)} \right) \\
&+ \left[ \frac{e^{-it_2^2/\gamma} e^{iQ}(t_1^2+\gamma)}{8i^2 R^+ Q} - \frac{e^{-it_2^2/\gamma} e^{-it_2^2/\gamma}}{8i^2 Q(Q + R^+)} \right] \\
&\quad \times \left\{ \frac{e^{i(R+S)(t_1^2+\gamma)} - e^{iQ}(t_1^2+\gamma)}{i(R^+ + S)} + \frac{-e^{i(R+S)(t_2^2+\gamma)} + e^{iS_t} e^{iR}(t_2^2+\gamma)}{iS} \right\}
\end{align*}
\]

\[
\begin{align*}
&+ \frac{1}{4} e^{-it_2^2/\gamma} \left[ \frac{e^{-it_2^2/\gamma} e^{i(Q+R^+)(t_1^2+\gamma)} + e^{i(Q^++R^+)(t_1^2+\gamma)} - e^{-it_2^2/\gamma}}{i316Q^+(Q^++R^-)S^+} \\
&\quad + \frac{e^{iQ}(t_1^2-\gamma)}{i316Q^+ R^- S^+} \left( e^{iS_t - e^{iS}(t_2^2-\gamma)} \right) \right] \\
&+ \frac{1}{4} e^{-it_2^2/\gamma} \left[ \frac{e^{-it_2^2/\gamma} e^{iQ^+}(t_1^2+\gamma) + e^{iQ}(t_1^2-\gamma)}{i316Q^+ R^- S^+} \\
&\quad + \frac{e^{i(R^-+S^+)(t_2^2-\gamma)} - e^{i(R^-+S^+)(t_2^2-\gamma)}}{i316Q^+ R^- S^+} \left( e^{iS_t - e^{iS}(t_2^2-\gamma)} \right) \right] \\
&+ \frac{1}{4} e^{-it_2^2/\gamma} \left[ e^{iQ}(t_2^2+\gamma) \left( e^{iS_t - e^{iS}(t_2^2-\gamma)} \right) \right] \\
&\quad - \frac{e^{-it_2^2/\gamma} e^{iQ^+}(t_2^2+\gamma) + e^{iQ}(t_2^2-\gamma)}{i316Q^+ R^- S^+} \\
&\quad + \frac{e^{iR^-}(t_2^2+\gamma) \left( e^{iS_t - e^{iS}(t_2^2-\gamma)} \right)}{i316Q^+ R^- S^+}
\end{align*}
\]
\[
+ \frac{1}{4} e^{-it_2^0 \pi / \tau_0} \left[ e^{i t_2^0 \pi / \eta} e^{i t_2^0 \pi / \tau_2} e^{i(1^2 + Q^-)(t_2^0 + \eta)} + e^{i(1^2 + R^-)(t_2^0 + \tau_2)} e^{i t_2^0 \pi / \eta} \right.
\]
\[
\quad \times \frac{1}{i^2 16 Q^- R^+ S^+} \left( e^{i(1^2 + \tau_2) + i t_2^0 \pi / \eta} e^{i Q^- R^+ (t_2^0 + \eta)} + e^{i Q^- R^+ (t_2^0 - \eta)} \right) \]
\[
+ \frac{1}{4} e^{i t_3^2 \pi / \gamma_3} \left[ e^{-i t_3^2 \pi / \gamma_3} e^{i (Q^+ + R^-)(t_3^1 + \gamma_1)} + e^{i (Q^+ + R^-)(t_3^2 - \gamma_2)} e^{-i t_3^2 \pi / \gamma_3} \right] \\
\quad \times \left( e^{i (R^- + S^-)(t_3^2 + \gamma_2)} - e^{i (R^- + S^-)(t_3^3 - \gamma_3)} \right) \\
\quad \times \left( e^{i (R^- + S^-)(t_3^1 + \gamma_2)} - e^{i (R^- + S^-)(t_3^3 - \gamma_3)} \right) \\
\quad \times \left( e^{i (R^- + S^-)(t_3^1 + \gamma_2)} - e^{i (R^- + S^-)(t_3^3 - \gamma_3)} \right)
\]
\[
\begin{align*}
&+ \left[ \frac{e^{+it_2 \pi/\tau} e^{i(Q+R^-)(t_2^0 + \gamma_1)} + e^{i(Q+R)(t_2^0 - \gamma_1)} - e^{iQ(t_2^0 - \gamma_1)} e^{iR(t_2^0 + \gamma_1)}}{8i^3 Q (Q + R^-) S} \right] \\
&- \frac{e^{+it^0_2 \pi/\tau} e^{i(Q^- + R^-)(t_2^0 + \gamma_1)}}{8i^3 R^- Q S^-} \left[ \frac{1}{4} e^{+it_2 \pi/\tau} e^{iS^- t - e^{iS^- (t_2^0 - \gamma_1)}} \right] \\
&+ \left[ \frac{e^{+it_2 \pi/\tau} e^{iQ(t_2^0 + \gamma_1)}}{8i^2 R^- Q} - \frac{e^{iQ(t_2^0 - \gamma_1)} e^{+it_2 \pi/\tau}}{8i^2 Q (Q + R^-)} \right] \frac{1}{4} e^{+it^0_2 \pi/\tau} \left\{ \frac{e^{i(R^- + S^-)(t_2^0 + \gamma_1)} - e^{iQ(t_2^0 + \gamma_1)}}{i(R^- + S^-)} + \frac{-e^{i(R^- + S^-)(t_2^0 + \gamma_1)} + e^{iS^- t e^{iR(t_2^0 + \gamma_1)}}}{iS^-} \right\} \\
&+ \left[ \frac{e^{-it^0_2 \pi/\tau} e^{i(Q^- + R^-)(t_2^0 + \gamma_1)} + e^{i(Q^+ + R)(t_2^0 - \gamma_1)} e^{-it^0_2 \pi/\tau}}{i^3 16 Q^+(Q^+ + R^-) S} \right] \\
&+ \frac{e^{iR^-(t_2^0 + \gamma_1)} e^{+it_2 \pi/\tau} e^{iQ^+(t_2^0 + \gamma_1)} + e^{iQ(t_2^0 - \gamma_1)}}{i^3 16 Q^+ R^- S} \right\} \left( e^{iS^t - e^{iR^0 (t_2^- - \gamma_1)}} \right) \\
&+ \left[ \frac{e^{+it_2 \pi/\tau} e^{-it^0_2 \pi/\tau} e^{iQ^+(t_2^0 + \gamma_1)} + e^{iQ(t_2^0 - \gamma_1)}}{i^3 16 Q^+ R^- S} \right] \\
&\times \frac{e^{i(R^- + S^0)(t_2^0 + \gamma_1)} - e^{i(R^- + S^0)(t_2^0 - \gamma_1)}}{i^3 16 Q^+ R^- S} \\
&+ \left[ \frac{e^{+it_2 \pi/\tau} e^{-it^0_2 \pi/\tau} e^{iQ^+(t_2^0 + \gamma_1)} + e^{iQ(t_2^0 - \gamma_1)}}{i^3 16 Q^+ R^- S} \right] \\
&\times \frac{e^{iR^-(t_2^0 + \gamma_1)} e^{iS^t - e^{iS^t (t_2^0 + \gamma_1)}}}{i^3 16 Q^+ R^- S} \\
&+ \left[ \frac{e^{+it_2 \pi/\tau} e^{-it^0_2 \pi/\tau} e^{iQ^+(t_2^0 + \gamma_1)} + e^{iQ(t_2^0 - \gamma_1)}}{i^3 16 Q^+ R^- S} \right] \\
&\times \frac{e^{iR^- (t_2^0 + \gamma_1)} e^{iS^t - e^{iS^t (t_2^0 + \gamma_1)}}}{i^3 16 Q^+ R^- S}
\end{align*}
\]
\[ + \left[ \frac{e^{+i\frac{\theta}{2}}/\eta_e^{+i\frac{\theta}{2}}/\eta e^{i(Q^--R^-)(t^3_0+\eta)} + e^{i(Q^--R^-)(t^0_2-\gamma_2)} e^{+i\frac{\theta}{2}}/\eta}{i^316Q^-(Q^-+R^-)S} \right. \\
+ \left. \frac{e^{iQ(t^3_0-\eta)} \left( e^{iR^-(t^0_2+\eta)} e^{+i\frac{\theta}{2}}/\eta + e^{iR(t^0_2-\gamma_2)} \right)}{i^316Q^-R^-S} \right. \\
+ \left. \frac{e^{iR^-(t^0_2+\eta)} e^{+i\frac{\theta}{2}}/\eta \left( e^{+i\frac{\theta}{2}}/\eta e^{iQ^-t^0_2+\gamma_2} + e^{iQ(t^0_2-\gamma_2)} \right)}{i^316Q^-R^-S} \right] \left( e^{iSt} - e^{i(t^3_0-\gamma_2)} \right) \\
\]

\[ + \frac{e^{+i\frac{\theta}{2}}/\eta \left( e^{iQ^-t^0_2+\gamma_2} + e^{iQ(t^0_2-\gamma_2)} \right)}{i^316Q^-R^-S} \times \frac{e^{iR^-(t^0_2+\gamma_2)} \left( e^{iSt} - e^{iS(t^3_0+\gamma_2)} \right)}{i^316Q^-R^-S} \]

\[ + \left[ \frac{e^{+i\frac{\theta}{2}}/\gamma e^{i(Q^+R^-)(t^0_2+\eta)} + e^{i(Q+R^-)(t^0_2-\gamma_2)} - e^{iQ(t^0_2-\gamma_2)} e^{iR(t^0_2-\gamma_2)}}{8i^3Q(Q^+R^-)S} \right. \\
+ \left. \frac{e^{+i\frac{\theta}{2}}/\gamma e^{i(Q^+R^-)(t^0_2+\gamma_2)} \left( e^{iS(t^3_0-\gamma_2)} \right)}{8i^3R^-QS} \right] \left( e^{iSt} - e^{iS(t^3_0-\gamma_2)} \right) \\
+ \left[ \frac{e^{+i\frac{\theta}{2}}/\gamma e^{iQ(t^0_2+\gamma_2)} - e^{iQ(t^0_2-\gamma_2)} e^{+i\frac{\theta}{2}}/\gamma}{8i^2R^-Q} \right. \\
+ \left. \frac{e^{i(Q+S)(t^0_2+\gamma_2)} - e^{iQ(t^0_2+\gamma_2)} e^{+i\frac{\theta}{2}}/\gamma}{8i^2Q(Q^++R^-)} \right] \times \frac{e^{i(R+S)(t^0_2+\gamma_2)} - e^{iQ(t^0_2+\gamma_2)} e^{iSt} e^{iR(t^0_2+\gamma_2)}}{i(R^-+S)} + \frac{e^{i(R+S)(t^0_2+\gamma_2)} + e^{iSt} e^{iR(t^0_2+\gamma_2)}}{iS} \right\} \]
\[ + 2e^{+it_0^2/\gamma_2} \frac{1}{4} e^{-it_0^2/\gamma_3} \left[ \frac{e^{-it_0^2/\gamma_1} e^{it_0^2/\gamma_2} e^{-i(Q^+ + R)(t_0^2 + \gamma_2) + e^{i(Q^+ + R^-)(t_0^2 - \gamma_2)}}}{i^3 16Q^+(Q^+ + R)S^+} \right. \\
\left. + e^{iQ(t_0^2 - \gamma_1)} \left( e^{iR(t_0^2 + \gamma_2)} e^{it_0^2/\gamma_2} + e^{iR^-(t_0^2 - \gamma_2)} \right) \right] \left( e^{iS^+ t} - e^{i(t_0^2 - \gamma_3)} \right) \]

\[ + 2e^{+it_0^2/\gamma_2} \frac{1}{4} e^{-it_0^2/\gamma_3} e^{it_0^2/\gamma_2} \left( e^{-it_0^2/\gamma_1} eQ^+(t_0^2 + \gamma_2) + e^{iQ}(t_0^2 - \gamma_2) \right) \]

\[ + \frac{e^{iR(t_0^2 + \gamma_2)} e^{it_0^2/\gamma_2} \left( e^{-it_0^2/\gamma_1} eQ^+(t_0^2 + \gamma_2) + e^{iQ}(t_0^2 - \gamma_2) \right)}{i^3 16Q^+ RS^+} \times \left( e^{i(R+S^+)(t_0^2 + \gamma_2)} - e^{i(R+S^+)(t_0^2 - \gamma_2)} \right) \]

\[ + 2e^{+it_0^2/\gamma_2} \frac{1}{4} e^{-it_0^2/\gamma_3} e^{it_0^2/\gamma_2} \left( e^{-it_0^2/\gamma_1} eQ^+(t_0^2 + \gamma_2) + e^{iQ}(t_0^2 - \gamma_2) \right) \]

\[ \left. + e^{iR(t_0^2 + \gamma_2)} \left( e^{iS^+ t} - e^{i(t_0^2 + \gamma_3)} \right) \right] \frac{e^{iR(t_0^2 + \gamma_2)} \left( e^{iS^+ t} - e^{i(t_0^2 + \gamma_3)} \right)}{i^3 16Q^+ RS^+} \]

\[ + 2e^{+it_0^2/\gamma_2} \frac{1}{4} e^{-it_0^2/\gamma_3} \left[ e^{+it_0^2/\gamma_1} e^{it_0^2/\gamma_2} e^{-i(Q^- + R)(t_0^2 + \gamma_2) + e^{i(Q^- + R^-)(t_0^2 - \gamma_2)}}}{i^3 16Q^-(Q^- + R)S^+} \right. \\
\left. + e^{iQ(t_0^2 - \gamma_1)} \left( e^{iR(t_0^2 + \gamma_2)} e^{it_0^2/\gamma_2} + e^{iR^-(t_0^2 - \gamma_2)} \right) \right] \left( e^{iS^+ t} - e^{i(t_0^2 - \gamma_3)} \right) \]

\[ + 2e^{+it_0^2/\gamma_2} \frac{1}{4} e^{-it_0^2/\gamma_3} e^{it_0^2/\gamma_2} \left( e^{-it_0^2/\gamma_1} eQ^-(t_0^2 + \gamma_2) + e^{iQ}(t_0^2 - \gamma_2) \right) \]

\[ + \frac{e^{iR(t_0^2 + \gamma_2)} e^{it_0^2/\gamma_2} \left( e^{-it_0^2/\gamma_1} eQ^-(t_0^2 + \gamma_2) + e^{iQ}(t_0^2 - \gamma_2) \right)}{i^3 16Q^- RS^+} \times \left( e^{i(R+S^+)(t_0^2 + \gamma_2)} - e^{i(R+S^+)(t_0^2 - \gamma_2)} \right) \]

\[ + 2e^{+it_0^2/\gamma_2} \frac{1}{4} e^{-it_0^2/\gamma_3} e^{it_0^2/\gamma_2} \left( e^{-it_0^2/\gamma_1} eQ^-(t_0^2 + \gamma_2) + e^{iQ}(t_0^2 - \gamma_2) \right) \]

\[ \left. + e^{iR(t_0^2 + \gamma_2)} \left( e^{iS^+ t} - e^{i(t_0^2 + \gamma_3)} \right) \right] \frac{e^{iR(t_0^2 + \gamma_2)} \left( e^{iS^+ t} - e^{i(t_0^2 + \gamma_3)} \right)}{i^3 16Q^- RS^+} \]
\[
+ \left[ \frac{e^{it_2\pi /\gamma_1}e^{i(Q+R)(t_2^0 + \gamma_1)} + e^{i(Q+R^-)(t_2^- - \gamma_2)} - e^{iQ(t_2^- - \gamma_2)}e^{iR^-(t_2^- - \gamma_2)}}{8i^3 Q(Q + R)S} \right. \\
- \frac{e^{it_2\pi /\gamma_1}e^{i(Q+R)(t_2^0 + \gamma_1)}}{8i^3 RQS^+} \left. 2e^{iR^+(t_2^0 + \gamma_1)} \frac{1}{4} e^{-it_2\pi /\gamma_3} \left( e^{iS^+ - e^{iS^+(t_2^0 - \gamma_3)} \right) \right] \\
+ \left[ \frac{e^{it_2\pi /\gamma_2}e^{iQ(t_2^0 + \gamma_2)}}{8i^2 RQ} \right. \\
- \frac{e^{iQ(t_2^- ^- - \gamma_2)}e^{it_2\pi /\gamma_2}}{8i^2 Q(Q + R)} \left. 2e^{iR^+(t_2^- ^- + \gamma_2)} \frac{1}{4} e^{-it_2\pi /\gamma_3} \right] \\
\times \left\{ \frac{e^{i(Q+S^+)(t_2^0 + \gamma_2)} - e^{iQ(t_2^0 + \gamma_2)}}{i(R + S^+)} \right. \\
+ \frac{-e^{i(R^- + S^-)(t_2^- + \gamma_2)} + e^{S^+}e^{iR^-(t_2^- + \gamma_2)}}{iS^+} \right\}
\]

\[
+ 2e^{iR^+(t_2^0 + \gamma_2)} \frac{1}{4} e^{iR^+(t_2^0 + \gamma_2)} \\
\frac{e^{iQ(t_2^- - \gamma_1)} \left( e^{iR(t_2^0 + \gamma_1)}e^{it_2\pi /\gamma_2} + e^{iR^-(t_2^- - \gamma_2)} \right)}{i^3 16Q^+(Q + R)S^-} \\
+ \frac{i^3 16Q^+ RS^-}{e^{iR(t_2^0 + \gamma_1)}e^{it_2\pi /\gamma_2} \left( e^{iR^+(t_2^0 + \gamma_1)} + e^{iQ(t_2^- - \gamma_1)} \right)} \left( e^{iS^- - e^{iS^+(t_2^- - \gamma_3)} \right) \\
+ \frac{2e^{iR^+(t_2^0 + \gamma_2)} \frac{1}{4} e^{iR^+(t_2^0 + \gamma_2)} e^{iR^+(t_2^- + \gamma_2)} + e^{iQ(t_2^- - \gamma_1)}}{i^3 16Q^+ RS^-} \\
\times \frac{e^{i(R^- + S^-)(t_2^- + \gamma_2)} - e^{i(R^- + S^-)(t_2^- - \gamma_3)}}{i^3 16Q^+ RS^-} \\
2e^{iR^+(t_2^0 + \gamma_2)} \frac{1}{4} e^{iR^+(t_2^0 + \gamma_2)} e^{iR^+(t_2^- + \gamma_2)} \left( e^{iR^+(t_2^- - \gamma_3)} + e^{iQ(t_2^- - \gamma_1)} \right) \\
+ \frac{e^{iR^+(t_2^- + \gamma_2)} \left( e^{iS^- - e^{iS^+(t_2^- + \gamma_2)} \right)}{i^3 16Q^+ RS^-} \\
\times \frac{e^{iR^+(t_2^- + \gamma_2)} \left( e^{iS^- - e^{iS^+(t_2^- + \gamma_2)} \right)}{i^3 16Q^+ RS^-}
\]
\[ + 2e^{it_0^2 \pi/n_2} \frac{1}{4} e^{it_0^2 \pi/n_1} e^{i(Q^- + R)(t_0^2 + \gamma_1)} + e^{iQ^-(R^-)(t_0^2 - \gamma_2)} e^{it_0^2 \pi/n_2} \]
\[ \times \frac{e^{i(Q(t_0^2 - \gamma_1))(e^{it_0^2 \pi/n_1} e^{iR^-(t_0^2 - \gamma_2)} + e^{iR^-(t_0^2 - \gamma_2)})}}{i36Q^- (Q^+ + R)S^-} \]
\[ + \frac{i36Q^- RS^-}{i36Q^- RS^-} \left( e^{iR^+(t_0^2 + \gamma_2)} - e^{iR^+(t_0^2 - \gamma_3)} \right) \]
\[ + \frac{i36Q^- RS^-}{i36Q^- RS^-} \left( e^{iR^+(t_0^2 + \gamma_2)} - e^{iR^+(t_0^2 - \gamma_3)} \right) \]
\[ + \left[ \frac{e^{it_0^2 \pi/n_1} e^{i(Q+R)(t_0^2 + \gamma_1)} + e^{i(Q+R^-)(t_0^2 - \gamma_2)} - e^{iQ(t_0^2 - \gamma_1)} e^{iR^-(t_0^2 - \gamma_2)}}{8i3Q(Q + R)S^-} \right] \]
\[ \times \left\{ \frac{e^{iR^+(t_0^2 + \gamma_2)} - e^{iQ(t_0^2 + \gamma_1)}}{i(R + S^-)} + \frac{-e^{i(R^- + S^-)(t_0^2 + \gamma_2)} + e^{iS^- t e^{iR^-(t_0^2 + \gamma_2)}}}{iS^-} \right\} \]
\[ + 2e^{it_2\pi/\gamma_2} \left[ \frac{e^{-it_0^2\pi/\gamma_1} e^{it_0^2\pi/\gamma_2} e^{i(Q^+ + R)(t_1^0 + \gamma_1)} + e^{i(Q^+ + R^-)(t_2^0 - \gamma_2)} e^{-it_0^2\pi/\gamma_1}}{i^316Q^+(Q^+ + R)S} \right. \\
+ \frac{e^{-it_0^2\pi/\gamma_1} (e^{R(t_1^0 + \gamma_1)} e^{it_0^2\pi/\gamma_2} + e^{R^-(t_2^0 - \gamma_2)})}{i^316Q^+ R_S} \\
- \frac{e^{-it_0^2\pi/\gamma_1} e^{it_0^2\pi/\gamma_2} (e^{Q^+ (t_1^0 + \gamma_1)} + e^{iQ(t_1^0 - \gamma_1)})}{i^316Q^+ R_S} \left( e^{iS(t_2 - t_1)} - e^{i(t_2^0 - \gamma_2)} \right) \right] \\
+ \frac{2e^{it_0^2\pi/\gamma_2} e^{it_0^2\pi/\gamma_2} (e^{-it_0^2\pi/\gamma_1} e^{iQ^+(t_1^0 + \gamma_1)} + e^{iQ(t_1^0 - \gamma_1)})}{i^316Q^+ R_S} \\
\times \frac{(e^{(R + S)(t_1^0 + \gamma_1)} - e^{(R + S)(t_1^0 - \gamma_1)})}{i^316Q^+ R_S} \\
+ \frac{2e^{it_0^2\pi/\gamma_2} e^{it_0^2\pi/\gamma_2} (e^{-it_0^2\pi/\gamma_1} e^{iQ^+(t_1^0 + \gamma_1)} + e^{iQ(t_1^0 - \gamma_1)})}{i^316Q^+ R_S} \\
\times \frac{e^{iR(t_1^0 + \gamma_1)} (e^{iS(t_2 - t_1)} - e^{iS(t_2^0 + \gamma_2)})}{i^316Q^+ R_S} \right]
\]
Clearly, inclusion of a pulse profile in the perturbative formalism generates an arduous number of terms. However, perhaps a better approach exists in the sech function. As a crude approximation of a true Gaussian profile, it is at least as legitimate as the $\cos^2$ function examined in the previous section.

However, it does have an advantage in the context of the perturbative integrals at hand. The reader is directed to Appendix A wherein a method for solving the non-trivial integration of the sech function to an arbitrary finite limit is laid out. Presently, the result of Appendix A equation A.12 will be used.

\[
\int_{-\infty}^{t} e^{iQ't'} \text{sech}(\gamma(t' - t_{0}))dt' = -\frac{e^{iQt_{0}}}{\gamma} \text{sech}(\frac{\pi Q}{2\gamma}) + \sum_{\text{modd}} 2i\frac{e^{iQt_{0}}e^{-m\gamma(t-t_{0})}}{Q + im\gamma} \quad (2.37)
\]
The second iteration becomes

\[
\int_{-\infty}^{t'} e^{iRt''} \text{sech} (\gamma_2(t'' - t_2^0)) \left[ -\frac{e^{iQt_1^0}}{\gamma_1} \text{sech} \left( \frac{\pi Q}{2\gamma_1} \right) + \sum_{\text{modd}} 2i \frac{e^{iQt_1^0} e^{-m\gamma(t'' - t_2^0)}}{Q + im\gamma_1} \right] dt'' =
\]

\[
- \frac{e^{iQt_1^0}}{\gamma_1} \text{sech} \left( \frac{\pi Q}{2\gamma_1} \right) \left[ -\frac{e^{iRt_2^0}}{\gamma_2} \text{sech} \left( \frac{\pi R}{2\gamma_2} \right) + 2i \frac{e^{iRt_2^0} e^{-m\gamma(t'' - t_2^0)}}{R + im\gamma_2} \right] +
\]

\[
\frac{2ie^{m\gamma_1 t_1^0} e^{iQt_1^0}}{Q + im\gamma_1} \left[ -\frac{e^{i(R + im\gamma_1)t_2^0}}{\gamma_2} \text{sech} \left( \frac{\pi (R + im\gamma_1)}{2\gamma_2} \right) + 2i \frac{e^{i(R + im\gamma_1)t_2^0} e^{-m\gamma(t'' - t_2^0)}}{(R + im\gamma_1) + im\gamma_2} \right]
\]

(2.38)

where the summations over the odd positive indices \( n \) and \( m \) are implied. This expression can be rearranged into a form \( A + Be^{-n\gamma t'} \):

\[
[2.38] = \frac{e^{iQt_1^0} e^{iRt_2^0}}{\gamma_1 \gamma_2} \text{sech} \left( \frac{\pi Q}{2\gamma_1} \right) \text{sech} \left( \frac{\pi R}{2\gamma_2} \right) - 2i \frac{e^{iQt_1^0} e^{iRt_2^0} e^{-m\gamma_1 t_2^0} e^{i(R + im\gamma_1)t_2^0}}{(Q + im\gamma_1) \gamma_2} \text{sech} \left( \frac{\pi (R + im\gamma_1)}{2\gamma_2} \right)
\]

\[- 2i e^{iQt_1^0} e^{iRt_2^0} e^{-m\gamma_1 t_2^0} \left( \frac{Q + im\gamma_1 (R + im\gamma_1 + im\gamma_2)}{\gamma_1 (R + im\gamma_2)} e^{-n\gamma t'} \right) \]

(2.39)

The third and final level of integration becomes:

\[
\int_{-\infty}^{t} e^{iSt'} \text{sech} \left( \gamma_3(t' - t_3^0) \right) \left( A + Be^{-n\gamma t'} \right) dt'
\]

\[
= A \left( -\frac{e^{iS t_1^0}}{\gamma_3} \text{sech} \left( \frac{\pi S}{2\gamma_3} \right) + 2i \frac{e^{iS t_1^0} e^{-\gamma_3 (t' - t_3^0)}}{S + i\gamma_3} \right)
\]

\[+ B \left( -\frac{e^{i(S + im\gamma_2)t_3^0}}{\gamma_3} \text{sech} \left( \frac{\pi (S + im\gamma_2)}{2\gamma_3} \right) + 2i \frac{e^{i(S + im\gamma_2)t_3^0} e^{-\gamma_3 (t' - t_3^0)}}{S + im\gamma_3 + i\gamma_3} \right)
\]

(2.40)

Thus, the time portion of the \( i \) time ordering (Equation 2.19) is expressed. Simple permutation of the entries for \( Q, R, \) and \( S \) provides the remaining time orderings (Equations
2.21–2.25). The sum of these six terms provides the third order transition amplitude, the modulus of which yields the scattering probability - i.e. output pulse profile as a function of frequencies, delays, physical state energies, and time.

2.7 Conclusion

The notion of inserting a temporal modulation in the perturbative fields for multi-photon scattering has been daunting because of the large number of terms involved in high order calculations. However, with a suitable pulse shape, a relatively simple solution can be had. Moreover, the expression is compact enough to allow for a fourth time integration, opening the door for time analysis of four-photon processes such as Degenerate Four Wave Mixing (DFWM), Coherent Stokes Raman Scattering (CSRS), and Coherent Anti-Stokes Raman Scattering (CARS). Application of the sech based pulsed formula developed in this chapter to numerical simulation may be useful in predicting quantum oscillation, dephasing, and other temporal effects which may become probable with contemporary short pulse width lasers, and to separate the coherence effects of the lasers from the physical relaxation of the probed material.
3.1 Introduction

Temperature behavior of light reflection, scattering and Second Harmonic Generation (SHG) from solid water films collected on a Si-SiO₂ substrate demonstrate irreversible and metastable behavior which is associated with the amorphous-cubic-hexagonal family of phase transitions of solid water. The large changes in reflectivity observed exceed that anticipated for either Silicon or solid water. It is shown that the oxide layer itself plays a vital role in this phenomenon, suggesting a strain-induced change in the dielectric function. This effect serves well as an enhanced, sensitive and hitherto unexploited probe for the study of the phase transitions in microlayers of solid water.

Further, documentation of the effect of solid water on the strain of the oxide layers of the substrate is crucial for cryogenic surface optical studies. Any optical or physical process dependent upon the behavior of the surface oxide layer will be influenced by this effect. Strain induced enhancement of the Second Harmonic susceptibility has been predicted by Govorkov [3], and the observations at hand not only support that prediction, but suggest that the linear susceptibility may also be influenced mechanically. While Silicon and it’s surfaces have been very well characterized for thermal temperatures, the cryogenic behavior has not. This effect, therefore, may point the way to a better understanding of the characteristics of the Si-SiO₂ interface.

A brief and separate review of the known characteristics of both the family of solid
water transitions and bulk Silicon will serve to preface the observations of the interaction of the two together.

3.2 Forms of Solid Water

The phase diagram of solid water has been mapped to reveal nine distinct crystal phases (Ice$_1$–Ice$_9$)[4] in addition to two amorphous forms[6] (also called "vitreous" phase[7]). Of these nine crystal structures, only Ice$_1$ has a density less than that of the liquid phase. The other denser phases are formed at high pressures. Ice$_1$ itself is further divided into two subgroups (Figures 3.2–3.1), Ice$_h$, hexagonal ice (space group P63/mmc), and Ice$_c$, cubic ice (space group Fd3m)[5], the latter of which is a metastable subset of the former. The amorphous form is not accessible from the liquid phase [8] but rather from the vapor phase directly to yield low density (0.94 gm cm$^{-3}$) Ice$_3$ or indirectly by applying 10 kbar pressures to crystalline ice $I_h$ to yield high density (> 1.17 gm cm$^{-3}$) amorphous Ice$_4$[9].

Likewise, the cubic phase is reached from one of two paths, either by heating low density amorphous ice or by depressurizing high pressure Ice$_5$ (space group A2/2 with a twenty-eight member unit cell). It is the first method which is relevant to the present work. Shallcross and Carpenter find that samples lowered in temperature to beneath -160 °C are deposited in the amorphous or vitreous form. Heating allows energy to assist frozen water to migrate to a crystalline phase. On the way to the natural low pressure $I_h$ the metastable $I_c$ structure emerges at temperatures no lower than -120 °C[10].

It has been observed that the intermediate $I_c$ phase is never pure and is always mixed with some fraction of amorphous grade solid water, as evidenced by neutron diffraction peak widths. This is true even as the temperature rises through the $I_c$ $I_h$ transition[11].
Figure 3.1: Three dimensional ray-traced representation of Oxygen placement in the hexagonal phase (from Fletcher[5]).
Figure 3.2: Three dimensional ray-traced representation of Oxygen placement in the cubic phase (from Fletcher[5]).
The final change from cubic to hexagonal occurs at temperatures above -80 °C. Dowell and Rinfret fit transition rates to the following formula: \( t = 2.58 \times 10^{12} e^{-0.126T} \) for this transition. In this formula, \( t \) represents the phase conversion time (in minutes) and \( T \) is the temperature in Kelvin. Sugisaki et. al. finds the Ice I\(_c\) → Ice I\(_h\) transition occurring in two steps with latent heats of 21.3 and 44.7 kJ/mole by monitoring changes in specific heat[12]. Elarby-Aouzerat tracks the Ice I\(_c\) → ice I\(_h\) transition with neutron diffraction using the 100 peak emergence for Ice I\(_h\) as the phase indicator yielding a -108 °C transition temperature[11]. The Electron Diffraction experiments of Blackman and Lisgarten show cubic forms at -140 °C to -120 °C, mixed cubic and hexagonal structures from -120 °C to -100 °C, and a pure hexagonal phase above -100 °C[13].

### 3.3 Index of Refraction of Silicon

The dielectric function is a reflection of the band structure of the bulk material. The characteristic cusps and peaks in the dielectric function for Silicon are linked to four principal interband critical points in the Silicon Brillouin zone identified as \( E_0 \), a gap at the zone origin \( k=000\), \( E_1 \) and \( E'_1 \), two gaps at the \( k=111\) zone edge, and \( E_2 \), a gap at the 100 zone boundary[15]. The energetic values and temperature dependence of these transition points are presented in Table 3.3.

The first observation to be had from this table is the fact that the primary transitions are far more energetic than photons in the optical regime. This is important, because the perturbative effects of temperature will change the band gap energies of the critical points, and therefore alter the dielectric function preferentially at the peaks corresponding to these transition points. The change in the dielectric function for optical frequencies, far
Figure 3.3: Temperature behavior of the index of refraction of bulk Silicon. From coefficients from Palik [14]
Table 3.1: Temperature dependence of the transitional critical points in the band structure of Silicon (from Lautenschlager[16]).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$E'_0$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E'_1$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>703</td>
<td>3.42</td>
<td>3.2</td>
<td>4.15</td>
<td></td>
</tr>
<tr>
<td>296</td>
<td>3.32</td>
<td>3.38</td>
<td>4.31</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>3.35</td>
<td>3.45</td>
<td>4.31</td>
<td>5.37</td>
</tr>
<tr>
<td>30</td>
<td>3.36</td>
<td>3.45</td>
<td>4.32</td>
<td>5.39</td>
</tr>
<tr>
<td>5</td>
<td>3.40</td>
<td>3.45</td>
<td>4.44</td>
<td>5.50</td>
</tr>
</tbody>
</table>

The second observation is that the change in transitional critical point energies over cryogenic temperature ranges is itself small. The dielectric function, and the index of refraction, experience a very small fractional change with temperature for optical wavelengths. This is born out in Figure 3.3. One would therefore expect only small fractional changes in the reflectivity of Silicon undergoing cryogenic cooling.

3.4 Light Scattering

Linear scattering experiments were conducted on two Si-SiO$_2$ substrates under cryogenic conditions. Contrary to the expectations leading from the above characteristics of Silicon, significant optical variations were observed. The first substrate was a 100- surface Silicon wafer with an 300-400 Å thick SiO$_2$ "thermal oxide" layer created by annealing at high temperature in an oxygen rich environment. This wafer was cut to $\sim$ 3 cm x 3 cm and affixed to a copper cold finger (Figure 3.6) and cooled from room temperature to -180°C in an evacuated chamber ($10^{-6}$-$10^{-8}$ Torr) for various durations of time. As
Figure 3.4: Linear scattering from SiO₂ surface.
probing the role of water contamination of the evacuated environment, water vapor could be introduced explicitly via a metering valve feeding a directed spigot near the substrate surface. The upper limit of the ensuing solid water film thicknesses was calculated from quartz micro balance measurements to be 100 Å. The reflectance\(^1\) of a P polarized\(^2\) 632.8 nm laser beam was monitored (Figure 3.5) during cooling and reheating to reveal a curious and highly reproducible temperature behavior. Pronounced reflectivity depression occurred at temperatures below -120 °C, and continued to fall even after the temperature bottomed out at -180 °C. Raising the temperature did not affect this reflectivity trend until the temperature -75 °C was reached, whereupon the reflectivity was restored (Fig. 3.7). If the temperature was not initially taken below -120 °C, then this transition was not seen when the sample was heated through the -75 °C region (Figure 3.8). An intense increase in the brilliance off-axis scattering accompanied this transition (Figures 3.8 and 3.9) and was monitored by a neutral density-filtered photomultiplier tube (Figure 3.5). A second brilliant scattering event even more intense than the first was observed repeatedly to occur at a higher temperature around -35 °C (Figure 3.9).

### 3.5 The Role of Water

The temperature characteristics of the first event were reminiscent of those of the Ice \(I_{as} \rightarrow I_{c} \rightarrow I_{h}\) family of transitions. In exploring the role of water, it was found that withholding water vapor reduced the magnitude of the scattering and reflectivity change. As it was not possible with the apparatus at hand to suppress the \(H_2O\) partial pressure

---

\(^1\)The reflectances shown in the data are not absolute reflectivities. They represent the quotient of reflected intensity and the fraction of the source split to the reference. At room temperature, the absolute reflectivity for the first wafer was 20% for P and 45% for S polarized beams at 45°.

\(^2\)P \(\equiv\) parallel to the plane of reflection, S \(\equiv\) normal to the plane of reflection. Total P reflectance \(\equiv\) unanalyzed reflection, P Reflection \(\equiv\) P-analyzed detector, S Reflection \(\equiv\) S-analyzed detector.
Figure 3.5: Cryogenic SiO$_2$ beam truncations.
Figure 3.6: Cryogenic sample mount with gas sampling line. The sample was clamped into a copper cold finger with a 1-inch diameter aperture. A copper sampling line directed water vapor to the sample as pictured. The thermocouple junction was clamped at the lower right screw. A length of NiChrome wire coiled about a ceramic rod and inserted into another ceramic cavity was clamped to the reverse side of the mount (not pictured) and served as the contact heater.
Figure 3.7: Temperature behavior of the reflectance for cryogenic Silicon with a thick oxide surface. Holding the temperature low while an ice film developed suppressed the reflectivity. As the temperature was allowed to rise, the repressed reflectivity increased asymmetrically at a critical temperature. By the time room temperature had been reached the reflectance had returned to the same level it began (origin not pictured). This is the total P reflectance.
Figure 3.8: Heating from below -120 °C gives a reflectivity recovery accompanied by off-axis scattering in all directions. Cooling to only -95 °C, however, does not demonstrate reversibility. This is consistent with the metastable cubic ice picture. This is unpolarized reflectance.
Figure 3.9: Second scattering excursion. Higher in temperature than the event associated with the Ice \( I_e \rightarrow I_h \) transition, this scattering is twenty times more intense (Note: a 5% transmission neutral density filter was inserted between scattering events in this run).

below \( 10^{-7} \) Torr, the influence of water was difficult to eradicate completely. Even following chamber and substrate baking (the latter limited to temperatures of temperatures of 50 °C), Residual Gas Analyzer (RGA) measurements revealed the tenacity of water vapor. To help, the cooling phase of the temperature cycle was conducted with a localized NiChrome coil contact heater active slightly, so as to allow preferential adsorption of water molecules on the relatively colder portions of the cold finger and cryostat apparatus. Comparison of Figures 3.10 and 3.11, cooling cycles which differed in that water vapor was introduced in one but not the other demonstrates the correlation between water and the reflection recovery. These effects were highly reproducible.
Figure 3.10: Reflectance throughout the cooling cycle on the thermal oxide (300 – 400 Å) substrate. This measurement was made after 3 days of evacuation and no water vapor was explicitly introduced. This represents the total P reflection.
Figure 3.11: Reflectance throughout the cooling cycle on the thermal oxide (300 – 400 Å) substrate. This measurement was made immediately after that of Figure 3.10 and differs from it in that water vapor was introduced via a sampling line. Note that despite the fact that H$_2$O was introduced early, it is not until the temperature of -120 °C that the reflectivity responds. This is consistent with the fact Ice I$_c$ and vitreous layers are formed only below this temperature. This is the total reflectance from a P-polarized incident beam.
Figure 3.12: S reflectivity of a P-polarized beam measured through the cooling cycle on a native oxide (50 Å) surface in the presence of applied water vapor. This is the S polarization. Note the vertical axis scale. It is important to note that the magnitude of the reflectivity change was reduced by an order of magnitude with the reduction in oxide layer thickness. The P reflectance change is also of the same scale (not pictured).

3.6 The Role of the Oxide Layer

But the causality of these effect cannot be limited to ice films alone. To demonstrate this, a second substrate, a 100-surface Silicon wafer with a native (unannealed in O\textsubscript{2}) oxide layer only 50 Å thick was used. The magnitude of both the reflectivity suppression and the off-axis scattering was greatly reduced by this change in substrate oxide layer thickness. Comparison of the magnitudes of Figure 3.8 (thick SiO\textsubscript{2} layer) and Figure 3.12 (thin SiO\textsubscript{2} layer) demonstrates nearly an order of magnitude reduction in the degree of optical behavior. This observation counters the notion that the scattering behavior is due
to interference within an ice layer alone. Rather, the inference to be made is that water molecules migrate \textit{into} the oxide layer itself.

### 3.7 Scattering Profile

Further investigation of the off-axis scattering events were made by placing a 255 element photodiode array (Appendix E) at the exit window of the cryostatic vacuum chamber. The scattering was found not to be isotropic, but to have a definite forward pitch in the differential cross section, as born out by Figure 3.13. Application of this scattering intensity pattern to the critical opalescence formalism of Ornstein and Zernike [17], in which the transition from isotropic to forward scattering is a major feature, is not entirely inappropriate.

This theory was developed for a liquid-gas model, in which fluctuations in the density of scattering "domains" make for, at a critical density and temperature, a distinct change in the isotropy and frequency dependence of the scattered light. The situation at hand is not a liquid, and this caveat should be noted in what follows. However, the Ornstein-Zernike theory treats the scattering domain in a general manner. A domain is a cell of uniform and coherent scattering matter. It can represent a macroscopic dust mote, a single atom, or a local density fluctuation of gas. The low density amorphous solid water Ice I$_a$ has likewise been characterized with a limit on the extent of order in any local parcel of the solid, of $\sim 0.7$ nm, and polycrystalline ice only allows these grain boundary sizes to increase as the temperature rises\cite{18}.

The static structure factor for a critical scattering assembly is given by Wang \cite{19}...
Figure 3.13: Image of the anisotropy of the off-axis scattering during the opalescent excursion. The individual channels of the 255 element imaging array are 25 μm in width and separated by 25 μm.
Slope = $1.63 \times 10^8 \, \text{Å}^2$

Y-Intercept = .857

Figure 3.14: Inverse off-axis scattering intensity vs. inverse momentum transfer during the opalescent phase of the heating cycle.
as

\[ S(q) = \frac{kT\rho_0\chi_T < N >}{1 + q^2\xi^2} \]

where

- \( k = \) Boltzmann's constant
- \( T = \) Temperature in Kelvin
- \( \rho_0 = \) equilibrium density of scattering domains
- \( \chi_T = \) isothermal compressibility
- \( q = \) momentum transfer
- \( \xi = \) correlation length
- \( S(q) = \) \( \equiv \int_{-\infty}^{\infty} d\omega S(q, \omega) \)

and \( S(q, \omega) \) is the dynamic structure factor, and is a measure of the scattering intensity as a function of both scattering angle and wavelength. Plotting the inverse of the scattering intensity against \( q^2 \) should produce a straight line with slope \( \xi^2/kT\rho_0\chi_T < N > \) and intercept \( kT\rho_0\chi_T < N > \). The square root of the product of these values obtained from Figure 3.14 yields a scattering correlation length of \( 1.2 \times 10^4 \text{ Å} = 1.2 \mu\text{m} \).

Inspection of Atomic Force Microscopy scans of the SiO₂ surfaces used in this series of experiments presented in Figures 3.15 reveals that while there are pores and microfissures, their spacing is well within this scattering length.

### 3.8 Second Harmonic Generation

Second Harmonic Generation (SHG) was performed on the thick oxide surface using the doubled fundamental of a Nd:YAG laser. The 532 nm beam was reflected from the surface during the cooling cycle. In order to normalize the SHG signal for laser power fluctuation part of the source beam was focused upon a KTP doubling crystal and the ensuing doubled UV was monitored by a PMT suitably filtered with a green blocking UG5 filter. In this manner the \( I^2 \) dependence of the SHG was introduced into the normalization.
Figure 3.15: Atomic Force Micrographs of both the thermal (left) and native (right) oxide surfaces. The top micrographs represent a $1\mu m \times 1\mu m$ image and the bottom pair represent $10\mu m \times 10\mu m$ scan areas.
Figure 3.16: SHG optical apparatus. UG5 filters block the 532 nm beam while passing the collinear UV SHG beam. In this configuration, two references, one for the fundamental power and one for the doubled power are collected.
Figure 3.17: Coherent Second harmonic generation on cryogenic SiO$_2$. These data represent the total scattering from a P-polarized incident 532 nm fundamental. Note the three tiered character of the SHG signal. The drops in SHG intensity are centered at points corresponding to the $I_{c}\rightarrow I_{h}$ transition near $\sim -75$ °C, the second scattering event at $\sim -35$ °C, and $I_{h}\rightarrow$liquid water transition at 0 °C.

The linear reflection of the 532 nm beam was also monitored and its normalization was achieved in the usual manner (Figure 3.16).

Coherent SHG is a highly surface and symmetry sensitive probe in which a non-linear polarization doubled in frequency from that of the applied field is induced and is described in terms of the macroscopic second-order susceptibility tensor (Equation 3.1).

$$P(2\omega) = \chi^{(2)} : E(\omega)E(\omega)$$

The symmetry sensitivity arises from the fact that quantum selection rules for SHG event forbid the transition in regions of centrosymmetry. This requirement automatically makes
the innate symmetry breaking represented by the material - vacuum interface the prefer-
tential zone for SHG to occur. What's more, the symmetry in the plane of the surface can
also accentuate or inhibit the SHG conversion efficiency.

In the case of the SiO₂, Three distinct steps in SHG response were noted at the
temperatures corresponding to both first and second linear scattering events as well as
the final phase change to liquid water (Figure 3.17). This is strong evidence of structural
changes with symmetry reorganization within the surface layers of the film-vacuum interface.
Following Kulyuk's proposal that surface SHG on Si-SiO₂ is generated primarily at the first
10 Å of oxide at the Si-SiO₂ interface[20] leads to a model in which water is allowed to
migrate via pores and microfissures into the oxide layer.

3.9 Estimation of Solid Water Film Depth

In order to estimate the depth of the solid water film deposited on the Silicon
substrate, a special quartz micro balance was built (Figure 3.18). The principle of operation
is quite simple. A quartz crystal tuned oscillator circuit is regulated by the capacitance of
the quartz resonator. Piezoelectrically driven vibrations cause an oscillating capacitance due
to the fluctuating thickness of the quartz dielectric. The resonant frequency of this quartz
dielectric can be changed by loading the surface with a damping mass of material. By
measuring the change in resonant frequency of a quartz oscillator while a film is deposited,
one may deduce the mass, and therefore the thickness, of a film of known density. While
this type of micro balance is used routinely for the measurement of vapor deposited films,
commercial units are not suitable for the kind of cryogenic application needed in this case.
Instead, a simple crystal oscillator was built with an exposed RF quartz crystal with contacts
Figure 3.18: Simple Quartz controlled oscillator. The crystal used was a 4.47 MHz RF crystal.
Figure 3.19: Partial pressure of H₂O during the cooling cycle for the micro balance measurement. This data was taken by means of an RGA affixed to the chamber. To protect the filament, the unit was turned off during the temperature and pressure excursion following the addition of water vapor at t=120 minutes.
Figure 3.20: The apparent thickness of the film deposited on the quartz microbalance surface over the course of cooling. Note that the curvilinear increase in virtual thickness levels off when the temperature does. Water vapor was introduced via metering valve at t=120 minutes.
Figure 3.21: Detailed plot of the transient region of Figure 3.20 following water vapor introduction. Note the difference in thickness before and after the transient temperature and pressure excursion. It is asserted that this is the change in frequency which corresponds to true film growth.
fused to the chip itself. The thickness of the film may be calculated from the resonant frequency change by:

\[
t = [(N_q D_q) / (\pi D_f Z F_c)] \arctan(Z \tan(\pi(F_q - F_c) / F_q))
\]

where

- \( t \) thickness in Angstroms
- \( N_q \) frequency constant, \( 1.668 \times 10^{13} \text{ Hz} \cdot \text{Angstrom} \)
- \( D_q \) mass density of Quartz, \( 2.658 \text{ gm/cm}^3 \)
- \( D_f \) mass density of film, \( 0.93 \text{ gm/cm}^3 \) for solid water
- \( Z = (D_q U_q) / (D_f U_f) \)
- \( U_q \) shear modulus of Quartz
- \( U_f \) shear modulus of film
- \( F_q \) frequency of the oscillator before film deposition
- \( F_c \) frequency of the loaded oscillator

The Silicon sample was replaced with the Quartz, and the appropriate electrical feedthrough were established. A cooling cycle typical of the SiO\textsubscript{2} work was carried out and the frequency, temperature and partial pressures monitored. The thickness calculated by means of equation 3.2 appears to increase with time even before water was explicitly introduced into the chamber. However, since this change tracks the temperature rather than H\textsubscript{2}O pressure curve in Figure 3.19, this change was taken as an indication of the change of the Quartz' resonant qualities due to its temperature change alone.

Water vapor was introduced via metering valve after the temperature had reached a steady state minimum. The ensuing transient pressure and temperature excursion can be seen in Figures 3.19–3.22. After the pressure re-equilibrated, a change in oscillator frequency corresponding to about 100 Å remained (Figure 3.22). As the pressure and temperature conditions were similar between the optical experiments and the microbalance measurements,
Figure 3.22: Corrected map of film thickness. In this plot, the initial frequency for equation 3.2 is taken at the steady state value just before the introduction of water vapor. Doing this asserts that the apparent change in thickness shown in 3.21 at this point is an artifact of cooling quartz and not due to surface loading. This plot most veridically represents the net ice deposition on the Quartz surface.
one can infer that similar amount of material were deposited in both scenarios, assuming similar sticking coefficients for molecular H₂O.

3.10 Conclusion

It is evident from SHG, linear and off-axis scattering observations that a structural phase transition occurs in or on the SiO₂ surface layer of cryogenically manipulated films. The well studied band structure of the bulk does not in any way support the kind of behavior observed. The fact that the addition of water vapor accentuates the optical behavior suggests that the phenomena is either partly or wholly due to the action of ice. The fact that the temperature behavior of the first event closely mimics that of the amorphous → cubic → hexagonal series of phase changes in solid water further implicates its
role. However, the fact that reduction of the oxide layer thickness reduces the magnitude of the effect would imply that this layer itself is directly involved. What's more, microbalance measurements predict ice films far smaller than would be required for elipsometric interference effects due to the adsorbate layer alone to be responsible.

The remarkable aspect of this mode of detection of this phase transition is that it is highly sensitive. In contrast to the neutron scattering, electron scattering, and calorimetric studies comprising the bulk of the Ice literature cited, in which layers μm thick were used, this method picks up on phase changes with microscopic levels of ice material. This is, therefore, at the very least, a novel mode of detection of the structural changes in solid water. But the role of the oxide layer itself cannot be discounted, and exploration of the physical interplay between the solid water adsorbate and the oxide structure is warranted.

It may be that ice in porous microfissures within the oxide stresses the film laterally, changing symmetry and dielectric functions of the combined ice - oxide region. Proposal of such a mechanism is not inappropriate; Govorkov predicts large SHG $\chi^{(2)}$ changes for Si surfaces stemming from stress effects[3]. While he considers the strains induced by nonuniformly planted defects during ion implantation, the strains postulated in the present work would stem from the presence of a phase change in the structure of an adsorbate. Naive analysis of the scattering anisotropy would indicate that long range coherence is at work, and AFM scans would suggest that the porosity is well within that range. Certainly such mechanisms have been proposed by those who study the photoluminescence associated with chemical etching of Silicon. The changing porosity of surfaces treated with hydrofluoric acid gives rise to a transient orange glow, and attempts to explain this phenomenon have ranged
from "quantum wire" models and quantum confinement theories to transient amorphous reconstruction scenarios to exotic surface species formation pictures [21], [22],[23].

Future studies which would prove useful would include a more complete SHG study with an oriented sample to determine symmetries of the scattering zones and scattering from oxides other than SiO₂. Water deposition on an oxide surface ion milled with an appropriate grating could reveal the lateral stresses induced by interstitially collected solid water through changes in diffraction efficiency. Raman spectroscopy of the O–H stretch in water would serve as an indicator of changing stresses on the H₂O molecules.
Chapter 4

Waveguided CARS Spectroscopy

Coherent Anti-Stokes Raman Scattering (CARS) is a four-photon process which, when conducted within the boundary conditions of a wave guiding medium, can serve as an enhanced surface and bulk probe. With the current trend in computing development turning toward low heat, high frequency integrated optical switching, nonlinear waveguide technology holds promise as photonic gates\cite{24}. As emphasized by Oliver\cite{25}, characterization of purely linear thin film devices is important in the fields of microelectronics and optoelectronics, where optical efficiency, band structure, defect states and free carrier effects may be ascertained and their impact on device operation determined. This chapter will describe an experiment performed on such a waveguide.

4.1 Classical Picture

For macroscopic media, Maxwell's equations describe the relation between fields and matter in terms of induced polarizations\cite{26}.

\[
\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}
\]

\[
\nabla \times \mathbf{B} = -\frac{1}{c} \frac{\partial (\mathbf{E} + 4\pi \mathbf{P})}{\partial t} + \frac{4\pi}{c} \mathbf{J}
\]

\[
\nabla \cdot (\mathbf{E} + 4\pi \mathbf{P}) = 4\pi \rho
\]

\[
\nabla \cdot \mathbf{B} = 0
\]

where \( \mathbf{P} \) is the local, linear polarization of the medium due to the applied field:

\[
\mathbf{P} = \chi^{(1)}(\mathbf{k}, \omega) \cdot \mathbf{E}(\mathbf{k}, \omega)
\]
However, if the applied field is intense enough, the polarization of the material can exhibit nonlinear responses. If the applied field is strong enough to drive the matter anharmonically, yet still weak enough to allow for a power series expansion of $\mathbf{P}$, then the nonlinear, nonlocal generalization of the polarization, $\mathbf{P}$ can be written thus\cite{27},

$$\mathbf{P}(k, \omega) =$$

$$\chi^{(1)}(k, \omega) \mathbf{E}(k, \omega) +$$

$$\frac{\chi^{(1)}(k, \omega)}{\mathbf{P}^{(1)}(k, \omega)}$$

$$\chi^{(2)}(k = k_1 + k_2, \omega = \omega_1 + \omega_2) : \mathbf{E}(k_1, \omega_1) \mathbf{E}(k_2, \omega_2) +$$

$$\frac{\chi^{(2)}(k, \omega)}{\mathbf{P}^{(2)}(k, \omega)}$$

$$\chi^{(3)}(k = k_1 + k_2 + k_3, \omega = \omega_1 + \omega_2 + \omega_3) : \mathbf{E}(k_1, \omega_1) \mathbf{E}(k_2, \omega_2) \mathbf{E}(k_3, \omega_3) +$$

$$\frac{\chi^{(3)}(k, \omega)}{\mathbf{P}^{(3)}(k, \omega)}$$

$$\vdots$$

$$\chi^{(n)}(k = k_1 + k_2 + \ldots + k_n, \omega = \omega_1 + \omega_2 + \ldots + \omega_n) : \mathbf{E}(k_1, \omega_1) \mathbf{E}(k_2, \omega_2) \ldots \mathbf{E}(k_n, \omega_n)$$

$$\frac{\chi^{(n)}(k, \omega)}{\mathbf{P}^{(n)}(k, \omega)}$$

These nonlinear polarizations are response of the matter to the driving applied fields at a local level and are subject to the microscopic structure and symmetries of the material. Depending, then, on the type of fields applied and the local structure probed, any number of interesting polarization responses can be induced, with the emission of detectable radiation.

Examples of such disparate phenomena include Parametric Oscillation, 4-Wave Mixing, Second and Third Harmonic Generation, Sum and Difference Frequency Generation, and Coherent Stokes and Anti-Stokes Raman Scattering. It is the latter that was used in a guided wave spectroscopy experiment.
Figure 4.1: Two possible time orderings for a four photon CARS event. Levels a and b are physical matter states, while the others are virtual states. Since only two virtual states are involved in the first time ordering pictured, it will dominate in it's contribution to the intensity of $\omega_4$.

4.2 Quantum Picture

In terms of quantum interactions, the generation of light differing in frequency from that of the applied field is treated as multi-photon interaction events at a microscopic center. A discussion of this picture may be found in Chapter 2. CARS is a four photon process in which two incident photons, $\omega_1$ and $\omega_3 = \omega_1$ are annihilated, $\omega_2$ emission is stimulated and a fourth photon at $\omega_4$ emerges (Figure 4.1). Note that the physical states probed are of the same parity and that energy is conserved in the total process. The Raman shift corresponds to the difference in energy of the two physical levels probed, and is given as $E = h\omega_1 - h\omega_2$. The frequency of the emitted photon $\omega_4$ is equal to $2\omega_1 - \omega_2$. Note that in this text $\omega_3$ refers to the third photon in the perturbative sequence but it is degenerate in energy to $\omega_1$. Some authors refer to $\omega_3$ as the CARS signal, here denoted $\omega_4$. 
Shen[27] shows the CARS signal intensity’s functional dependence on $\chi^3$ to be:

$$I_4 = \frac{2\pi\omega_4^2}{c\epsilon_4} |\chi^3|^2 r_1^2 r_2^2 \frac{\sin^2 \left( \frac{\Delta k - 1}{2} \right)}{\Delta k^2}$$

(4.1)

where $\Delta k$ represents the phase matching vector, the difference between the output photon wave vector and the corresponding input wave vectors.

### 4.3 Guided Waves

The asymmetric wave guide solutions are given by Mazely et al. [28]:

$$E_j = \frac{1}{2} \chi f_j(z) a_j(y) e^{i(\omega_j t - \beta_j y)} + c.c.$$  \hspace{1cm} (4.2)

where

$$C_j = 2\kappa_j \left[ \left( 2h + \frac{1}{\delta_j} + \frac{1}{\gamma_j} \right) \left( \kappa_j^2 + \delta_j^2 \right) \frac{\beta_j}{\omega_j \mu_0} \right]^{-1/2}$$

$$\gamma_j^2 = \beta_j^2 - n_3^2 k^2$$

$$\kappa_j^2 = n_2^2 k^2 - \beta_j^2$$

$$\delta_j^2 = \beta_j^2 - n_1^2 k^2$$

(4.3)

the field distribution is

$$f(z) = \begin{cases} 
  e^{-\delta_j(z-h)} & \text{superstrate (}z > h) \\
  \cos[\kappa_j(z-h)] - \left( \frac{\delta_j}{\kappa_j} \sin[\kappa_j(z-h)] \right) & \text{waveguide (}h > z > -h) \\
  \left[ \cos(2\kappa_j h) + \left( \frac{\delta_j}{\kappa_j} \right) \sin(2\kappa_j h) \right] e^{\gamma_j(z+h)} & \text{substrate (}z < -h) 
\end{cases}$$

and the propagation constants are related through the following recursion relation:

$$\tan(2h\kappa_j - m\pi) = \kappa_j \frac{\delta_j + \gamma_j}{\kappa_j^2 - \delta_j \gamma_j}$$

(4.4)
Figure 4.2: Propagation angles for TE modes in a waveguide of index 1.83. These data are presented in the most general fashion by plotting the angles against the ratio $\lambda / T$ where $T$ represents the thickness of the waveguide.

These formulae may then be used to determine the propagation angles, $\beta$, for various modes for a given material, thickness and wavelength. Figure 4.2 illustrates the family of propagation angles for the waveguide used in the experiment described in section 4.4. In order to generate these curves, Equation 4.4 was iterated using the code listed in appendix I.

The intensity of the CARS output photon $\omega_4$ produced by the interaction of these
fields is given by inserting the guided field distributions into expression 4.1.

\[ I_{\omega_4} = \left| \frac{1}{4} k e_0 \right|^2 |C_1^2 C_2^* C_3^*|^2 |\epsilon_4 \cdot F : \epsilon_1 \epsilon_3 \epsilon_2^*|^2 / L^2 I_{\omega_1} I_{\omega_2} \sin^2(\phi)/\phi^2 \]  

(4.5)

In this expression \( \phi \) represents the deviation from perfect phase matching (ideally \( \sum_k k = 0 \)) and the tensor \( F \) an effective susceptibility. It is the integral over the entire depth of the system of the field intensities and the actual \( \chi^{(3)} \):

\[ F = \int_{-\infty}^{\infty} \chi^{(3)} f_1(z) f_2(z) f_3(z) \, dz \]

This weighted tensor is the key for wave guided CARS to serve as a powerful probe for both surfaces and bulk material. Because one ostensibly has the freedom to choose the coupling modes, and therefore the transverse field structure pattern (the \( f(z) \)'s), one can select combinations which either interfere constructively or destructively over the bulk and substrate portions of the spatial integral.

For bulk CARS, constructive interference through even parity transverse field profiles for all photons gives a strong coherent guided field intensity. As an alternative for standard Raman profiling of a material, the extra intensity is valuable, since the response depends on the square of the intensity of \( \omega_1 \).

For surface spectroscopy, the rewards are even greater. Selection of a mode combination which has odd parity over the bulk region minimizes the overall contribution from the bulk. Meanwhile, the evanescent fields will always add constructively, enhancing the response of the surface nonlinearities or adsorbates.

Using the programs "Alamode" and "Alaint" (see Appendix I) to generate mode angles and then the ratio of the surface portion of Equation 4.5 to the bulk portion for a
Figure 4.3: Pictograph of the data found in Table 4.1, surface to bulk contrast ratios for surface CARS in a wave guide of index 2.18.
### Table 4.1: Waveguided CARS interference ratios for various mode combinations, n=2.18.

The wavelengths are given in terms of the ratio $t/\lambda$ where $t$ is the film thickness. The interference is given in terms of the ratio of the surface CARS signal $I_s$ to the bulk CARS signal $I_b$. In this case, the best contrast comes from mode combination 2-3-2. This information is presented in Figure 4.3.

<table>
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<th>$t/\lambda_2$</th>
<th>$I_s/I_b$</th>
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<tr>
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<td>0.55</td>
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</tr>
<tr>
<td>D</td>
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<td>0.55</td>
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</table>
wave guide of index 2.18, a huge contrast ratio was found at a mode combination of 2-3-2. Figure 4.3 and Table 4.1 show other combinations as well. It should be noted that these computations assume identical native susceptibilities for the bulk and the surface species. This is not true in general. In practice, an adsorbate, particularly an Organic one, might have a large susceptibility. In this case the contrast is even further enhanced.

4.4 Waveguided CARS

An experiment in constructive interference in a waveguide was performed using SiO$_2$N$_y$ material. The waveguide consisted of 7500 Å of SiO$_2$N$_y$ laid onto a Corning 7059 glass substrate via plasma enhanced chemical vapor deposition (Figure 4.4). SrTiO$_3$ prisms 10 mm on a side were spring clamped into contact with the surface of the guiding film to serve as couplers. While this method of coupling is practicable, it is not greatly efficacious, with a combined input/output coupling efficiency of 8% in the lowest order mode. This is because the theoretical coupling made by perfectly fused surfaces (see Figure 4.5) is defeated by imperfect contact. Therefore, the coupling in this system resembles evanescent wave coupling rather than simple refraction and the efficiency is reduced. The phase matching and coupling angles were produced by using a 6-inch diameter, f=26.8 cm lens as both a common focusing steering element. An f=80 cm correction lens was placed in the path of $\omega_1$ to ensure a common focal point in the waveguide for the crossed beams (Figure 4.6). The Gaussian waist at the focal spot was 300 μm with resultant power densities at the interaction zone of about 2100 mw/cm$^2$ and 700 mw/cm$^2$ for $\omega_1$ and $\omega_2$ respectively (the power directed to the coupling prisms was 2 mW and 6 mW respectively).

The sources of $\omega_1$ and $\omega_2$ radiation were two folded-cavity synchronously pumped
Figure 4.4: Atomic Force Micrograph of the SiO$_x$N$_y$ waveguide surface described in the text. This is an unpolished surface, so the super lattice domains are evident.

Figure 4.5: Refractive path through a coupling prism.
Figure 4.6: Guided wave CARS. Beams $\omega_1$ and $\omega_2$ are coupled into and out of the waveguide by means of contact prisms. The coherent interaction produces a beam of frequency $\omega_4$ as a coupled mode.
Figure 4.7: Optical paths for the dual dye lasers for the CARS experiment. Dark elements belong to \( \omega_1 \), light elements to \( \omega_2 \). Any element not explicitly labeled is a beam splitter. Elements labeled "M" are mirrors while those labeled "P" are Glan-Thompson polarizers. Ovals are converging lenses and right triangles are prisms. The apparatus was assembled on a 9' \( \times \) 15' optical bench.
pulsed high gain tunable dye lasers (Figure 4.7. Discussion of the wet chemistry and frequency monitoring of these lasers can be found in Appendix D. \( \omega_1 = \omega_2 \) came from a 6 mW tunable laser manually locked into a "fixed" frequency of 566 nm. \( \omega_2 \) was then scanned over a range of about 570 – 615 nm to provide the CARS spectrum. Tuning this source by computer was a formidable task which involved simultaneous interfacing with two tuning elements and the monochromator. Discussion of these issues may be found in Appendices B, E, F, H and D.

In order to compensate for radical and frequent power fluctuations of the Nd:YAG pump source and its effect on the dye lasers, intensity windowing was implemented in the software used to collect the data. After a laser shot was recorded, the datum was either kept or rejected if the reference intensity fell beyond a set range. In this way, the non-linear response to \( \omega_1 \) power was limited in it's noise impact on the spectrum.

Additionally, normalization of the signal was achieved by monitoring the intensities of the source lasers. The following background elimination scheme was implemented. Each laser had a solenoid driven shutter inserted in its cavity, which, when tripped by the computer, would extinguish lasing. These will be denoted \( S_1 \) and \( S_2 \). Each laser had a PIN photo diode intensity reference. The output of these diodes will be denoted \( R_1 \) and \( R_2 \). The signal apprehended at the waveguide by PMT, though filtered with a dielectric bandpass filter, apertures, and a 60 degree dispersive prism, still had scattered background contributions. The PMT signal will be denoted \( P \).

With \( S_1 \) and \( S_2 \) closed, \( E(R_1), E(R_2) \) and \( E(P) \) were measured. Since no light at all was issued with both lasers extinguished, these quantities represent the electronic
background provided by dark current, amplifier noise, and baseline biases. With $S_1$ off and $S_2$ on, $R_2 - E(R_2) = BR_1$ represents light scattered into the $\omega_2$ reference from $\omega_1$ and $P - E(P) = B1$ represents the $\omega_1$ contribution to the PMT signal. With $S_2$ off and $S_1$ on, $R_1 - E(R_1) = BR_2$ represents light scattered into the $\omega_1$ reference from $\omega_2$ and $P - E(P) = B2$ represents the $\omega_2$ contribution to the PMT signal.

Next, the assumption that the scattering contributions to these background signals are linear with respect to the sources.

$$BR_1 = \alpha_1 I\omega_1$$  \hspace{0.5cm} (4.6)

$$BR_2 = \alpha_2 I\omega_2$$  \hspace{0.5cm} (4.7)

$$B1 = \beta_1 I\omega_1$$  \hspace{0.5cm} (4.8)

$$B2 = \beta_2 I\omega_2$$  \hspace{0.5cm} (4.9)

$$I\omega_1 = R_1 - E(R_1) - BR_2 = R_1 - E(R_1) - \alpha_2 I\omega_2$$  \hspace{0.5cm} (4.10)

$$I\omega_2 = R_2 - E(R_2) - BR_1 = R_2 - E(R_2) - \alpha_1 I\omega_1$$  \hspace{0.5cm} (4.11)

$$P = E(P) + I\omega_4 + B1 + B2$$  \hspace{0.5cm} (4.12)

Solving these equations simultaneously gives the corrected signal intensities.

$$I\omega_1 = \frac{R_1 - E(R_1)\alpha_2 (R_2 - E(R_2))}{1 - \alpha_1 \alpha_2}$$  \hspace{0.5cm} (4.13)

$$I\omega_2 = \frac{R_2 - E(R_2)\alpha_1 (R_1 - E(R_1))}{1 - \alpha_1 \alpha_2}$$  \hspace{0.5cm} (4.14)

$$I\omega_4 = P - e(P) - \beta_1 I\omega_1 - \beta_2 I\omega_2$$  \hspace{0.5cm} (4.15)

In practice, since this background routine involves so many shutter combinations, background was taken on every 200th data point. A typical spectrum would contain 4000 –
Figure 4.8: CARS signal produced by constructive interference in the SiO$_x$N$_y$ waveguide described in the text. These data are the convolution of five scans over the frequency range. 8000 points. The Si-O vibrational Raman spectrum produced (Figure 4.8) was thus achieved after signal averaging over 2000 pulse trains per data point.

4.5 Conclusion

As a means of characterizing the internal structure of wave guiding materials the interference provided by the transverse mode structure of guided waves actually enhances what is an otherwise weak process.

While CARS conducted through waveguides has vast potential for surface spectroscopy, this has not been demonstrated experimentally by this work. However, the enhancement in contrast between the surface nonlinear response and the bulk contribution has been demonstrated through computation, and the source code has been presented.
Chapter 5

Conclusion

The issues explored in this work are many. All revolve around the physics of light-matter interactions.

First, an original analytic expression for the time dependent multiphoton transition amplitude corresponding to a microscopic susceptibility was derived. The resultant expression allows for the general solution of the transition probability for any desired set of pulse widths, delays and frequencies. The generality of this expression in no way implies triviality, however; the degrees of freedom built into the expression allow for maximum utility.

Second, observation of an adsorbate-controlled change in both first and second order susceptibilities ($\chi^{(1)}$ and $\chi^{(2)}$) of a surface oxide layer demonstrated (i) the impact of an adsorbate on the optical properties of the host (ii) a means of introducing stress in an oxide layer without ion implantation or macroscopic loading and (3) a system for the study of the phase changes in solid water sensitive to very small amounts of material.

Third, Coherent Anti-Stokes Raman Scattering was performed inside a planar optical waveguide. This experiment not only measured the Raman profile for the characterized guide, but demonstrated the efficacy of waveguided CARS. In the course of achieving this measurement, a working nonlinear spectrometer was built utilizing computer assisted tuning techniques, drift correction, and an original birefringent filter design.
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APPENDICES
Appendix A

Fourier Method for Finite Integration

The following represents a method for evaluating a definite integral of a function in terms of the infinite integral of the same function by means of Fourier methods.
A.1 The Fourier Transform of a Product is Equal to the Convolution of their Fourier Transforms

Proof.

\[ G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} g(t) \, dt \]

and \( g(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} G(\omega) \, d\omega \)

and let \( F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega t} f(t) \, dt \)

and \( f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} F(\omega) \, d\omega \)

\[ \int_{-\infty}^{\infty} g(t) f(t) e^{i\omega t} \, dt = \quad (A.1) \]

\[ = \int_{-\infty}^{\infty} f(t) e^{i\omega t} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{Gi\omega t}(\omega) e^{-i\omega t} d\omega \, dt \]

\[ = \frac{1}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} F(\omega) G(\omega) e^{i(a-\omega-\omega)t} d\omega \, dt \]

\[ \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(a-\omega-\omega)t} \, dt \equiv \delta(a - \omega - \omega) \right\} \]

\[ = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} F(\omega) G(\omega) e^{i(a-\omega-\omega)t} \, dt \, d\omega \]

\[ = \int_{-\infty}^{\infty} F(a - \omega) G(\omega) \, d\omega \]
A.2 Creating the Finite Limit

Sometimes a definite integral with a finite limit is harder to solve than the concomitant definite integral with an infinite limit. By rewriting the integrand of a finite limit integral as the product of the original integrand and a Heavyside step function, the limits may be extended to infinity:

\[
\int_{-\infty}^{T} f(t) dt = \int_{-\infty}^{\infty} f(t) g(t) dt \text{where} g(t) = \Theta(T - t) \begin{cases} \hfill 0 & \hfill t > T \\ \hfill 1 & \hfill t < T \end{cases} \tag{A.2}
\]

The transform becomes:

\[
G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i(\omega + \delta)t} \Theta(T - t) dt
\]

\[
= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{T} e^{i(\omega + \delta)t} dt
\]

\[
= \frac{1}{\sqrt{2\pi}} \left. \frac{e^{i(\omega + \delta)t}}{i\omega + \delta} \right|_{-\infty}^{T}
\]

\[
= \frac{1}{\sqrt{2\pi}} \frac{e^{i\omega T}}{i\omega}
\]

Where \(\delta\) is allowed to approach an arbitrarily small real positive value.

A.3 An Example

In this section the Fourier method will be used to analyze the finite integral

\[
\int_{-T}^{T} e^{iax} \cos(bx) dx \tag{A.3}
\]
which is easily integrated in the standard way:

\[
\int_{-T}^{T} e^{iax} \cos(bx) \, dx = \int_{-T}^{T} e^{iax} e^{ibx} + e^{-ibx} \, dx
\]

\[
= \frac{e^{i(a+b)x}}{2i(a+b)} + \frac{e^{i(a-b)x}}{2i(a-b)} \bigg|_{-T}^{T}
\]

\[
= \frac{e^{i(a+b)T} - e^{-i(a+b)T}}{2i(a+b)} + \frac{e^{i(a-b)T} - e^{-i(a-b)T}}{2i(a-b)}
\]

\[
= \frac{\sin(a+b)T}{a+b} + \frac{\sin(a-b)T}{a-b}
\]  

(A.4)

Using the masking method, the finite limits on the integral in expression A.3 are made infinite by inserting Heavyside step functions in the integrand:

\[
\int_{-T}^{T} e^{iax} \cos(bx) \, dx = \int_{-\infty}^{\infty} e^{iax} \cos(bx) \Theta(T-t) \Theta(x+T) \, dx
\]

where \( \Theta(T-x)\Theta(t+T) = \begin{cases} 
0 & t < -T \\
1 & -T < x < T \\
0 & t > T
\end{cases} \)
\[ = \int_{-\infty}^{\infty} f(x)g(x) \, dx \]

\[ = \int_{-\infty}^{\infty} F(a)G(a') \, da \]

where \( f(x) = \cos(bx) \)

\( g(x) = \Theta(T - x)\Theta(t + T) \)

\[ F(a) = \int_{-\infty}^{\infty} e^{iat}f(x) \, dx \]

\[ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{iat} e^{ibx} + e^{-ibx} \, dx \]

\[ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{i(a+b)x} + e^{i(a-b)x}}{2} \, dx \]

\[ = \frac{1}{\sqrt{2\pi}} \frac{1}{2\pi} (\delta(a+b) + \delta(a-b)) \]

\[ G(a' - a) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i(a'-a)x}g(x) \, dx \]

\[ = \frac{1}{\sqrt{2\pi}} \int_{-T}^{T} e^{i(a'-a)x} \, dx = \frac{1}{\sqrt{2\pi}} \frac{e^{i(a'-a)x}}{i(a'-a)} \bigg|_{-T}^{T} \]

\[ = \frac{1}{\sqrt{2\pi}} \left( \frac{e^{i(a'-a)T} - e^{-i(a'-a)T}}{i(a'-a)} \right) \]

\[ = 2 \frac{\sin((a' - a)T)}{a' - a} \]
\[ F(a)G(a' - a) = \frac{1}{2} \left[ \delta(b - a) + \delta(a + b) \right] \left[ 2 \frac{\sin((a' - a)T)}{a' - a} \right] \]

\[ \int_{-\infty}^{\infty} F(a)G(a' - a) = \frac{1}{2} \left[ \delta(b - a) + \delta(a + b) \right] \left[ 2 \frac{\sin((a' - a)T)}{a' - a} \right] da \]

\[ = \frac{\sin(b - a')T}{b - a'} + \frac{\sin(b + a')T}{b + a'} \]

which agrees with the result of the standard integration (eq.A.4).

### A.4 Application to the sech pulse shape

The above method can now be employed to simplify the finite limit integral

\[ \int_{-\infty}^{t} e^{iQt'} \text{sech}(\gamma(t' - t_0)) dt' \quad (A.5) \]

by letting

\[
g(t) = \Theta(t' - t) = \begin{cases} 
0 & t' > t \\
1 & t' < t 
\end{cases} \quad (A.6)\]

and

\[ f(t') \equiv \text{sech}(\gamma t') \quad (A.7)\]

The Fourier transform of the sech function is itself a sech function, which is why it is chosen as a viable pulse shape for the iterated high order perturbative calculations in the text.

\[ F(Q) = \int_{-\infty}^{\infty} e^{iQt'} \text{sech}(\gamma(t' - t_0)) dt' = \text{sech}(\frac{\pi Q}{2\gamma}) \quad (A.9)\]

This can be born out through the complex plane integration over the path illustrated in Figure A.4. Making the transformation from real to complex time, \( t' \rightarrow z = x + iy \)
the integrand has a an infinite family of singularities periodically spaced in the imaginary direction. \( e^{iQz} \text{sech}(\gamma(z - t_0)) = \frac{e^{iQz}}{\cosh(\gamma(z - t_0))} \) has a zero denominator when the argument of the \( \text{cosh} \) function, \( \gamma(z - t_0) \), equals \( m\pi/2 \) where \( m \) is a signed odd integer. This means that the poles in the complex plane sit at the positions \( z = \frac{m\pi}{2\gamma}i - t_0 \). The residues at these poles are given by

\[
R_m = \lim_{z \to \frac{m\pi}{2\gamma}i - t_0} (z \frac{m\pi}{2\gamma}i - t_0) \frac{e^{iQz}}{\cosh(\gamma(z - t_0))}
\]

Application of L'Hopital's rule by differentiating the numerator and denominator before taking the limit yields:

\[
R_m = \lim_{z \to \frac{m\pi}{2\gamma}i + t_0} \frac{(z \frac{m\pi}{2\gamma}i + t_0)iQe^{iQz} + e^{iQz}}{\gamma\sinh(\gamma(z - t_0))} = \frac{1}{\gamma} e^{-Qm\pi/(2\gamma)e^{iQ_t_0}}
\]
The closed path of integration indicated in Figure A.4 encloses only one of these poles, and can be separated into four legs:

\[
\oint e^{iQz} \text{sech}(\gamma (z - t_0)) = \int_{-X}^{X} e^{iQx} \text{sech}(\gamma (z - t_0)) dx \tag{I}
\]

\[
= \int_{-\pi/\gamma}^{\pi/\gamma} e^{iQ(x+iy)} \text{sech}(\gamma (X + iy - t_0)) dy \tag{II}
\]

\[
+ \int_{-X}^{X} e^{iQ(x+\pi/\gamma)} \text{sech}(\gamma (x + i\pi / \gamma - t_0)) dx \tag{III}
\]

\[
+ \int_{X}^{\pi/\gamma} e^{iQ(x+iy)} \text{sech}(\gamma (X + iy - t_0)) dx \tag{IV}
\]

In the limit as \(X \to \infty\) the integrands in parts II and IV are driven to zero. Inspection of the argument of term III and utilization of the fact that \(\text{sech}(\theta + i\pi) = -\text{sech}(\theta)\) allows the limits of this term to be reversed. This done, it is apparent that the two integrals I and III are proportionate:

\[
\oint e^{iQz} \text{sech}(\gamma (z - t_0)) = \int_{-\infty}^{\infty} e^{iQx} \text{sech}(\gamma (z - t_0)) dx \tag{I}
\]

\[
+ e^{-\pi Q / \gamma} \int_{-\infty}^{\infty} e^{iQx} \text{sech}(\gamma (x - t_0)) dx \tag{III}
\]

\[
= \left(1 + e^{-\pi / \gamma}\right) \int_{-\infty}^{\infty} e^{iQx} \text{sech}(\gamma (x - t_0)) dx
\]

Further, by the residue theorem, the closed path integration will equal \(2\pi i \sum \Re_{\text{enclosed}}\).
\[
(1 + e^{-\pi Q/\gamma}) \int_{-\infty}^{\infty} e^{iQx} \text{sech}(\gamma(x - t_0)) dx = \frac{2\pi i}{\gamma} e^{iQ\pi/(2\gamma)}
\]

\[
\int_{-\infty}^{\infty} e^{iQx} \text{sech}(\gamma(x - t_0)) dx = \frac{2\pi i e^{-Q\pi/(2\gamma)} e^{iQt_0}}{(1 + e^{-\pi Q/\gamma})} = \frac{2\pi i e^{iQt_0}}{\gamma \left( e^{iQ\pi/(2\gamma)} + e^{-\pi Q/2\gamma} \right)} = \frac{i\pi e^{iQt_0}}{\gamma \text{sech}(\frac{\pi Q}{2\gamma})}
\]

(A.10)

This is simply the Fourier transform of the sech function. The integral at hand, eq. A.5 has yet to be solved. Using the Fourier transforms of the integrand and the masking function eq. A.5 may be rewritten with infinite limits.

\[
\int_{-\infty}^{\infty} e^{iQ't} \text{sech}(\gamma(t' - t_0)) dt' = \frac{i}{2\gamma} \int_{-\infty}^{\infty} \frac{e^{i(Q-Q')t}}{i(Q - Q')} e^{i(Q/Q')} \text{sech}(\frac{\pi Q'}{2\gamma}) dQ'
\]

(A.11)

The same sort of infinite series of poles in the imaginary direction exist in this integrand as were in the previous sech transform. This integral differs, however, in that a denominator which is resonant at \(Q' = Q\) exists. This sets another pole on the real axis with which to contend when the transformation to the complex plane occurs. With \(Q' \to z = x + iy\) the residues are, at \(z = Q\)

\[
\mathbb{R}_0 = \lim_{z \to Q} \frac{i (z - Q) i(-t + t_0)e^{i(Q-z)t}e^{izt_0} + e^{i(Q-z)t}e^{izt_0}}{i(Q - z) \frac{\pi}{2\gamma} \sinh \left( \frac{\pi z}{2\gamma} \right) - i \cosh \left( \frac{\pi z}{2\gamma} \right)}
\]

\[
= \frac{-1}{2\gamma} e^{iQt_0} \text{sech}(\frac{\pi Q}{2\gamma})
\]

\(1\)less the factor of \(1/\sqrt{2\pi}\)
Figure A.2: Complex contour integration path for the convolution of the finite-$t$ mask and the sech transforms. The arc extends infinitely, encompassing the entire set of negative valued residues.
and at \( z = \text{i} \gamma \):

\[
R_m = \lim_{z \to \text{i} \gamma} \frac{\text{i} (z - \text{i} \gamma) (z + t_0) e^{i(Q-z)t} e^{\text{i} t_0} + e^{i(Q-z)t} e^{\text{i} t_0}}{i(Q - z) \frac{\pi}{2 \gamma} \sinh \left( \frac{\pi z}{2 \gamma} \right) - i \cosh \left( \frac{\pi z}{2 \gamma} \right)}
\]

\[
= \frac{1}{\pi} \frac{e^{iQ t_0} e^{m \gamma (t_0)}}{Q - \text{i} \gamma}
\]

The existence of that resonant term in the denominator introduces a lone pole on the real axis breaks the symmetry that made equally spaced integral paths parallel to the real axis proportional to another in the earlier Fourier transform of the sech function. Therefore, the entire set of residues will have to be collected under and infinite path. This means that the solution will wind up being an infinite summation. However, inspection of the formula for \( R_m \) shows that the series is convergent for negative \( m \). In fact, it is the negative imaginary half plane that the infinite arc must trace in order for that leg of the path integral to vanish, so it is indeed the negative \( m \) values that will be used. Invocation of the residue theorem, then, provides the final solution to equation A.11.

\[
\int_{-\infty}^{t} e^{iQ t'} \text{sech} \left( \gamma (t' - t_0) \right) dt' = -\frac{e^{iQ t_0}}{\gamma} \text{sech} \left( \frac{\pi Q}{2 \gamma} \right) + \sum_{\text{modd}} 2i e^{iQ t_0} e^{-m \gamma (t_0 - t_0)}
\]

(A.12)

The above expression redefines \( m \) as being a positive index, and the appropriate signs have been changed to account for this.
Appendix B

Four Plate Birefringent Filter for High Gain Pulsed Dye Laser Tuning

B.1 Introduction

Introduced to study the solar corona spectrum in the 1930's [34][35], birefringent or Lyot filters continue to find application in solar spectroscopy today, where planar imaging precludes diffractive spectroscopy [36][37]. Similar filters are used as selective tuning elements in broadband cw dye laser cavities. As such, the theory behind these filters has been treated for both single [38] and multiple [39] stage filters. Temperature effects have also been studied [40]. However, as observed by Holtom [41], implementation in a high-gain laser leads to unwanted sideband transmission.

Birefringent filters exploit Brewster angle reflection loss of S-polarized radiation in order to reject all but certain frequency orders by means of controlled polarization retardation. Although the term Lyot filter strictly denotes a system of birefringent plates sandwiched between linear polarizers, the term will be used presently to include filters without polarizer stages as well. However, the equations governing multiple stage Lyot filters allow for successive phase retardations to produce, in addition to the desired passband, comparatively weak satellite solutions representing unwanted sidebands.

While implementation in low gain dye lasers prevents these sidebands from emerging, high gain, pulsed dye lasers provide less contrast between main orders and satellite orders. As a result, the utility of commercial Lyot filters used in such cavities is compromised. A quantitative analysis of a four plate Lyot filter assists in the design of a working
Figure B.1: A single birefringent plate in the presence of an incident beam with both S and P components. The plate is tilted at $\theta =$ Brewster's angle in the $kP$ plane (see also fig. B.5). The P component will pass through the plate, but will emerge as a combination of P and S, the mixing ratio being frequency dependent.

A tunable filter with good linewidth and free spectral range.

B.2 Theory

With a dye jet oriented at Brewster's angle and pumped with $P$ polarized (horizontal) light, the $P$ polarization mode is the prevalent cavity mode. Placement of a single $z$-cut birefringent plate in the cavity at Brewster's angle, with the $P$ direction approximately halfway between the $n_e$ and $n_o$ directions, or 45 degrees from the optic axis, has several effects. First, the Brewster orientation introduces partial reflection loss for any incident $S$
(vertical) radiation. Second, exiting radiation will experience a relative phase retardation. Some $P$ amplitude will be transferred to $S$, while some $S$ will be transformed to $P$. Third, the retardation is dispersion-dependent. For a specific family of frequencies, those for which the difference between ordinary and extraordinary optical path lengths is an integer number of vacuum wavelengths, $[n_o(\nu) - n_\phi(\nu)]L = n\lambda$, no retardation occurs, and the $P$ amplitude passes unchanged.

Following Pruess and Gole[39], utilization of the Jones matrix of a single birefringent plate, tilted and rotated with respect to the input beam axes (fig. B.1), describes the polarization transformation

$$
\begin{pmatrix}
E^\text{out}_S \\
E^\text{out}_P
\end{pmatrix}
= M(\theta, \phi)
\begin{pmatrix}
E^\text{in}_S \\
E^\text{in}_P
\end{pmatrix}
$$

(B.1)

where

$$
M(\theta, \phi) =
\begin{pmatrix}
SS & SP \\
PS & PP
\end{pmatrix}
$$

(B.2)

and

$$
SS = \frac{e^{i\delta}(n_o^2 - \sin^2 \theta) \cos^2 \phi + e^{i\delta} n_\phi^2 \sin^2 \phi}{(n_o^2 - \cos^2 \phi \sin^2 \theta)}
$$

(B.3)

is the amplitude of incident $S$ preserved as $S$,

$$
PP = \frac{e^{i\delta}(n_o^2 - \sin^2 \theta) \cos^2 \phi + e^{i\delta} n_\phi^2 \sin^2 \phi}{(n_o^2 - \cos^2 \phi \sin^2 \theta)}
$$

(B.4)

is the amplitude of incident $P$ preserved as $P$,

$$
SP = \frac{[e^{i\delta} - e^{i\delta}](n_o \sin \phi \cos \phi) |n_o \sin \theta|}{(n_o^2 - \cos^2 \phi \sin^2 \theta)}
$$

(B.5)
is the amplitude of incident $P$ transformed to $S$, and $PS = SP$. In this expression, $\theta$ is the angle between the plate normal and the ray axis (ideally $\theta = \theta_{\text{Brewster}}$), and $\phi$ is the azimuthal angle about the filter body axis, measured between the ordinary axis of the plate and the $S$ polarization direction. The phases of the field components along the extraordinary and ordinary directions are:

$$
\delta_e = \delta_e(\theta, \phi, t) = 2\pi n_e t \tilde{\nu} \left( 1 + \sin^2 \theta \cos^2 \phi \left( \frac{1}{n_e^2} - \frac{1}{n_o^2} \right) \right) \left( 1 - \sin^2 \theta \left( \frac{\sin^2 \phi}{n_e^2} - \frac{\cos^2 \phi}{n_o^2} \right) \right)
$$

(B.6)

and

$$
\delta_o = \delta_o(\theta, t) = 2\pi n_o t \tilde{\nu} \sqrt{1 - \frac{\sin^2 \theta}{n_o^2}}
$$

(B.7)

where $t$ = plate thickness, and $\tilde{\nu} \equiv 1/\lambda_{\text{vac}}$ is the frequency in cm$^{-1}$.

As both Zhu[38] and November and Stauffer[37] point out, the phase angle equations may be inverted in $\tilde{\nu}$ yielding the family of frequencies experiencing $\pi$-phase shifts. This is similar to the approach Preuss and Gole use in their design analysis, in which the set of frequencies which drive only the $PP$ term to unity are found. By this approach, a multiple stage filter is designed by superimposing the orders of three single plates of different thicknesses to provide the bandwidth of the thickest plate with the free spectral range (FSR) of the thinnest.

But this method has several weaknesses. First, by considering only the frequencies which drive the transmission coefficient to unity, one generates orders of global maxima only. This method is therefore insensitive to local maxima with peak heights less than unity. Second, by considering the $PP$ term alone, the contribution of the $SP$ matrix component is
neglected. For a single plate with a pure $P$ input and 100% $S$ attenuation of the output, this would be adequate. However, a multiple stage filter, even with a pure $P$ input, will generate $S$ fields at the output of each plate by virtue of the $SP$ element of the transformation tensor $M$. This $S$ component will then provide immediately successive plates with an $S$ input, as the Brewster attenuation is not 100%, but only about 17% at each surface. The ultimate transmission spectrum is therefore not the superposition of the individual free plate profiles, but is compounded by the successive trading between the two polarization modes caused by all tensor components, not just $PP$. These intermediate transformations manifest themselves as sidebands in the $P$ output which can, in fact, experience the gain of the $P$ polarized pump. Dye lasers operated in cw mode allow for many passes through a multistage filter, enabling the Brewster reflection loss to effectively suppress these sidebands. But a Q-switched, modelocked, high gain pulsed dye laser may provide only a few passes, allowing the sidebands to compromise the spectral purity. A true Lyot filter of the kind used in solar astronomy employs polarizers between stages to eliminate intermodal transfer. But this may not be a practical alternative in a laser tuning system. In addition to increasing the length of the filter and the magnitude of beam displacement, placing stationary polarizers between rotating birefringent plates is complicated. A full analysis of a multistage system therefore requires the repeated use of $E_{P_{out}} = PPE_{P_{in}} + PSE_{S_{in}}$ and $E_{S_{out}} = SSE_{S_{in}} + SPE_{P_{in}}$ at each plate.

It is a simple matter to iterate the Jones matrix over each stage, including a reflection loss factor at each face. Rather than search for maxima, one merely generates the actual transmission over all frequencies to see the sidebands that are present in actual use.
The dispersion relation used incorporated tabular dispersion data[14] for quartz in a third order polynomial fit, yielding:

\[ n_e = 1.52431 + 2.72477 \times 10^{-6}\nu - 1.02969 \times 10^{-10}\nu^2 + 2.54850 \times 10^{-15}\nu^3 \]

\[ n_e = 1.52431 + 2.72477 \times 10^{-6}\nu - 1.02969 \times 10^{-10}\nu^2 + 2.96919 \times 10^{-15}\nu^3 \]

The computer program used for the simulation also allows for separate variation of each plate angle, thus allowing one to see the effects of angular misalignment of the optic axes, information which proved valuable in the alignment of the finished filter. Various three-plate combinations were modeled, and in every case sidebands of various separations and magnitudes were apparent in the transmission profile. Addition of small fractions of $S$ radiation to the incident field only exacerbate the problem. Yet small $S$ components from the dye source may be present in practice.

The best combination turned out to be a four plate ensemble. The ratio of 1:2:4:8 plates yields minimal sideband transmission and a combined FSR of 1685 cm$^{-1}$ (fig. B.2). The contrast ratio between the principal transmission band and the largest sideband in a five-pass simulation is 270. One may compare this to the transmission profile generated by the commercial ratios 1:2:15 and 1:4:16 which yield contrast ratios of only 3.2 and 29 respectively. The overlapping FSR argument suggests that integer thickness ratios should perform best. The commercial ratio 1:2:15, which does not conform to this restriction, performs poorly (fig. B.3). Yet another combination 1:4:16 also used commercially shows a sideband structure (fig. B.4).

Notice that while the four plate assembly affords two additional surfaces for Brewster loss to compensate for the fewer passes in a high gain cavity, the sideband structure
Figure B.2: A simulation of a 1:2:4:8 quartz plate ratio filter rotated axially by $\phi = 39.06$ degrees with a 90/10 P/S input field ratio. In this calculation, 5 passes were iterated to yield this, the $P$ transmission function, normalized to unity. While the sidebands (barely visible here) are not completely eradicated, they are satisfactorily suppressed. The free spectral range is 1685 cm$^{-1}$ in this region of the spectrum. The sidebands remain even in the absence of an incident $S$ input. The sidebands do not appear if the $SP$ and $PS$ elements of the Jones matrix are ignored.
Figure B.3: The calculated $P$ transmission function of a 1:2:15 plate ratio system. This commercial design is particularly ineffective, with large sidebands being present in this simulation. Smaller sidebands are broadened to a near continuum. This calculation again iterated 5 passes with a 90/10 P/S field ratio.
Figure B.4: Calculated $P$ transmission profile for the 1:4:16 plate ratio. Another commercial ratio in which, despite the integer multiple thicknesses, sideband structure is evident, and in fact is large enough to lase, given the gain. Mere superposition of individual plate profiles does not predict these sidebands. The calculation used in this simulation couples the behavior of all plates to yield this structure. Again, a 90/10 P/S input and 5 passes were used to generate this normalized $P$ transmission profile.

cannot be completely suppressed. But this combination does drive the transmission peaks sufficiently low so as to eliminate lasing. This is not necessarily true for the other models. The calculated spectra are multi-pass transmission profiles of the filters alone; other cavity gain and loss mechanisms are not incorporated into this calculation. As a result, the calculated linewidths are actually broader than those found in practice.
B.3 Filter Construction and Performance

Four 1-inch diameter quartz plates of thickness 1.027, 2.054, 4.107, and 8.215 mm (+ .1µm) were offset axially to account for the displacement of a beam incident at Brewster's angle (fig. B.5). Each plate is thus held off axis by its own plate holder. The surfaces of each plate are held 2mm apart. Each plate holder is itself held to the main cylindrical housing (4.4 cm diameter) by its own radial setscrew, meaning that each plate may be rotated independently. This is generally acknowledged as extremely useful for finely tuning the filter upon assembly[42].

The filter was assembled in the laser cavity, successively introducing each plate. Rough alignment was made by matching the plate manufacturer’s indication of the optic axis direction. Fine angular alignment required that the laser output be monitored through a one-meter monochromator. A photodiode array replaced the slit at the monochromator exit allowing a small range of the spectrum to be viewed as an oscilloscope trace while leaving the monochromator grating fixed. In this manner, the angle ϕ of each new plate could be adjusted so that a single target peak was emphasized. However, auxiliary peaks still existed. The smallest pair was eliminated by passing the laser beam through a P transmitting linear polarizer, indicating that a finite amount of S mode lasing does occur.

The plates were adjusted so that the remaining peaks formed symmetric lobes on either side of the target peak. This procedure was repeated with the addition of each plate in succession. After four plates, the next lasing order was pushed just beyond the range of the dye. Rotation about the filter body axis moves the peak through the dye profile. Since each plate’s ϕ angle is adjusted independently to center on the peak, one thus corrects
Figure B.5: Four plate filter design. Plates of thickness 1.027, 2.054, 4.107, and 8.215 mm are spaced by 2 mm. The surfaces are specified at $\lambda/10$ at 632.8 nm. The plates are staggered by the indicated offsets to account for the beam displacement. Plates 1-3 are held in independent plate holders which are free to turn with respect to the main housing which also holds plate 4. This main casing is slotted (not pictured) to allow rotational access to plate holders 1-3. Once each plate’s individual $\phi$ angle is so adjusted, each plate is locked to the main cylinder with its own set screw. It should be noted that as the plates are mounted off center from the holder’s rotational axis, independent adjustment yields a slight plate translation as well as a rotation. Nevertheless, only small angular adjustments are necessary during initial alignment. After the plates are locked, the unit may be rotated as a whole to tune the laser.
Figure B.6: Spectra of the synchronously-pumped dye laser described in the text with and without the 1:2:4:8 birefringent filter.
for imperfect parallelism and plate thickness. Accordingly, the optic axes may be slightly misaligned. It is therefore crucial to note that this alignment is good only for this particular order maximum. If the filter is rotated to allow the next order into the range, it may have sidebands associated with it due to the axes' misalignment. It is important, therefore, to pin the range over which the filter is allowed to rotate. In the case of this design, the maximal orders are separated by rotations of the filter housing of 18 degrees.

The linewidth produced by the filter in a high gain pulsed dye laser was measured to be 4.5 cm\(^{-1}\) and the spectrum is shown in fig. B.6. The laser had a cavity length of 1.5 m and a Rhodamine 610/ethylene glycol dye jet in the folded region. It was pumped with the frequency-doubled output of a 500 Hz Q-switched, mode-locked, cw Nd:YAG laser. The green pulse train consisting of thirty 100 ps pulses. Pulses in the train were separated by 10 ns. Further linewidth reduction was made by inserting a piezoelectrically-controlled etalon into the cavity. By simultaneously controlling the Lyot filter tuning angle and the etalon spacing via a computer interface, a 0.2 cm\(^{-1}\) wide line may scanned continuously through the range of the dye, 16700 - 17300 cm\(^{-1}\).

B.4 Conclusion

For high gain applications, all terms in the transformation tensor are relevant for the analysis of a multistage birefringent filter. Further, it is insufficient to superimpose single plate profiles. Rather, the equations for each plate must be coupled to account for all polarization amplitudes. For a four plate filter, the ratio 1:2:4:8 delivers the best profile with the most attenuated sidebands. In future designs, the Brewster loss at each face might be accentuated by the use of birefringent plates of higher index, such as sapphire.
Appendix C

Nd:YAG Laser

The keystone of the experimental apparatus is the Nd:YAG laser. This section will briefly outline its operation.

The gain medium is crystalline Yttrium Aluminum Garnet, Y₃Al₅O₁₂, with Neodymium Nd³⁺ atoms substitutionally doped in the lattice at Y³⁺ sites. More information about the optical properties of this material can be found in Table C.1.

The Nd:YAG laser used was a modified mode-locked, pulsed Quantronix 114 water cooled laser Q-switched at 500 Hz (Figure C.1). The 30 pulses comprising each train were 10 ns in duration, separated by 100 ps. In order to pump the dye lasers, the 1064 nm Nd:YAG fundamental was frequency doubled by means of a type II phase matched KTP crystal¹ 3mm × 3mm × 8mm with anti-reflection coatings for both 1064 nm and 532 nm. With a conversion efficiency of 40%, 950 mW of pulsed infrared radiation produced 380 mW

¹CSK Optronics DVAR SHG 1064 #1867

![Diagram of Nd:YAG laser setup](image_url)

Figure C.1: Nd:YAG laser described in the text.
Table C.1: properties of Nd:YAG (from Koechner [43])

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dopant Level by weight</td>
<td>0.725%</td>
</tr>
<tr>
<td>Dopant Level by atoms</td>
<td>1.0%</td>
</tr>
<tr>
<td>Nd density</td>
<td>$1.38 \times 10^{20}/\text{cm}^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>1970 °C</td>
</tr>
<tr>
<td>Density</td>
<td>4.56 g/cm³</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>1.82</td>
</tr>
<tr>
<td>Coefficients of Thermal Expansion [100]</td>
<td>$8.2 \times 10^{-6} \text{C}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>[110] $7.7 \times 10^{-6} \text{C}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>[111] $7.8 \times 10^{-6} \text{C}^{-1}$</td>
</tr>
<tr>
<td>Relaxation Time $^4I_{11/2} \rightarrow ^4I_{9/2}$</td>
<td>30 ns</td>
</tr>
<tr>
<td>Radiative Lifetime $^4F_{3/2} \rightarrow ^4I_{11/2}$</td>
<td>550 μsec</td>
</tr>
</tbody>
</table>

of a 2mm birefringent Quartz plate, and the unconverted collinear IR radiation filtered by means of an infrared reflecting mirror oriented at Brewster's angle.
Appendix D
Dye Lasers

The sources for the $\omega_1$ and $\omega_2$ photons were two synchronously pumped, high-gain, tunable dye lasers. Each had a circulating dye jet oriented at Brewster’s angle in the folded region of its respective cavity (Figure 4.7).

$\omega_1$ was tuned by means of a rotatable double prism dispersive element in tandem with an adjustable etalon. $\omega_2$ was tuned by means of a custom designed four-plate birefringent filter (see Appendix B) and a piezoelectrically controlled tunable etalon.

D.1 Frequency Monitoring

Both lasers were coupled via a fiber optic link to a one-meter monochromator. The frequency reference for $\omega_1$ was split from the beam after the exit face of laser $\omega_1$. The $\omega_2$ frequency reference, however, was tapped from a surface reflection from the $\omega_2$ etalon within the laser cavity. This was done in the interest of both minimizing the loss of usable spectroscopic power and maximizing the frequency reference power. Calibration over the entire lasing range verified that the surface reflection used was locked in frequency to the beam from the laser’s exit face.

Although both lasers were tunable, only laser $\omega_2$ was interfaced for automated tuning by computer. The frequency of $\omega_1$ would be set manually at the beginning of an experiment by monitoring via the fiber link to the monochromator. After this initial calibration, the monochromator would be scanned to the wavelength of laser $\omega_2$, where
Figure D.1: Linear position monitor circuit for detection of the frequency drift of laser $\omega_1$. 
it would remain parked for the duration of the experiment. The tuning algorithms (see Appendix H) required constant access to the spectral profile garnered by the pixillated linear image interface of the monochromator (see Appendix E).

As a result, any drift in $\omega_1$ would be unrecorded, and the Raman shift probed would in fact differ. In order to monitor the frequency stability of $\omega_1$, a dedicated frequency sensor was built. The frequency reference ordinarily directed to the coupling fiber for the monochromator could be redirected by means of a series of mirrors on translation stages to a double prism jig. The dispersed beam was allowed to travel 2.5 meters before focusing onto a special linear position detector element\textsuperscript{1}

A 1 mm high, 12 mm long strip of photo-resistant material produces a different voltage (when biased) at either end based on the position of the photocharge producing spot on the sensor. This analog system is quite different from the digitized linear imaging used in the monochromator proper. While the ratio of the voltages of the dual anodes should give a measure of the position with respect to the sensor’s center, fluctuations in laser intensity make for a noise fraught reading.

To remedy this weakness, the amplifier electronics illustrated in Figure D.1 were built. After initial stages of transimpedance amplification, both anode signals were processed by analog sum ($\Sigma$) and difference ($\Delta$) amplifiers. The outputs of these stages were then sent to a division circuit (not pictured) based on an analog transconductance multiplier IC\textsuperscript{2}. The resultant ratio $\Delta/\Sigma$ is therefore immune to baseline fluctuations to first order.

The output of the divider circuit was suitable for interfacing and incorporating

\textsuperscript{1}Hamamatsu S3932 one-dimensional position sensitive detector.
\textsuperscript{2}Analog Devices AD533 Multiplier, Divider, Square Rooter
### Table D.1: Characteristics of Rhodamine B (from Brackmann [44])

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
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<tr>
<td>Formula</td>
<td>C&lt;sub&gt;28&lt;/sub&gt;H&lt;sub&gt;31&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;Cl</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>479.02</td>
</tr>
<tr>
<td>Absorption Maximum in CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>552 nm</td>
</tr>
<tr>
<td>Fluorescence Maximum in CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>580 nm</td>
</tr>
<tr>
<td>Tuning Center</td>
<td>582 nm</td>
</tr>
<tr>
<td>Lasing Range (532 nm pump)</td>
<td>577 - 601 nm</td>
</tr>
</tbody>
</table>

Into the CARS data acquisition software. In practice however, due to chronic thermal instabilities of the etalon for ω<sub>1</sub>, the sensor was used only to monitor major frequency excursions corresponding to bimodal lasing caused by FSR drifts allowing more than one lasing peak into the gain zone rather than the subtle drifts in the absolute position of the single peak used in normal operation.

#### D.2 Laser Dyes

The gain medium for the two dye lasers were solutions of Rhodamine B for ω<sub>1</sub> and Rhodamine 6G for ω<sub>2</sub> in ethylene glycol. The structures for these two organic molecules are presented in Figures D.2 and D.3. Both afford a near continuum of vibrational modes excitable by a 532 nm pump. The resultant fluorescence peaks are given in Tables D.1 and D.2.

To prepare the dyes, 2 grams were dissolved in 100 mL of methyl alcohol and forced into solution by mild heating and prolonged magnetic stirring for 24 hours. 1.50 L of ethylene glycol were placed in the dye circulation path, which included a 1 L filter vessel.
Figure D.2: Structure of Rhodamine B (from Brackmann [44]).

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<tr>
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<td>Fluorescence Maximum in CH_3CH_2OH</td>
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Table D.2: Characteristics of Rhodamine 6G (from Brackmann [44]).

Figure D.3: Structure of Rhodamine 6G (from Brackmann [44]).
with a wound bleached cotton filter with a 1 μm aperture weave. In the case of w₂, the Rhodamine 6G: solution was drawn into a 60 mL syringe with a 22 guage needle and was transferred gradually to the circulating ethylene glycol. Addition via syringe allowed for maximal control of the concentration of dye within the ethylene glycol. Once the concentration was brought to the lasing threshold, the beam was channeled to a photodiode. The laser intensity was thus monitored and additional dye was injected slowly over the course of twenty minutes until the intensity began to fall. Finally additional ethelyne glycol was injected in order to reduce the concentration to achieve the density which maximized the intensity. In this way, the balance between dye concentration and opaqueness was met empirically. In the end, a total of 80 mL of Rhodamine 6G: methyl alcohol was combined with 1.55 L of ethylene glycol to give an optimized concentration of 2.23 Mole/L.

³Part # C1A-4A, Filterite Co., Timonium, MD
Appendix E

Monochromator Electronics

The key to being able to continuously tune the dye laser is the ability to monitor its spectral output electronically. In order to achieve this, as 256 element photodiode array\(^1\) was placed at the exit slit of a one-meter monochromator.

The digitizing electronics were designed around the self scanning diode array's clocking requirements and fabricated on a 3" by 7" printed circuit board. The acquisition sweep begins after a 1 \(\mu\)s delay from the Q-switch driver for the Nd:YAG laser. A 250 kHz TTL clock pulse sequentially poles each element in the array. The array affords two outputs, one representing the addressed live diode element, and another representing an optically shielded dummy diode element. These signals are amplified differentially by a wideband op amp\(^2\) in order to eliminate common switching transients.

After the charge is drawn, amplified, sampled and held, the diode is reset with a -10 volt recharge pulse. The sampled and held signal is sent serially to a digitization stage. The digitized signal is then stored in a memory bank. After all 256 elements have been poled and stored, an active-low blanking signal allows the memory the addressed by a counter sequence initiated by a request pulse from an interfaced computer.

---

\(^1\)Part # RL256G, EG&G Reticon, Sunnyvale, CA

\(^2\)Part # OPA621, Burr-Brown, Tucson, Az
Figure E.1: Diode video electronics outline
Figure E.2: Diode video circuit
<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
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<td>7404 Inverter</td>
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<tr>
<td>U2</td>
<td>7402 Buffer</td>
</tr>
<tr>
<td>U3</td>
<td>74123 Monostable Multivibrator</td>
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<tr>
<td>U4</td>
<td>74123 Monostable Multivibrator</td>
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<tr>
<td>U5</td>
<td>RLG256K 256 element linear photodiode array</td>
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<tr>
<td>U6</td>
<td>OPA670 High Bandwidth Op Amp</td>
</tr>
<tr>
<td>U7</td>
<td>SHC5320 High Bandwidth Sample/Hold Amplifier</td>
</tr>
<tr>
<td>Q1</td>
<td>SN4260 PNP Switching Transistor</td>
</tr>
<tr>
<td>R1</td>
<td>500 kΩ pot</td>
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<tr>
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<tr>
<td>R3</td>
<td>500 kΩ pot</td>
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<td>C6</td>
<td>.022 pF</td>
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</tbody>
</table>

Table E.1: Diode Video Components
Figure E.3: Diode Blanker Circuit

Table E.2: Blanker Components

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<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>U1</td>
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</table>

Table E.2: Blanker Components
Figure E.4: Data bus architecture
Appendix F

CARS Data Acquisition Software

In order to perform the spectroscopic measurements, software to control dye lasers, normalization shutters, data acquisition and signal averaging was written. This chapter will outline the structure of the software with the code to follow.

F.1 Data Assignment

There are five A/D converters referred to as "hard channels" and addressed at hex port address H30A. There are nine logical data arrays, referred to as "soft channels" or "arrays", to which can be assigned various functions performed on the data from the hard channel data from the A/D converter port. Entry of a hard channel number in an array text box will assign the data from that channel to that data array. An entry of "0" will leave that array blank. Two, three, or four hard channel numbers separated by slashes will assign the corresponding quotient of hard channel data to that array. The four letter phrases "wave", "wvno", "ramn", and "time" will assign the energy of $\omega_2$ in wave numbers, the wavelength of $\omega_2$ in nanometers, the Raman shift $\omega_2 - \omega_1$ in wavenumbers, and the time in seconds to the logical array corresponding to the text box used. All of these data functions are performed on a shot by shot basis before signal averaging.

"Shots" determines the number of individual laser pulses over which to signal average. One "shot" is equivalent to one 30-pulse train.

"EtSweep" will lock the Lyot filter in place and sweep the etalon, recording the
spectral maximum position in array 1 and intensity in array 2. The result will be an image of the Lyot filter profile.

"LyotSweep" will lock the etalon in place and sweep the Lyot filter, recording the spectral maximum position in array 1 and intensity in array 2. The result will be an image of the etalon profile.

All settings may be saved to or recalled from a resource file (extension .rc). The "Files" menu provides the appropriate dialog box. Data may likewise be saved or recalled via these dialog boxes.

F.2 Lyot, Etalon and Monochromator Control

The Monochromator Controls menu displays the current position of the monochromator grating stage's stepper motor, the lyot filter's stepper motor, and the etalon control word. The current peak position and intensity of the linear diode array are also displayed on a range of 0 – 255. Finally, the position of the center pixel in nm space is displayed.

The definition of the current lyot filter and monochromator stepper motor positions can be changed immediately simply by changing their values within their text boxes. Both stepper motors and the etalon can be queued by the control buttons below the text boxes.

The "MonoGo" button will invoke a dialog box prompting for the absolute destination position in monochromator grating counts to which to queue the grating. "MonoSeek" is identical to "MonoGo" except that the destination is given in nanometers rather than grating steps. A brief pause is to be expected after invoking this command while a search algorithm determines the grating position corresponding to the requested wavelength.

"Rotate" will turn the lyot filter by the indicated number of steps. The value
entered in the dialog box should be a signed integer. The command “Squeeze” will send a control word to the etalon controller. The word consists of an integer from 0 to 4095. The D/A converter in the etalon supply will convert this word to the appropriate high voltage (0-450 V) to be sent to the piezoelectric element in the etalon mount.

F.3 Signal Averaging and Intensity Windowing

In order to minimize the effects of fluctuating laser intensity, an intensity gate filter is set in the data integrating loop. Shots in which any of the A/D hard channels’ values fall beyond the upper and lower limits set on the HLIMS menu will be disregarded. These entries are made in units of A/D counts, i.e. 1 to 4096.

F.4 Graphing

The “Display” option of the “Graph” menu of the main form will display a graph of the data arrays entered in the dx and dy text boxes. The domain of the graph is set by the value of the “points” text box. Although this value defaults to the maximum number of points in the data field, it can be overridden simply by entering the desired value in the text box. After the graph is displayed in graphics mode, a crosshair can be superimposed on the display graph and positioned with the right and left arrow keys. This is useful for determining various global extrema, as well as for determining the values of specific plotted points. The values of the current data point are displayed in the upper left hand corner of the graphics display. Table F.1 lists the functions of the crosshair navigation keys.
move crosshair right on data point
← move crosshair left one data point
pgup  move crosshair right 50 data points
pgdwn move crosshair left 50 data points
↑ place crosshair at y-array global maximum
↓ place crosshair at x-array minimum

Table F.1: Displayed graph crosshair controls

F.5 Editing Data

Data amassed in the nine logical arrays may be displayed and edited in columnar format under the "Edit Data" form. This form displays five list boxes. The vertical ribbon will scroll the list box position. The logical array displayed is set with the horizontal scroll bar beneath each list box. The maximum and minimum entry for the data for each list box assigned array are displayed in the control buttons atop and beneath each list box. A single mouse click on either of these control buttons will advance the list box to the corresponding global extremum in the array data.
Appendix G

Thermocouple Information

The cryogenic Silicon experiments required a continuous monitor of the temperature of the cold finger to which the substrate was attached. To that end, an unsheathed fine gauge K type Nickel-Chromium Vs. Nickel-Aluminum (Chromel-Alumel) thermocouple manufactured by Omega International was attached to the lowest portion of the mounting substrate.

The output of the compensated dual junction was amplified differentially and computer interfaced to the CARS data acquisition program. Data from the manufacturer¹ was fit to a fourth order polynomial using a least square regression, and the resultant function was utilized in the software to record temperature directly.

The reference junction was clamped into a 3 kg Aluminum thermal mass and immersed in an ice bath. In this way, the potentials created by the feed through connections to the vacuum chamber could be negated by the reverse biased second junction. A differential stage of amplification was inserted between the compensated junction output and the A/D converter feeding the data acquisition computer.

¹Complete temperature measurement handbook and encyclopedia
Omega Engineering 1985
Omega International
One Omega Drive
Stamford, CT 06907
Figure G.1: Schematic for K-type thermocouple dual junction with constant reference.
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Table G.1: Thermocouple Voltage Response
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<th>°C</th>
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Table G.2: Continuation of G Table Thermocouple table
Appendix H

CARS Data Acquisition Source Code

The enclosed disk holds the source code written in Microsoft Visual Basic for MS-DOS\(^1\) for the program "CARS". This program controls and automates the execution of a CARS spectroscopy experiment, including recursive tuning of \(\omega_2\) via interface to a stepper motor driven Lyot filter, a piezoelectrically controlled etalon, a stepper driven one-meter monochromator and a 255 element digitizing array. Normalization for the four photon process is handled through a series of background elimination calls to interfaced solenoids.

The forms and modules reside in directory a:\cars.

\(^1\)"Microsoft", "Visual Basic" and "MS-DOS" are trademarks of Microsoft, Inc.
Appendix I

Waveguide Mode Calculation Source Code

The enclosed disk holds the source code for the program "Alamode4" which was used to generate the mode propagation angles $\beta$ for the asymmetric planar optical waveguide described in the text. The sole input parameter is the index of refraction. The output is in the form of a comma separated value file with data arrays for the first 10 TE mode angles vs. the ratio of guide thickness to wavelength.

The code resides in directory a:\modes\alamode.
Appendix J

Waveguide Interference Calculation Source Code

The enclosed disk holds the source code for the program "Alaint" which used the mode propagation angles $\beta$ generated by "Alamode" to determine the interference for optimal surface enhancement of CARS. The sole input parameter is the file produced by "Alamode" and the index of refraction. The output is in the form of a series of comma separated value files with data arrays showing the ratio surface to bulk CARS response vs. the ratio of guide thickness to wavelength. A variety of mode combinations are attempted, and some 20 files are produced.

The code resides in directory a:\modes\alaint.