ANALYSIS FOR COHERENT ANTI-STOKES RAMAN SPECTROSCOPY (CARS)

PERFORMING ORGANIZATION NAME AND ADDRESS
The University of Michigan
Department of Electrical and Computer Eng.
Ann Arbor, MI 48109

MONITORING AGENCY NAME AND ADDRESS (if different from Controlling Office)
AFOSR/NP
Boiling AFB DC 20332

ABSTRACT
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A number of different computer codes have been developed to solve the equations at different levels of complexity. With them numerical investigation of the effects of various physical factors on saturation was carried out. Some of the results are presented graphically.
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(CARS)

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by

Herschel Weil
Radiation Laboratory
The University of Michigan
Ann Arbor, Michigan 48109

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Bolling AFB, D.C. 20332

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Abstract

Coupled differential equations have been formulated which model the generation of coherent anti-Stokes Raman radiation in molecular gases. The equations include not only the basic term which involves the coherent interaction of incident pump and idler (Stokes) waves to generate the anti-Stokes radiation, but also include additional terms which model other radiation and absorption processes, both stimulated and coherent, which occur simultaneously. These are important in determining saturation effects due to population depletion of the lowest energy level. Other effects have also been considered. These are a finite idler beam bandwidth (simultaneous excitation of more than one vibration frequency) a quasi-monochromatic idler beam slightly off the true Stokes frequency; laser pulse shape; modification of the result for different rotational levels.

A number of different computer codes have been developed to solve the equations at different levels of complexity. With them numerical investigation of the effects of various physical factors on saturation was carried out. Some of the results are presented graphically.
I. INTRODUCTION

Coherent anti-Stokes Raman Spectroscopy is a form of Raman spectroscopy which has developed with the advent of laser light. In it the medium--usually gas or liquid--is irradiated by two waves, the pump wave at frequency $\omega_p$ and a lower frequency wave, the idler wave, at $\omega_i$. When their frequency difference matches a vibrational frequency $\omega_v$ characteristic of the molecule the idler wave is then at the Stokes frequency $\omega_s = \omega_p - \omega_v$. One result is coherent generation of a new wave at the anti-Stokes frequency $\omega_a = 2\omega_p - \omega_s = \omega_p + \omega_v$ provided the incident wave intensities are adequate to excite the third order nonlinear terms in the electric susceptibility of the gas. For collinear phase-matched beams the intensity or power per unit area, $I_a$, in the new wave is roughly proportional to the square of the incident pump intensity, $I_p$, times the incident Stokes intensity, $I_s$, and also is proportional to the square of the distance over which the phase matched interaction occurs. Thus a very intense anti-Stokes output can be generated, orders of magnitude greater than spontaneous Raman scattering. Furthermore, unlike spontaneous Raman scattering, it is directional so that all the anti-Stokes radiation can be readily collected. Because of these two properties as well as others the generation of CARS spectra offers a potentially very practical tool for the measurement of molecular species concentrations and temperature in gases. It is especially useful as a probe of combustion gases since these commonly contain many particulates which can so strongly scatter incident radiation and also, due to the laser heating, radiate themselves, they can cause relatively weak spontaneous Raman radiation to be lost in the particle generated "noise"
while the far stronger CARS scattering would not be. Even with no particles in the gas ordinary spontaneous Raman scattering is in fact much weaker than the Rayleigh scattering which arises from the gas molecules and there is also interference due to fluorescent radiation. Because of these considerations AFAPL is actively laying the groundwork for the use of CARS as an eventually routine diagnostic tool for combustion systems.¹,²,³

The relation between measured CARS spectra for gases and the usually desired quantities; molecular species concentrations and temperature must be made on the basis of theory taking into account both the particular experimental setup as well as modification of the internal molecular structure of the constituent molecules by the applied and internally generated electromagnetic fields. The theory also requires a combination of quantum mechanical considerations regarding the populations of the molecular vibrational and rotational energy levels and transitions between them and classical wave propagation. The latter accounts for the coherency in the interactions between the various waves which is a fundamental part of the CARS generation of the anti-Stokes wave.

By limiting the theory to the most essential physical factors which explain CARS a convenient basic analytical formula for the CARS intensity results which gives the proportionalities discussed above. While the formula has clearly been of great value in a general understanding of CARS it is inadequate for the accurate quantitative prediction of the CARS spectra under certain conditions. In particular, it is quite inadequate to predict saturation effects which occur as
I_p, I_s or both are increased. It is also inadequate to treat the case when the idler beam is not quasi-monochromatic but contributes to excitation of more than one vibrational line simultaneously. For saturation effects to be accurately predicted requires the inclusion of stimulated generation and absorption of the pump, idler and anti-Stokes waves as well as stimulated and coherent generation of the second order Stokes wave at the frequency \( \omega_x = \omega_p - 2\omega_v = 2\omega_s - \omega_p \) "symmetrical" with the anti-Stokes frequency \( 2\omega_p - \omega_s \). This is the so-called "scissors" CSRS process. All these processes occur simultaneously with CARS.

In this report we outline the derivation of the governing differential equations very concisely since much of it directly parallels results already in the literature except that here some additional physical processes and refinements are included. Aspects of the numerical integration problem are discussed and numerical results presented with emphasis on effects occurring due to depletion of the population of the lowest vibrational energy level.
II. DERIVATION OF EQUATIONS TO MODEL CARS

A. Physical Basis for CARS

To describe the generation of CARS spectra we consider the vibrational energy level diagram, Figure 1, showing the potential energy function and the ground state and two higher vibrational energy levels for a diatomic molecule. When a gas of such molecules is pumped by intense laser radiation of circular frequency $\omega_p$, the set of simultaneous coherent photon-molecule interactions illustrated in Fig. 1 can be set up by coherent interaction of the electromagnetic and vibrational waves; absorption of two pump photons, emission of a photon at $\omega_s = \omega_p - \omega_1$, the Stokes frequency and at $\omega_a = 2\omega_p - \omega_s = \omega_p + \omega_1$. 

Figure 1. CARS
the anti-Stokes frequency. If the gas is also irradiated by an external source at the Stokes frequency the emission of anti-Stokes radiation is greatly increased, primarily because the nonlinear term proportional to $|E_p|^2 E_s^*$ in the induced polarization of the gas is enhanced. In the CARS experimental systems at AFAPL, the gas is irradiated by collinear pump and idler laser beams of the same polarization. These are focussed into a small region in the gas so as to obtain a high resolution as well as a high intensity. In the focal region the beams "neck down" to a short cylindrical region in which they may be considered to have plane phase fronts. These conditions will be assumed in what follows.

Along with CARS there are other coherent Raman processes which take place; inverse CARS and coherent secondary Stokes Raman (leading to CSSRS spectroscopy) and its inverse. These are illustrated by the diagram in Fig. 2 where it is seen that the CSSRS frequency $\omega_x = 2\omega_s - \omega_p = \omega_p - 2\omega_y$. There are also stimulated emissions which occur independently of one another nad do not combine coherently as in CARS. These are shown in Fig. 3.

These processes are all induced by the lowest order electric field dependent--hence nonlinear--term in the susceptibility of the gas. In this point of view the induced molecular polarization may be written in terms of the electric field susceptibility tensors $\chi^{(1)}$ and $\chi^{(3)}$ as

$$P_{t}(t) = \chi^{(1)}_{\alpha}(t) + \chi^{(3)}_{\alpha\beta\gamma} E_{\alpha} E_{\beta} E_{\gamma}$$

or as

$$P(t) = P^{(1)}(t) + P^{(3)}(t)$$
Note: the populations of the vibrational level (1) and ground level (0) do not change because of these processes.

Figure 2. Coherent Raman Processes.

Note: the populations of the vibrational level and ground levels change as each process proceeds.

Figure 3. Stimulated Raman Scattering.
The vector $\textbf{E}$ is made of the sum of pump, idler, secondary Stokes and anti-Stokes components all with the same direction of propagation and the same linear wave polarization.

The stimulated processes alter the populations of the ground and energy levels. Furthermore, while all the processes shown in Figs. 1 through 3 involve only levels 0 and 1 the effect on the population of the additional process shown in Fig. 4.

![Diagram](image)

Figure 4. Stimulated Raman Scattering Involving Third Vibrational Level.

This difference Stokes frequency, $\omega_{s2} = \omega_p - (\omega_2 - \omega_1)$ differs from the Stokes frequency $\omega_s = \omega_p - \omega_1$ by a small percentage only. The difference is due to the lack of symmetry of the potential function as explained in Herzberg. Hence both processes will be stimulated by an incoming idler beam of even small bandwidth. For the equations to be presented in the following section we will ignore the process in Fig. 4. It will be considered again in Section D.
B. Two-Level Equations

The incident waves are assumed to be quasi-monochromatic collinear waves with the same wave polarization. Then the incident CARS and stimulated waves will also be collinear and with the same polarization as the incident waves. Accordingly, the total electric field may be written as a scalar sum

\[ E(x,t) = \sum_{\alpha=1}^{4} \left[ A_\alpha(x,t) \exp(-i\omega_\alpha t + ik_\alpha x) + \text{cc} \right], \]  

(3)

where \( \alpha_1 \) stands for pump (p), \( \alpha_2 \) for idler (I), \( \alpha_3 \) for anti-Stokes (a), \( \alpha_4 \) for secondary Stokes (x), and \( \text{cc} \) means complex conjugate. If the idler frequency is not the true Stokes frequency \( \omega_I \neq \omega_S = \omega_p - \omega_1 \) then by \( \omega_a \) and \( \omega_x \) in the following we will mean, respectively, \( 2\omega_p - \omega_I \) and \( 2\omega_I - \omega_p \). This is done to avoid additional notation such as possibly \( \omega_\text{al} \) and \( \omega_\text{XI} \). We are including the possibility of \( \omega_I \neq \omega_S \) to be able to evaluate the rate of drop off in the anti-Stokes field with small deviations from the ideal resonant condition \( \omega_I = \omega_S \).

Substitution of Eq. (2) into Maxwell's equations and elimination of the magnetic field in the usual way leads to the wave equations

\[ \frac{\partial^2 E}{\partial x^2} - \frac{n^2}{c} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} p(3)(x,t) \]  

(4)

When Eqs. (3) and (1) are substituted in (4) and terms with a common frequency equated one finds a set of equations for the \( E_\alpha \).
\[
\frac{\partial^2 E}{\partial x^2} + \frac{n^2 \omega^2}{c^2} E = -\frac{4\pi}{c^2} \omega^2 \rho^{(3)}(x) \tag{5}
\]

These equations for the \( E \) are coupled through the \( \rho^{(3)}(x) \); these are terms which require expressions for the \( x_{1a8y}^{(3)} \) of Eq. (1) before they can be expressed explicitly. For proper quantum mechanical derivations of the third order susceptibilities we refer to Druet and Taran \(^5\) where it is shown that, for the waves with frequencies \( \omega_p - \omega_{\alpha'} \), they take the form for stimulated scattering

\[
\chi^{(3)}_{\alpha \beta} = \frac{N}{\hbar} \frac{(N_{v''} - N_{v'}) c \hbar}{\omega_{\beta}^{\alpha}} \left( \frac{d\sigma}{d\Omega} \right) v' (\omega_{v''} - \omega_{v'}) = \omega_p + \omega_{\alpha'} + \Gamma_{v''} v' \tag{6}
\]

or its conjugate for coherent scattering. Here \( \alpha' \) represents Stokes, anti-Stokes or secondary Stokes and the transition in question is between vibrational levels \( v' \) and \( v'' = v' + 1 \). \( N_{v''} \) and \( N_{v'} \) are their respective population densities and \( N = N_{v''} + N_{v'} \). \( (d\sigma/d\Omega) \) is the spontaneous Raman scattering cross section.*

*The cross section used here is \( \omega_s/\omega_p \) times the cross section in Druet and Taran.\(^5\)
In addition to the above considerations we use

\[ \frac{\partial^2 E_\alpha}{\partial x^2} = \frac{\partial^2 A_\alpha}{\partial x^2} \exp(-i\omega t + k_\alpha x) = \frac{\partial^2 E_\alpha}{\partial x^2} + 2ik \frac{\partial E_\alpha}{\partial x} - k^2 E_\alpha. \]  

(7)

The explicit equations which result from the substitution of the forms like Eq. (6) into (1) and (5) and then equating coefficients of \( -i\omega t \) and \( e^{-\alpha} \) are

\[ \frac{\partial A_\alpha}{\partial x} = F_\alpha \]  

(8)

\[ \frac{\partial F_\alpha}{\partial x} = -4\pi v_\alpha i(F_\alpha - iF_\alpha) \]  

(9)

where \( \alpha \) represents pump, idler, anti-Stokes and secondary Stokes, i.e., \( p, I, a \) and \( X \), respectively, and:

\[ v_\alpha = \text{inverse wavelength (cm)} \]

\[ f_a = 12\pi^2 v_\alpha [x_p^* A_p^* A_p^2 e^{i\delta k} + x_{ap} A_a^* |A_p|^2 + x_{IX} A_p^* A_a^* e^{i\delta k}] \]  

(10)

\[ f_i = 12\pi^2 v_\lambda [x_p^* A_p^* A_p^2 e^{i\delta k} + 4ix_{ap} A_p A_a A_a^* e^{i\delta k} + x_{IX} A_p^* |A_p|^2] \]  

(11)

\[ f_I = 12\pi^2 v_\lambda [x_{ap} A_p^* A_p^2 e^{i\delta k} + (x_p^* |A_p|^2 A_a + x_{IX} |A_a|^2) A_a] \]  

(12)

\[ f_p = 12\pi^2 v_\lambda [(x_p I_\lambda |A_p|^2 + x_{ap} |A_a|^2) A_p + (x_{ap} A_a A_p^* e^{-i\delta k} + x_{IX} A_a^* |A_a|^2)] \]  

(13)
Here

\[ \Delta k = 2k_p - k_I - k_a \]

\[ \delta k = k_p + k_I - k \chi - k_a \]

\[ Dk = 2k_I - k_p - k \chi \]  \hspace{1cm} (14)

Clearly, this set of equations could be cut almost in half and hence be simpler and much cheaper to solve numerically if the second derivatives in \( A_\alpha \), the \( \partial F_\alpha / \partial x \) terms governed by Eq. (9) were negligible. Furthermore, boundary conditions on the \( F_\alpha \) are not normally available from the experimental data so to integrate the present set one has to estimate the boundary conditions by an analytic iterative procedure. This is given in the Appendix.

From physical considerations one expects that the terms \( \partial F_\alpha / \partial x \) will have almost no influence on the results and we have verified this in a few numerical runs. In all other work we assumed that \( \partial F_\alpha / \partial x = 0 \).

For efficient computing separate codes based on setting (9) to zero

\[ F_\alpha = i f_\alpha \]  \hspace{1cm} (15)

were used when the \( \partial^2 A_\alpha / \partial x^2 \) terms were to be neglected.
In these equations we must also bear in mind that the population difference $(N_0 - N_1)$ is variable in time because of the stimulated Raman induced population changes indicated in Figure 2. In addition, there is decay from any value $N_1 > N_{10}$ to the value $N_{10}$ where $N_{10}$ is the thermal equilibrium value. This is due to collisional interactions in which the vibrational energy of the molecules is converted to vibrational energy. This takes place with a relaxation time which is characteristic of the molecule in question as well as the other molecules in the gas, the pressure and temperatures.

To derive a differential equation for the time variation of $N_0 - N_1$ we consider that the photon density $n$ in the incoming idler (Stokes) beam changes to $n + (\partial n/\partial x)dx$ in traversing a gas sample of length $dx$. The intensity of the incoming beam; i.e., the time averaged pointing flux, is

$$I_I = \frac{c}{2\pi} A_s A_s^* = n \frac{\nu_0}{(2\pi)}$$ (16)

so that

$$\frac{\partial n}{\partial x} = \frac{c}{\nu_0 I_I} \left( A_I^* \frac{\partial A_I}{\partial x} + A_I^* \frac{\partial A_I}{\partial x} \right).$$ (17)

We have

$$\frac{\partial A_I}{\partial x} = \left. i f_I \right|_{SRS}$$ (18)
where \( f_I \) is given by the stimulated Raman terms in Eq. (12);

\[
f_I|_{SR} = 12\pi^2 \nu_I \left\{ x_{PI}^* A_I |A_p|^2 + x_{IX} A_I |A_x|^2 \right\} .
\] (19)

Then we find that

\[
\frac{3\Delta}{\dot{\Delta}} + \frac{\Delta}{\tau} + \frac{24\pi |A_I|^2}{nN} \left( x_{PI}^* |A_p|^2 + x_{IX} |A_x|^2 \right) = \frac{\Delta_0}{\tau} 
\] (20)

and \( \Delta_0 \) is the value of \( \Delta \) at thermal equilibrium, \( \tau \) is the relaxation time for transition from levels \( v = 1 \) to \( v = 0 \). The subscript \( i \) indicates imaginary part. Here \( \Delta \) is the quantity

\[
\Delta = \frac{N_I - N_0}{N} = \frac{N_I - N_0}{N_1 + N_0} .
\] (21)

To find \( N_V \) we use the Maxwellian distribution

\[
N_V = N e^{-E_V/kT} / \sum_V e^{-E_V/kT} 
\] (22)

where

\[
E_V = \hbar c[\omega_e (v + 1/2) - \omega_{e\chi_e} (v + 1/2)]
\] (23)

The quantities \( \omega_e \) and \( \omega_{e\chi_e} \) are available in Herzberg\(^4\) for all diatomic molecules.
C. Simple CARS Formula

The dominant term in the generation of the anti-Stokes wave is the first term on the right-hand side of Eq. (10). This represents the coherent (CARS) process. To the extent that variation of \( A_1 \) and \( A_p \) and \( N_{v''} - N_{v'} \) (which enters into \( \chi_{PI} \) as shown in Eq. (6)) and the other terms on the right-hand side in the equation can be ignored one then has, on integrating over \( 0 < x < L \)

\[
A_a = -12\pi^2 v_a x_p A^*_a A^2 e^{i\Delta k} \sin \frac{L}{2} \Delta k \left( \frac{L}{2} \Delta k \right) L .
\]

(24)

Using

\[
I_a = \frac{c}{2\pi} A_a A_a^*
\]

we get

\[
I_a = \left( \frac{2\pi}{c} \right)^2 \left( 12\pi^2 v_a x_p \right)^2 I_{II_p}^2 \left( \sin \frac{L}{2} \Delta k \right)^2 \left( \frac{L}{2} \Delta k \right)^2 L^2 .
\]

(25)

One purpose of this investigation is to check how good a result (25) gives as one enters parameter ranges where the assumptions are not really valid.

D. Three-Level Equations

In this case \( v = 0, 1 \) and 2. Vibrational transitions directly between levels 0 and 2 are forbidden; their probability is so low we need only consider the 01 and 12 transitions. Then introducing the two idler waves \( I_1 \) and \( I_2 \) of slightly differing frequencies equal to
or near to $\omega_s$ and $\omega_{s_2}$ where $\omega_{s_1} = \omega_p - \omega_1$, $\omega_{s_2} = \omega_p - (\omega_2 - \omega_1)$

we are led to two anti-Stokes waves $\omega_{a_1} = 2\omega_p - \omega_2$ and $\omega_{a_2} = 2\omega_p - \omega_1$.

As in the earlier work the $\omega_{a_1}$ are not the "true" quantities $\omega_p + \omega_1$

and $\omega_p + (\omega_2 - \omega_1)$ unless $\omega_{s_1} = \omega_1$, $\omega_{s_2} = \omega_2$. We consider the two

incident fields $E_{I_1}$ and $E_{I_2}$ although in physical practice there will

likely be only one idler beam. The equations as written below can model

this situation whether the beam is purely monochromatic or has a band-

width sufficient to cover $\omega_{s_1}$ and $\omega_{s_2}$.

The equations for the $f_{a_1}$ are now found by replacing all the $\alpha$

subscripts by $a_j$, $j = 1$ or 2 except for subscript $\alpha = p$. The $\Delta k$, $\delta k$

and $D_k$ must likewise be subscripted 1 and 2. Thus, for example,

$$f_{I_j} = 12\pi^2 v_{I_j} \left[ x_{a_j}^{*} A_{a_j} A_p^2 e^{ix\Delta k_j} \right.$$

$$+ x_{pI_j} A_p |A_p|^2 A_{I_j} + x_{I_j} x_{j} A_x |A_x|^2 A_{I_j} \left. \right]$$

and similarly for $f_{a_{1j}}$ and $f_{a_{2j}}$. On the other hand the Eq. (13) for

$f_p$ is replaced by just one equation,

$$f_p = 12\pi^2 v_p \sum_{j=1}^{2} \left[ (x_{pI_j} |A_{I_j}|^2ight.$$

$$+ \chi_{a_p} |A_{a_p}|^2) A_p + (x_{pI_j} + x_{a_p})$$

$$A_{I_j} A_{a_p} A_p^* e^{-ix\Delta k_j} \left. \right]$$

$$+ x_{I_j} x_{j} A_x A_{I_j}^2 e^{ixD_k} \right]$$
We now have to obtain, for use in the \( x_{\alpha \beta j} \), both

\[
\Delta_1 = \frac{N_0 - N_1}{N} \quad \text{and} \quad \Delta_{12} = \frac{N_2 - N_1}{N}
\]

(24)

By a derivation directly analogous to that used for Eq. (16) but involving the stimulated Raman processes of both figures 3 and 4 we can obtain the appropriate equations. In terms of *

\[
\Delta_1 = \Delta \quad \text{and} \quad \Delta_2 = \frac{(N_2 - N_0)}{N}
\]

(25)

\[
\frac{\partial \Delta_1}{\partial t} = -\frac{12\pi}{\hbar N} |A_p|^2 \left( 2|A_{s1}|^2 x_{11} + |A_{s2}|^2 x_{21} \right) + \frac{1}{3} \left( \frac{1}{\tau_{20}} - \frac{1}{\tau_{21}} - \frac{4}{\tau_{10}} \right) (\Delta_1 - \Delta_{10})
\]

\[
+ \frac{2}{3} \left( \frac{1}{\tau_{21}} - \frac{1}{\tau_{20}} + \frac{1}{\tau_{10}} \right) (\Delta_2 - \Delta_{20})
\]

(26)

\[
\frac{\partial \Delta_2}{\partial t} = \frac{12\pi}{\hbar N} |E_p|^2 \left( |A_{s1}|^2 x_{11} + |A_{s2}|^2 x_{21} \right) + \frac{1}{3} \left( \frac{2}{\tau_{20}} + \frac{1}{\tau_{21}} - \frac{2}{\tau_{10}} \right) (\Delta_1 - \Delta_{10})
\]

\[
+ \frac{1}{3} \left( \frac{1}{\tau_{10}} - \frac{4}{\tau_{20}} - \frac{2}{\tau_{21}} \right) (\Delta_2 - \Delta_{20})
\]

(27)

*The equations in terms of \( \Delta_1 \) and \( \Delta_2 \) are much better suited for numerical integration than equations in terms of \( \Delta \) and \( \Delta_{12} \) or in terms of \( N_1 \) and \( N_2 \). This is because the rates of change of \( \Delta_1 \) and \( \Delta_2 \) are relatively slow while this is not true for \( N_2 \) and \( \Delta_{12} \) near \( t=0 \).
D. Rotational Levels

The rotational energy levels, $E_{v,j}$, associated with each vibration level $v$ have so far been ignored. If we limit ourselves to the $Q$ branch transitions between vibrational states there is no change in the $J$ value. For this case the previous equations are readily generalized so that they apply to a given rotational level $J$. Then one replaces formula (18) by the equilibrium values appropriate to the $J$th levels:

$$N_{v,Jo} = \frac{N(2J + 1)g_n e^{-(E_v+E_J)/(kT)}}{\sum_v e^{-E_v/kT} G_n kT/(2\pi B \hbar c)}$$

(28)

where $E_v$ is given still by (19), $\hbar = h/(2\pi)$,

$$E_J = B \hbar c \frac{J(J + 1)}{kT}$$

(29)

and $g_n$ and $G_n$ are constants characteristic of the molecules in question. (see Herzberg\textsuperscript{6}).

E. Measured Quantity-Energy

The main physical quantity which is measured experimentally is the anti-Stokes energy or power per unit area incident on a receptor surface at the end of the sample, integrated over the pulse time and the detector surface area. We are assuming uniform plane waves so the area integration is trivial. Hence the quantity we shall compute to model the experiment will be energy/area $\varepsilon_a$
Similarly we can compute the CSSRS energy

\[ E_a(t) = \frac{c}{2\pi} \int_0^T E_a^2 \left| \frac{x}{x_m} \right| dt = \int_0^T I_a \ dt . \]  

(30)

The \( E_a \) and \( E_x \) are evaluated at the end, \( x_m \), of the sample volume which extends to the right from \( x = 0 \), where it is irradiated.
III. COMPUTATIONS

A. Computer Codes

The equation sets of the previous section were programmed in FORTRAN IV for computation. For simplicity and speed in the computations separate programs, CARS0 through CARS5, were written for different cases.

<table>
<thead>
<tr>
<th>Code Name</th>
<th>Main Equations</th>
<th>Number of Energy Levels (including ground)</th>
<th>Is CSSRS Included?</th>
<th>Are second derivative terms included?</th>
<th>Integration Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARS0</td>
<td>(15), (20)</td>
<td>2</td>
<td>no</td>
<td>no</td>
<td>RK</td>
</tr>
<tr>
<td>CARS2</td>
<td>(22)-(27)</td>
<td>3</td>
<td>no</td>
<td>no</td>
<td>RK</td>
</tr>
<tr>
<td>CARS3</td>
<td>(15), (20)</td>
<td>2</td>
<td>no</td>
<td>no</td>
<td>A,M and G</td>
</tr>
<tr>
<td>CARS4</td>
<td>(8), (9), (20)</td>
<td>2</td>
<td>no</td>
<td>yes</td>
<td>RK</td>
</tr>
<tr>
<td>CARS5</td>
<td>(15), (20)</td>
<td>2</td>
<td>yes</td>
<td>no</td>
<td>RK</td>
</tr>
</tbody>
</table>

Here RK stands for 4th order Runge-Kutta, AM for Adams-Moulton and G for Gear's method. Provision was made in CARS0 to set individual terms equal to zero on the right. Also CARS5 was set up to compute either Gaussian or rectangular shaped pump and idler pulses whereas the other codes are limited to rectangular.

Numerical comparisons between sample CARS0 and CARS3 results showed no reason to favor AM or G over the RK method so RK was used for all the data presented.
The integration in space and time was organized to proceed between the discrete point \( mn \) shown in Figure 5 in a manner designed to minimize storage.

![Diagram to explain computation scheme.](image)

To describe it let the symbolic statement \( nm + (n + 1)m \) mean to carry out the integrations of the \( A_\alpha \) with respect to \( x \) between the points \( nm \) and \( (n + 1)m \) while \( nm + n(m + 1) \) means to integrate the equations for \( A \) (or \( A_1 \) and \( A_2 \)) with respect to time between \( nm \) and \( n(m + 1) \). The integrations between the points were carried out using many further subdivisions whose size is adjustable automatically to fit prestated accuracy requirements. Distance \( x \) ranged from 0 to \( L \) while time was measured from 0 to \( T \), with \( L \) and \( T \) chosen to correspond to values typical of experiments at AFAPL.
The computation was carried out using the following order and approximations:

\[ 11 \rightarrow 21 \] using \( \Delta_0 \) as initial value

\[ 11 \rightarrow 12 \] using \( \Delta_0 \) in computing \( \chi \)'s

\[ 12 \rightarrow 22 \] using \( \Delta_0 \) as initial value

\[ \ldots \]

\[ \ldots \]

\[ 1(n - 1) \rightarrow 1N \] using \( \Delta_0 \) in computing \( \chi \)'s

Then

\[ 21 \rightarrow 31 \] using \( \Delta(21) \) as initial value

\[ 21 \rightarrow 22 \] using linear interpolation between \( 21 \) and \( 22 \) in computing \( \chi \)'s

\[ 22 \rightarrow 32 \] using \( \Delta(22) \) as initial value

\[ \ldots \]

\[ \ldots \]

\[ (M - 1)N \rightarrow MN \] using \( \Delta((m - 1)N) \) as initial value.

Numerical comparison of simple CARSO and CARS4 results showed, as expected, almost no difference in the numerical results for the electric fields \( E_x \) or energies \( E_x \) as computed with the second derivative terms or neglecting them. Keeping them however led to so tremendous an increase in computing time, that it was impractical from a cost standpoint to extend the computations as far in distance and time as would correspond to the CARS experimental work at WPAFB. In light of these results all subsequent work was done without second derivative terms.

Another comparison which was made was to run the same data using CARSO and CARSS. The results showed that there was practically no change in \( E_x \); when CSSRS energy \( E_x \) developed it was not at the expense of \( E_x \).
B. Presentation of the Results

\( E_a \) for the various cases to be described has been plotted vs. 
\( |A_p|^4 |A_I|^2 \left( \frac{(2\pi/c)^3 I_{pI}^2}{p_I} \right) \) on log paper.

If the simple CARS formula (25) were to hold then the computed curves would simply be straight lines at 45° to the axes. These lines would intercept the vertical axis at a height

\[
\log \left( \frac{c}{2\pi} \right) \left( 12\pi^2 v_a^2 p_1 \right)^2 \sin \left( \frac{\Delta k}{2} \right) \frac{1}{(L/2)\Delta k} \left( L^2 T \right).
\]

As \( I_{pI}^2 \) increases the effect of the non CARS terms becomes non-negligible and with that goes the fact that changes in the energy population levels become important. The \( E_a \) vs. \( |E_p|^4 |E_I|^2 \) plots bend below the straight line which results when these phenomena are neglected. This bending is the saturation effect referred to in the abstract and introduction.

To show how the bending of the \( E_a \) curves is tied in with energy level depletion the corresponding curves of \( \Delta \) or \( \Delta_1 \) and \( \Delta_2 \) vs. \( |E_p|^4 |E_I|^2 \) are also plotted.

C. Data

Computations were made for \( N_2 \). The corresponding constants needed to compute \( \Delta_0 \) and the \( \chi \) were taken from Hertzberg. Relaxation times were taken from White and Millikan. In CARS2 we need several relaxation times. We could find no such detailed data and have simply used a common \( \tau \) value equal to the above. The actual data used
for the computational results presented in Section E is, (in Gaussian units)

\[ v_v = 0.2331 \times 10^4 \]
\[ v_I = 0.1207 \times 10^5 \]
\[ v_p = 0.1440 \times 10^5 \]
\[ d\omega/d\omega = 0.3300 \times 10^{-31} \]

**Notation:** 
(E04 = \(10^4\), etc.)

Case A:
\[ p = 0.7600 \times 10^5 \]
\[ T = 0.3000 \times 10^4 \]
\[ \tau = 0.400 \times 10^{-6} \]
\[ (\Delta_o = 0.5080 \times 10^0) \]

Case B:
\[ p = 0.7600 \times 10^5 \]
\[ T = 0.1000 \times 10^4 \]
\[ \tau = 0.1000 \times 10^{-4} \]
\[ (\Delta_o = 0.9328 \times 10^0) \]

These \(p\), \(T\) and \(\tau\) combinations are from the White and Millikan's empirical data and were chosen to illustrate the effects of varying \(\tau\). The \(\Delta_o\) values however also vary and their computed values are shown in parentheses.

**D. Discussion of Results**

Aside from the results discussed in the previous sections which do not lend themselves to graphical display we present a series of curves where \(I_p^2I_I\) is varied by changing \(I_p\) while keeping \(I_I\) fixed. Figure 1 illustrates the buildup of \(E_a\) with time by showing curves for \(T = 10\) ns and \(T = 20\) ns for each fixed level of pump and idler.
irradiation. The curves show that once saturation due to increasing \( I_p \) becomes strong very little or no additional anti-Stokes power is delivered in the last half of a 20 ns rectangular pulse. While \( \Delta \) drops closer to zero after 10 ns it has dropped so far from its initial value in 10 ns that very little further \( E_\Delta \) is generated. While examining the data in Figs. 1 through 5 note that the assumed temperature is quite high so that \( \Delta_0 = 0.508 \). CARS was used for curves A.1.

Figure 2 shows the effect of keeping the CARS term only in computing \( A_a \) assuming, when calculating \( x \), that \( A_p \) and \( A_I \) are constant but nevertheless allowing approximately for change in \( \Delta \) by use of Eq. (20). The \( E_\Delta \) and \( \Delta \) for this artificial case is labeled A.2 and is computed via CARSO. The \( \Delta \) variation is only approximate because \( A_p \) and \( A_I \) were kept constant. Comparing A.2 to a correctly computed curve A.3 and to the 45° line (for CARS only and \( \Delta = \Delta_0 \)) gives an idea of how much of the saturation effect is due to \( \Delta \) changing as opposed to how much is due to the neglect of the stimulated noncoherent generation of \( E_\Delta \).

Figure 3 illustrates the effect of using three vibrational levels instead of only two. The idler wave \( A_I \) in the three level case is taken in curves A.5 to be monochromatic so that \( A_{I1} = 10^3 \), \( A_{I2} = 0 \). For curves A.4 \( A_{I1} = A_{I2} = 10^3 \).

The two level corresponding curves are given by curve A.3. To Interpret the curves for A.5 \( A_2 \) actually becomes negative by virtue of stimulated emissions from level 1. We have plotted \( |A_2| \) using a dashed curve for the portion of the curve which is plotted when \( A_2 \) is negative. In some instances we have also used the symbols \( \oplus \) and \( \ominus \) to indicate the sign of \( \Delta_1 \) or \( \Delta_2 \).
is negative. We do not have enough data to draw in the curve in the missing intervening section corresponding to the $I^2_{p \Gamma}$ range in which $\Delta_2$ goes through zero.

We note that although the energy level populations are quite radically changed by the more complete analysis for curves A.4 and A.5 the $\mathcal{E}_a$ curves of A.3 and A.5 differ only by a relatively small uniform translation for all $I^2_{p \Gamma}$ values. The $\mathcal{E}_a$ plotted for curve A.4 is the sum of $\mathcal{E}_{a1} + \mathcal{E}_{a2}$. It corresponds to the energy a receptor of uniform sensitivity across a frequency band covering $\omega_{a1}$ and $\omega_{a2}$ would receive.

Figure 4 presents several comparisons. Curves A.3 vs. A.6 exhibit the effect of Gaussian pulses (curve A.6) as compared to a rectangular pulse (A.3). The two pulses have the same duration and peak power so that the incident Gaussian pump and idler pulses deliver 81% as much energy as the rectangular pulses. 81% of the $\mathcal{E}_a$ output for the rectangular pulse is shown as an additional curve in the figure.

Curves A.3 vs. A.9 exhibit the effect of achieving the same range of $I^2_{p \Gamma}$ by multiplying $I_\Gamma$ by 10 and dividing $I_p$ accordingly by $\sqrt{10}$. The large difference in results indicates inaccuracy in the simple CARS formula.

In Figure 5 the curves A.3 vs. A.10 exhibit the effect of changing $\tau$ from $\tau = 0.4 \ E - 06$ for (A.3) to $\tau = 0.1 \ E - 06$ for A.10, keeping all other parameters constant (even though $\tau$ is a function of, for example, temperature). The difference in output is less than the accuracy with which the figures are drawn.
Curves A.3 vs. A.7 show the effect of decreasing the coherence length by setting $\Delta k = D_k = \delta k = 10.7$ for A.7 against setting $\Delta k = D_k = \delta k = 0$ for A.3.

Figure 6 depicts the direct analog of Figure 3 but carried out for the data of Case B as given above in Section C. In this case the excitation $A_{11} = 10^3$, $A_{12} = 0$ corresponds to curve B.3 and $A_{11} = A_{12} = 10^3$ to curve B.3. The two-level case is curve B.2.
APPENDIX

Boundary Conditions

To solve the equations (8) and (9) requires boundary conditions on \( A_\alpha \) and \( F_\alpha = (2A_\alpha / 3x) \) at \( x = 0 \).

For the \( A_\alpha \) we have \( A_p \) and \( A_I \) given nonzero values (determined by the experimental set-up) while \( A_\alpha \) and \( A_x = 0 \). \( A_\alpha = 0 \) assumes no anti-Stokes is generated in the gas outside the test region—or at least that it is negligible.

To obtain boundary conditions on the derivatives is more difficult in a sense since these are not normally specified or measured. We use the following approximate procedure. Referring to Eqs. (8) through (13), we first consider \( x \)'s independent of \( x \) and \( F_\alpha = iF_\alpha \); i.e.,

\[
\frac{\partial A_\alpha}{\partial x} = iF_\alpha \quad \text{(A.1)}
\]

Then

\[
\frac{\partial F_\alpha}{\partial x} \bigg|_{x=0} = \frac{\partial^2 A_\alpha}{\partial x^2} \bigg|_{x=0} = \frac{i\partial F_\alpha}{\partial x} \bigg|_{x=0} \quad \text{(A.2)}
\]

where, in evaluating \( (\partial F_\alpha / \partial x)|_{x=0} \), we use the boundary conditions on \( A_\alpha \) and the fact that \( F_\alpha = iF_\alpha \). The result is that the \( (\partial F_\alpha / \partial x)|_{x=0} \) can be written explicitly as functions of \( A_p(0,t) \) and \( A_s(0,t) \). Then
\[ F_{\alpha} \bigg|_{x=0} = i \left[ \frac{1}{4\pi \nu} \frac{\partial F_{\alpha}}{\partial x} + f_{\alpha} \right]_{x=0} \]  \hspace{1cm} (A.3)

These are the values used to start the solutions of (8) and (9).

Specifically, one has

\[ \frac{\partial F_{\alpha}}{\partial x} \bigg|_0 = -12\pi^2 \nu_A A_p^2 A_s \left\{ 12\pi^2 [2 \nu_p |A_s|^2 + (\nu_a x + \nu_s x^*) |A_p|^2] + \Delta k \right\} \bigg|_{x=0} \]

\[ \frac{\partial F_s}{\partial x} \bigg|_0 = (12\pi^2)^2 \nu_s A_s |A_p|^2 x^* \left\{ \nu_d |A_p|^2 x^* - 2i |A_s|^2 \nu_p x_1 - |A_p|^2 \nu_s x^* \right\} \bigg|_{x=0} \]

\[ \frac{\partial F_p}{\partial x} \bigg|_0 = (12\pi^2)^2 x A_p |A_s|^2 \nu_p \left\{ 2 |A_p|^2 \left( i \nu_s x_1 - \nu_a x_1 \right) - \nu_p x |A_s|^2 \right\} \bigg|_{x=0} \]

where \( x = x_p + ix_1 \) and CSSRS has been neglected.
REFERENCES


Fig. 1 CARS energy; effects of excitation duration.
Fig. 2. CARS energy; effects of non-CARS terms.
Fig. 3 CARS energy; effects of third vibrational level (Case A data).
Fig. 4. CARS energy; effect of pulse shape; effect of changing $I_p$ and $I_1$ keeping $I_p^2I_1$ fixed.
Fig. 5 CARS energy; effect of vibrational relaxation time.

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Fig. 6 CARS energy: effects of third vibrational level (Case B data).