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Saturation effects in coherent anti-Stokes Raman scattering

A. D. Wilson-Gordon, R. Klimovsky-Barid, and H. Friedmann
Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel
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Saturation effects in coherent anti-Stokes Raman scattering (CARS) spectroscopy are discussed. The discussion is limited to Raman-resonant CARS ($\omega_l - \omega_s \simeq \omega_{21}$, where $\omega_{l,s}$ are the frequencies of the pump fields with powers $P_{l,s}$, and ω_{21} is the frequency of the Raman transition $|1\rangle \rightarrow |2\rangle$) with the possible addition of a one-photon resonance ($\omega_l \simeq \omega_{31}$ is the frequency of the electronic transition $|1\rangle \rightarrow |3\rangle$). For these cases we show that the CARS polarization $\mathcal{P}_{\text{CARS}}$ is proportional to the off-diagonal density-matrix element ρ_{21}. In order to determine ρ_{21}, we use Laplace transforms to solve the Bloch equations for the effective two-level system $|1\rangle$ and $|2\rangle$ when ω_l is far from resonance, or for the three-level system $|1\rangle$, $|2\rangle$, and $|3\rangle$, when $\omega_l \simeq \omega_{31}$. The steady-state expression for $\mathcal{P}_{\text{CARS}}$ in the former case gives $\mathcal{P}_{\text{CARS}} \propto P_l P_s^{1/2}$ at low powers and $\mathcal{P}_{\text{CARS}} \propto P_l^0 P_s^{-1/2}$ at high powers. In the three-level system, we show that when the pressure is low and at least one field is weak, the slow time dependence of ρ_{21} must be considered. When one field is strong and the other weak, the CARS spectrum is Stark split. When P_l is high, for example, $\mathcal{P}_{\text{CARS}} \propto P_l^0 P_s^{1/2}$ for $\omega_s \simeq \omega_{32}$ and $\mathcal{P}_{\text{CARS}} \propto (P_l P_s)^{1/2}$ when $\omega_s \simeq \omega_{32} \pm V_{13}$ where V_{13} is the one-photon Rabi frequency for the $|1\rangle \rightarrow |3\rangle$ transition. The Wilcox-Lamb approximation is used to reduce the three-level Bloch equations to rate equations containing one- and two-photon terms. When the fields are so weak that both one- and two-photon terms are small compared to the decay terms, the usual expression for $\mathcal{P}_{\text{CARS}}$ is reproduced. If only the direct two-photon processes are important, the effective-two-level-system results are reproduced. When both fields are intense and nearly resonant, the steady state is rapidly achieved. The results for the case where one field is much stronger than the other are essentially the same as those for one strong and one weak field. When the fields are of comparable strength, $\mathcal{P}_{\text{CARS}} \propto P_l^{1/2} P_s^0$ for $\omega_l \simeq \omega_{31}$ and $\omega_s \simeq \omega_{32}$, and the CARS spectrum is split into five components.

I. INTRODUCTION

Many techniques[1-4] have been devised to enhance the Raman-resonant contribution to CARS[5] (coherent anti-Stokes Raman scattering) with respect to the nonresonant background contribution. One of the most popular methods is resonance enhancement[3,4] in which one or more of the incident frequencies is tuned near to electronic resonances of the atom or molecule being studied. In most CARS experiments, saturation is deliberately avoided by decreasing the intensity of the incident lasers. Saturation effects[6] have, however, been reported but only for complicated systems which do not permit easy interpretation of the results obtained. To our knowledge, only one detailed analysis[7] of saturation effects in CARS exists, although there are several treatments of saturation effects in the related phenomena of two-photon resonant third-harmonic generation[8] and stimulated Raman.[9] The theory of intensity effects in CARS presented here differs from the treatment of Druet *et al.*,[7] in that it is based on the full solution of the appropriate Bloch equations, rather than a simple extension of the traditional approach[5] involving the third-order nonlinear susceptibility $\chi^{(3)}$ to higher-order susceptibilities.[10] Our approach also allows transient and relaxation effects to be discussed in an obvious manner.

In order to simplify the discussion, we consider only Raman-resonant contributions to the CARS process in which the two pump frequencies ω_l and ω_s (see Fig. 1) are such that

$$\omega_l - \omega_s \simeq \omega_{21} . \tag{1.1}$$

In addition, we limit our discussion to the case where either ω_l is nearly resonant with the molecular-electronic-transition frequency ω_{31}, so that the Bloch equations for the three-level system $|1\rangle$, $|2\rangle$, and $|3\rangle$ must be solved[11] (this is a particular case of doubly resonant CARS[3] and is analogous to resonance fluorescence), or where ω_l is sufficiently far from resonance with ω_{31} so that the three-level Bloch equations can be reduced to those of an effective two-level system[12,13] (singly resonant CARS,[3] which is analogous to resonance Raman

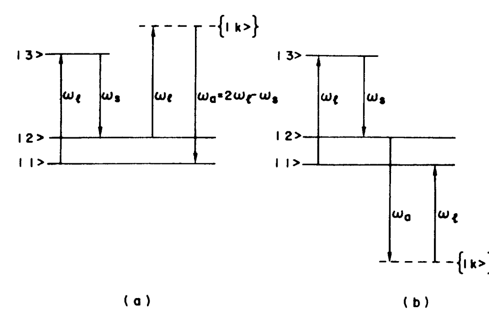

FIG. 1. Energy-level scheme for Raman-resonant CARS ($\omega_l - \omega_s \simeq \omega_{21}$) with additional one-photon resonance ($\omega_l \simeq \omega_{31}$). The pump frequencies are ω_l and ω_s and the coherent light is emitted at the anti-Stokes frequency $\omega_a = 2\omega_l - \omega_s$.

scattering). We do not consider the case where $\omega_a = 2\omega_l - \omega_s$, the coherent anti-Stokes frequency, is in near resonance with an electronic-transition frequency (another example of doubly resonant CARS[3]). This case could be treated by a straightforward modification of the theory presented here. Nor do we consider the case where both ω_l and ω_a are in near resonance with molecular-transition frequencies (triply resonant CARS[3]) which would require the solution of the four-level Bloch equations.[14]

In Sec. II A we derive, for the cases we wish to discuss, a general expression for the CARS polarization $\mathcal{P}_{\rm CARS}$ using projection-operator techniques[13] and show that it is proportional to the off-diagonal element of the density matrix ρ_{21}. In Sec. II B, we write the three-level Bloch equations[11] which must be solved in order to obtain ρ_{21} and hence $\mathcal{P}_{\rm CARS}$ for the case of doubly resonant CARS outlined above (Fig. 1). We include phenomenological decay terms in the equations which express both decay to lower levels of the three-level system and to a set of states $\{|l\rangle\}$ whose populations are assumed to remain in thermal equilibrium. In addition we derive the Bloch equations for the effective two-level system[12,13] from which ρ_{21} and hence $\mathcal{P}_{\rm CARS}$ can be obtained for the case of singly resonant CARS. In Sec. II C, we briefly discuss some of the techniques to be used in Sec. III to solve the Bloch equations: the Wilcox-Lamb approximation,[15] Laplace transforms, and an extension of the perturbation theory devised by Schenzle and Brewer.[16]

The Bloch equations for the effective two-level system are solved in Sec. III A in both the transient and steady-state regimes. We show that whereas at low intensities, the steady-state $\mathcal{P}_{\rm CARS} \propto P_l P_s^{1/2}$ where $P_{l,s}$ are the powers of the pump fields at frequencies $\omega_{l,s}$, at high values of P_l, $\mathcal{P}_{\rm CARS}$ becomes independent of P_l, and at high values of P_s, $\mathcal{P}_{\rm CARS} \propto P_s^{-1/2}$.

In the remaining subsections of Sec. III we solve the three-level Bloch equations for various limiting cases. In general we are interested in only the slowest-decaying and steady-state contributions to $\mathcal{P}_{\rm CARS}$. The existence of these slowly decaying contributions to $\mathcal{P}_{\rm CARS}$, for example, in low-pressure molecular CARS, has not been pointed out before. In order to obtain simple analytical expressions for these terms, we shall assume that $(1/T_1)_{3l}$, the rate of decay of population from level $|3\rangle$ to the reservoir $\{|l\rangle\}$, is the fastest decay rate in the system.

In Sec. III B, we consider the case where the $|1\rangle \rightarrow |3\rangle$ transition is saturated by the ω_l field, whereas the $|2\rangle \rightarrow |3\rangle$ transition is only weakly coupled to the ω_s field. We find that for time $t \gg (T_1)_{3l}$, $\mathcal{P}_{\rm CARS}$ is independent of P_l and proportional to $P_s^{1/2}$ when $\omega_s \simeq \omega_{32}$ and $\mathcal{P}_{\rm CARS} \propto (P_l P_s)^{1/2}$ when $\omega_s \simeq \omega_{32} \pm V_{13}$, where V_{13} is the one-photon Rabi frequency for the $|1\rangle \rightarrow |3\rangle$ transition. The existence of Stark splitting in the CARS excitation spectrum is also demonstrated. In addition we discuss the analogous case where the $|3\rangle \rightarrow |2\rangle$ transition is saturated by the ω_s field and the $|1\rangle \rightarrow |3\rangle$ is weakly coupled to the ω_l field. There we expect $\mathcal{P}_{\rm CARS} \propto P_l P_s^{-1/2}$ when $\omega_l \simeq \omega_{31}$ and $\mathcal{P}_{\rm CARS} \propto P_l$ and independent of P_s when $\omega_l \simeq \omega_{31} \pm V_{23}$.

In Sec. III C, we employ the Wilcox-Lamb approximation in order to reduce the three-level Bloch equations to rate equations which contain both one-photon terms relating to the $|1\rangle \rightarrow |3\rangle$ and $|2\rangle \rightarrow |3\rangle$ transitions and two-photon terms relating to the $|1\rangle \rightarrow |2\rangle$ transition. We show that when the intensity is sufficiently low so that the two-photon terms can be neglected, there are two slowly decaying contributions to $\mathcal{P}_{\rm CARS}$. In addition, we show that the usual low-intensity assumption $\rho_{ii} = \rho_{ii}^{\rm eq}$, where $\rho_{ii}^{\rm eq}$ is the population of level $|i\rangle$ at thermal equilibrium, is reproduced when the one-photon terms are small compared to the decay rates in the equations. On the other hand, when the intermediate level is sufficiently far from resonance and the intensity sufficiently high so that the one-photon terms can be dropped in favor of the two-photon terms, the effective two-level system steady-state result is reproduced. The slowly decaying contribution to ρ_{21} for this case is also evaluated.

In Sec. III D, we give the steady-state solutions for the case where both fields saturate and are near resonance with the appropriate transitions. In this case, all time-dependent contributions to ρ_{21} can be assumed to decay rapidly. We find that when $V_{13} \gg V_{23}$ or $V_{23} \gg V_{13}$, the results are also almost identical to those of Sec. III B where we considered the case of one saturated transition and one weakly excited transition. When, however, $V_{13} \simeq V_{23} \simeq V$, the CARS spectrum splits into five Stark split peaks. For example, when ω_s is varied, peaks are predicted at $\omega_s = \omega_{32}$, $\omega_{32} \pm V$, and $\omega_{32} \pm 2V$. When $\omega_s \simeq \omega_{32}$ and $\omega_l \simeq \omega_{31}$ we find that $\mathcal{P}_{\rm CARS} \propto P_l^{1/2}$ and independent of P_s.

We assume throughout that even in the presence of saturating fields, the CARS intensity[5] is still proportional to the absolute value squared of the coefficient of $\exp(-i\omega_a t)$ in the expression for $\mathcal{P}_{\rm CARS}$. In the absence of saturation this coefficient is proportional to $\chi_{\rm CARS} P_l P_s^{1/2}$ where $\chi_{\rm CARS}$ is the usual intensity-independent CARS susceptibility.

II. THE MODEL

A. General expression for CARS polarization

We begin by extracting from the total polarization vector (expressed in the interaction picture)

$$\vec{\mathcal{P}} = N\langle\Psi_I|\vec{\mu}_I|\Psi_I\rangle, \qquad (2.1)$$

those terms which derive from the processes shown in Fig. 1. In order to do this we define the projection operators P and Q[13] where

$$P=\sum_{i=1}^{3}|i\rangle\langle i|, \quad Q=\sum_{k\neq 1,2,3}|k\rangle\langle k|, \quad P+Q=1. \qquad (2.2)$$

Thus P refers to those levels which are nearly resonant with some combination of the pump frequencies ω_l and ω_s (see Fig. 1) whereas Q refers to those levels which are far from resonance with the incident frequencies. In a previous publication,[13(a)] we showed that the formal equations of motion for the P and Q levels are given by

$$i\hbar\frac{dP|\Psi_I(t)\rangle}{dt}=PV_IP|\Psi_I(t)\rangle-\frac{i}{\hbar}PV_IQ\int^t\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}QV_IQ\,dt''\right)QV_IP|\Psi_I(t')\rangle dt', \qquad (2.3)$$

$$Q|\Psi_I(t)\rangle=-\frac{i}{\hbar}\int^t\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}QV_IQ\,dt''\right)QV_IP|\Psi_I(t')\rangle. \qquad (2.4)$$

In Eqs. (2.3) and (2.4), the "chronologically ordered exponential"

$$\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}QV_IQ\,dt''\right)=1+\left(-\frac{i}{\hbar}\right)\int_{t'}^{t}QV_I(t'')Q\,dt''+\left(-\frac{i}{\hbar}\right)^2\int_{t'}^{t}\int_{t'}^{t''}QV_I(t'')QV_I(t''')Q\,dt'''\,dt''+\cdots, \qquad (2.5)$$

$$V_I=\exp(iH_0t/\hbar)V\exp(-iH_0t/\hbar), \qquad (2.6)$$

where H_0 is the Hamiltonian of the unperturbed molecular system with eigenstates $|n\rangle$:

$$H_0|n\rangle=\hbar\omega_n|n\rangle, \qquad (2.7)$$

and V is the matter-field interaction Hamiltonian which we write in the electric-dipole-moment approximation, assuming for simplicity that both the pump fields are linearly polarized with unit polarization vector $\hat{x}$,

$$V=V^l+V^s, \quad V^{l,s}=-\tfrac{1}{2}\vec{\mu}\cdot\hat{x}(\mathcal{E}_{l,s}e^{-i\omega_{l,s}t}+\text{c.c.}) \qquad (2.8)$$

with

$$\mathcal{E}_{l,s}=|\mathcal{E}_{l,s}|\exp[-i(\phi_{l,s}-k_{l,s}z)]. \qquad (2.9)$$

We further assume that $|\mathcal{E}_{l,s}|$ and $\phi_{l,s}$ are slowly varying functions of time.

It can be shown by integration by parts that if

$$\left|\frac{\dfrac{d\mathcal{E}(t)}{dt}}{\Delta\mathcal{E}(t)}\right|\ll 1, \quad \left|\frac{\dfrac{dP|\Psi_I(t)\rangle}{dt}}{\Delta P|\Psi_I(t)\rangle}\right|\ll 1, \qquad (2.10)$$

where Δ is the frequency offset of a typical far-from-resonance transition, we can write Eqs. (2.3) and (2.4) as

$$i\hbar\frac{dP|\Psi_I(t)\rangle}{dt}=\mathcal{H}(t)P|\Psi_I(t)\rangle \qquad (2.11)$$

and

$$Q|\Psi_I(t)\rangle=-\frac{i}{\hbar}\left[\int^t\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}QV_IQ\,dt''\right)QV_I(t')P\,dt'\right]P|\Psi_I(t)\rangle, \qquad (2.12)$$

where the effective Hamiltonian $\mathcal{H}(t)$ is given by

$$\mathcal{H}(t)=PV_IP-\frac{i}{\hbar}PV_IQ\int^t\mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}QV_IQ\,dt''\right)QV_IP\,dt'. \qquad (2.13)$$

We note that the second condition of Eq. (2.10) can be written in the rotating-wave approximation (RWA) as

$$|\Delta|\gg|\Delta\omega|, \qquad (2.14)$$

where $\Delta\omega$ is the frequency offset of a typical near-resonance transition.

This method of calculating the effective Hamiltonian $\mathcal{H}(t)$ has two distinct advantages over other methods[12]: first, it is applicable to any number of levels resonant with the incident fields and second, it describes the evolution of the nonresonant levels as well as the resonant ones. It is currently being used as the basis of a general theory of nonlinear coherent processes.[17]

Using Eqs. (2.1) and (2.2) we can now rewrite the total polarization vector as

$$\vec{\mathcal{P}} = N\langle\Psi_I|(P+Q)\vec{\mu}_I(P+Q)|\Psi_I\rangle . \tag{2.15}$$

In order to extract those terms that correspond to Fig. 1, we employ Eqs. (2.2), (2.6)–(2.9), and (2.12) to first order in $\mathcal{E}_l$ or $\mathcal{E}_l^*$. Thus

$$\begin{aligned}\mathcal{P}_{\text{CARS}} = \hat{x}\cdot\vec{\mathcal{P}}_{\text{CARS}} &= N\sum_k \langle\Psi_I|1\rangle\langle 1|\mu_I|k\rangle\left(\frac{i}{2\hbar}\mathcal{E}_l\int^t \langle k|\mu_I|2\rangle e^{-i\omega_l t'}dt'\right)\langle 2|\Psi_I\rangle + \text{c.c.}\\ &+ N\sum_k \langle\Psi_I|2\rangle\langle 2|\mu_I|k\rangle\left(\frac{i}{2\hbar}\mathcal{E}_l^*\int^t \langle k|\mu_I|1\rangle e^{i\omega_l t'}dt'\right)\langle 1|\Psi_I\rangle + \text{c.c.}\\ &= N\sum_k \mu_{1k}\mu_{k2}\left(\rho_{21}\mathcal{E}_l\frac{e^{-i(\omega_l+\omega_{21})t}}{(\omega_{k2}-\omega_l)} + \rho_{12}\mathcal{E}_l^*\frac{e^{i(\omega_l+\omega_{21})t}}{(\omega_{k1}+\omega_l)} + \text{c.c.}\right),\end{aligned} \tag{2.16}$$

where the density operator ρ is given by

$$\rho = |\Psi_I(t)\rangle\langle\Psi_I(t)| \tag{2.17}$$

and

$$\mu_{ij} = \langle i|\vec{\mu}\cdot\hat{x}|j\rangle . \tag{2.18}$$

We note that the sum over the states $|k\rangle$ in Eq. (2.16) includes the state $|3\rangle$. Now invoking the Raman resonance condition of Eq. (1.1) and defining

$$\Delta\omega = \omega_l - \omega_s - \omega_{21} , \tag{2.19}$$

$$\rho_{21}' = \rho_{21}\exp(i\Delta\omega t) , \tag{2.20}$$

Eq. (2.16) becomes

$$\mathcal{P}_{\text{CARS}} = \frac{N}{2\hbar}\sum_k \left[\rho_{21}'\mu_{1k}\mu_{k2}\mathcal{E}_l\left(\frac{1}{(\omega_{k2}-\omega_l)} + \frac{1}{(\omega_{k1}+\omega_l)}\right)e^{-i\omega_a t} + \text{c.c.}\right] . \tag{2.21}$$

Equation (2.21) is the fundamental result of this section. In Sec. III, we shall derive expressions for ρ_{21}' for several different cases. For example, for the simplest case where level $|3\rangle$ is far from resonance with the pump fields and the $|1\rangle \to |2\rangle$ two-photon transition is unsaturated, we find that in the steady-state regime

$$\rho_{21}'^{ss} = \frac{1}{4\hbar^2}\frac{\mathcal{E}_l\mathcal{E}_s^*}{\Delta\omega + i(1/T_2)_{21}}\sum_{k'}\mu_{1k'}\mu_{k'2}\left(\frac{1}{(\omega_{k'1}-\omega_l)} + \frac{1}{(\omega_{k'1}+\omega_s)}\right)(\rho_{22}^{eq} - \rho_{11}^{eq}) , \tag{2.22}$$

where ρ_{11}^{eq} and ρ_{22}^{eq} are the populations of levels $|1\rangle$ and $|2\rangle$ at thermal equilibrium and $(1/T_2)_{21}$ is the relaxation rate of the off-diagonal density-matrix element ρ_{21}. Substitution of Eq. (2.22) into Eq. (2.21) gives the traditional expression for the polarization of Raman-resonant (singly resonant) CARS.[3,7]

We note that the approximation introduced on going from Eq. (2.4) to Eq. (2.12) excludes possible modifications of ω_a in Eq. (2.21) due to the Stark effect. Since the CARS signal is measured as a function of the input frequencies (excitation spectrum) rather than the scattered frequency, this does not limit the validity of Eq. (2.21).

B. Bloch equations

1. Three-level system

In this section, we write the Bloch equations for the three-level system[11] $|1\rangle$, $|2\rangle$, $|3\rangle$ assuming that ω_l is near resonance with the $|1\rangle \to |3\rangle$ transition frequency ω_{31}. The von Neumann equation for the density-matrix operator defined in Eq. (2.17) is given by

$$i\hbar\frac{d\rho}{dt} = [V_I, \rho] \tag{2.23}$$

and on including phenomenological relaxation terms, the following Bloch equations are obtained:

$$\begin{aligned}\dot{\rho}_{11} &= iV_{13}(\rho_{31}' - \rho_{13}') + (1/T_1)_{21}(\rho_{22} - \rho_{22}^{eq})\\ &+ (1/T_1)_{31}(\rho_{33} - \rho_{33}^{eq}) - (1/T_1)_1(\rho_{11} - \rho_{11}^{eq}) ,\end{aligned} \tag{2.24}$$

$$\begin{aligned}\dot{\rho}_{22} &= iV_{23}(\rho_{32}' - \rho_{23}') + (1/T_1)_{32}(\rho_{33} - \rho_{33}^{eq})\\ &- (1/T_1)_2(\rho_{22} - \rho_{22}^{eq}) ,\end{aligned} \tag{2.25}$$

$$\dot{\rho}_{33} = -iV_{13}(\rho_{31}' - \rho_{13}') - iV_{23}(\rho_{32}' - \rho_{23}') - (1/T_1)_3(\rho_{33} - \rho_{33}^{eq}) , \tag{2.26}$$

$$\dot{\rho}_{21}'' = -iV_{13}\rho_{23}' + iV_{23}\rho_{31}' - [(1/T_2)_{21} - i\Delta\omega]\rho_{21}'' , \tag{2.27}$$

$$\dot{\rho}'_{31} = -iV_{13}(\rho_{33} - \rho_{11}) + iV_{23}\rho''_{21} - [(1/T_2)_{31} + i\Delta_{31}]\rho'_{31}, \tag{2.28}$$

$$\dot{\rho}'_{32} = -iV_{23}(\rho_{33} - \rho_{22}) + iV_{13}\rho''_{12} - [(1/T_2)_{32} + i\Delta_{32}]\rho'_{32}, \tag{2.29}$$

where the rapidly oscillating terms have been eliminated by the substitutions

$$\rho_{31} = \rho'_{31}(\mathcal{E}_l/|\mathcal{E}_l|)e^{i\Delta_{31}t}, \quad \rho_{32} = \rho'_{32}(\mathcal{E}_s/|\mathcal{E}_s|)e^{i\Delta_{32}t}, \tag{2.30}$$

$$\rho_{21} = \rho''_{21}(\mathcal{E}_s^*\mathcal{E}_l/|\mathcal{E}_l||\mathcal{E}_s|)e^{-i\Delta\omega t} = \rho'_{21}e^{-i\Delta\omega t}, \tag{2.31}$$

and

$$V_{13} = \mu_{13}|\mathcal{E}_l|/2\hbar, \quad V_{23} = \mu_{23}|\mathcal{E}_s|/2\hbar, \tag{2.32}$$

$$\begin{aligned}\Delta_{31} &= \omega_{31} - \omega_l, \quad \Delta_{32} = \omega_{32} - \omega_s, \\ \Delta\omega &= \Delta_{32} - \Delta_{31} = \omega_l - \omega_s - \omega_{21}.\end{aligned} \tag{2.33}$$

Following Schenzle and Brewer,[16] we have assumed that the molecules relax via spontaneous decay or collisions out of the states $|1\rangle$, $|2\rangle$, and $|3\rangle$ into lower levels or into a reservoir (labeled l) which remains in thermal equilibrium. The total decay rate for levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ are given by

$$\begin{aligned}(1/T_1)_1 &= (1/T_1)_{1l}, \\ (1/T_1)_2 &= (1/T_1)_{21} + (1/T_1)_{2l}, \\ (1/T_1)_3 &= (1/T_1)_{31} + (1/T_1)_{32} + (1/T_1)_{3l},\end{aligned} \tag{2.34}$$

where $(1/T_1)_{ij}$ (Ref. 18) is the rate of transitions from level $|i\rangle \to |j\rangle$. By redefining $(1/T_1)_1$ we can include the case of excited-state CARS.[19] In writing Eqs. (2.24)–(2.26), we have assumed levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ to be repopulated by the reservoir at the constant rates $(1/T_1)_i\rho_{ii}^{eq}$. The dephasing rates $(1/T_2)_{ij}$ for the off-diagonal density-matrix elements ρ_{ij} are given by

$$(1/T_2)_{ij} = \tfrac{1}{2}[(1/T_1)_i + (1/T_1)_j] + (1/T_2^*)_{ij}, \tag{2.35}$$

where $(1/T_2^*)_{ij}$ is the rate of phase-interrupting collisions.

Since population is not conserved in the three-level system, a full solution of Eqs. (2.24)–(2.29) requires the solution of nine equations. Before proceeding to solve these equations, we give the effective-two-level Bloch equations for the case where ω_l is far from resonance with ω_{31}.

2. *Effective-two-level system*

When ω_l is sufficiently far from resonance with any of the molecular-transition frequencies so that Eq. (2.14) holds, we can redefine the projection operator P of Eq. (2.2) such that

$$P = P' + Q', \quad P' = \sum_{i=1}^{2} |i\rangle\langle i|, \quad Q' = \sum_{k'} |k'\rangle\langle k'|. \tag{2.36}$$

The effective Hamiltonian for the $|1\rangle$, $|2\rangle$ two-level system can then be obtained by replacing P and Q by P' and Q' in Eq. (2.13) and invoking Eqs. (2.5)–(2.9), (2.14), and the RWA. We find that

$$\begin{aligned}\mathcal{H}_{ii} &= -\frac{1}{4\hbar}\sum_{k'} \mu_{ik'}\mu_{k'i} \times \left(\frac{2\omega_{k'i}}{\omega_{k'i}^2 - \omega_l^2}|\mathcal{E}_l|^2 + \frac{2\omega_{k'i}}{\omega_{k'i}^2 - \omega_s^2}|\mathcal{E}_s|^2\right) \\ &= \Delta E_i, \quad i = 1, 2\end{aligned} \tag{2.37}$$

and

$$\mathcal{H}_{21} = -\hbar\Omega(\mathcal{E}_l\mathcal{E}_s^*/|\mathcal{E}_l||\mathcal{E}_s|)e^{-i\Delta\omega t}, \quad \mathcal{H}_{12} = \mathcal{H}_{21}^*, \tag{2.38}$$

where ΔE_i is the ac Stark shift of the level $|i\rangle$ and the two-photon Rabi frequency Ω is given by[12]

$$\Omega = \frac{|\mathcal{E}_l||\mathcal{E}_s|}{4\hbar^2}\sum_{k'} \mu_{1k'}\mu_{k'2}\left(\frac{1}{\omega_{k'1} - \omega_l} + \frac{1}{\omega_{k'1} + \omega_s}\right). \tag{2.39}$$

We note that in order for Ω to be sufficiently large so that saturation of the two-level system can take place for reasonable powers of the pumping fields,[20] there must be at least one $|1\rangle \to \{|k'\rangle\}$ transition that is near resonance with ω_l while, of course, still maintaining the condition of Eq. (2.14):

$$|\Delta_{k'1}| \gg |\Delta\omega|, \tag{2.40}$$

where $\Delta_{k'1} = \omega_{k'1} - \omega_l$ and $\Delta\omega$ is defined in Eq. (2.33). Then Ω can be reexpressed in the notation of the previous section as

$$\Omega = \sum_{k'} \frac{V_{1k'}V_{k'2}}{\Delta_{k'1}}. \tag{2.41}$$

Using Eqs. (2.11), (2.17), (2.31), (2.37), and (2.38) and including relaxation terms as in the previous section, we obtain the following Bloch equations for the effective two-level system:

$$\begin{aligned}\dot{\rho}_{11} = i\Omega(\rho''_{21} - \rho''_{12}) &+ (1/T_1)_2(\rho_{22} - \rho_{22}^{eq}) \\ &- (1/T_1)_1(\rho_{11} - \rho_{11}^{eq}),\end{aligned} \tag{2.42}$$

$$\dot{\rho}_{22} = -i\Omega(\rho''_{21} - \rho''_{12}) - (1/T_1)_2(\rho_{22} - \rho_{22}^{eq}), \tag{2.43}$$

$$\dot{\rho}''_{21} = i\Omega(\rho_{11} - \rho_{22}) - [(1/T_2)_{21} - i\Delta\tilde{\omega}]\rho''_{21}, \tag{2.44}$$

where rapidly oscillating terms have been eliminated using the transformation of Eq. (2.31) and $\Delta\tilde{\omega}$ is defined as

$$\Delta\tilde{\omega} = \Delta\omega + (\Delta E_1 - \Delta E_2)/\hbar. \tag{2.45}$$

These equations are identical in form to the Bloch equations for the ordinary two-level system.[21]

C. Methods used in solving Bloch equations

1. Wilcox-Lamb approximation

This approximation[15] involves setting the time derivatives of the off-diagonal elements of the density matrix equal to zero. In this way, the n^2 n-level Bloch equations can be reduced to n n-level rate equations. A number of comparisons between the numerical solutions of the Bloch equations (or Schrödinger equations) and the rate equations have been made for multiphoton ionization of atoms[22] and multiphoton absorption and dissociation of molecules.[18(a),23] The general rule which emerges from these studies and which has recently been demonstated theoretically[24] is that rate equations are appropriate for those cases where coherent pumping processes are much slower than incoherent decay processes. Great care must be exercised in interpreting the results obtained using the Wilcox-Lamb approximation as it involves the assumption that the off-diagonal elements of the density matrix ρ_{ij} relax very rapidly to their steady-state values ρ_{ij}^{ss}. In fact, the time dependence of *all* the elements of the density matrix can be expressed as

$$\rho_{ij}=\sum_{k=1}^{n^2}\rho_{ij}^{(k)}\exp(Z_k t)+\rho_{ij}^{ss} \tag{2.46}$$

and so the assumption $\dot{\rho}_{ij}=0$ for $i\neq j$ implies the reliability of only the slowest-decaying contributions to ρ_{ii} obtained from the rate equations.

A number of authors have shown numerically[22] (but without presenting justification) that in the opposite limit (that is, when coherent pumping processes are much faster than incoherent relaxation processes) the rate equations give the time average of the populations obtained from the Bloch equations. We point out that in this limit all the states are so strongly coupled that all the real parts of Z_k in Eq. (2.46) are approximately equal and all the density-matrix elements achieve their steady-state values at the same rate as the fastest-decaying state. A critical discussion of the validity of the Wilcox-Lamb approximation in this regime has been given by Stone and Goodman.[18(a)]

2. Laplace transforms

We shall solve the Bloch equations of Sec. III (or the rate equations derived from them) by applying the Laplace transform

$$\rho_{ij}(Z)=\int_0^\infty \rho_{ij}(t)e^{-Zt}\,dt\,,$$
$$Z\rho_{ij}(Z)-\rho_{ij}(0)=\int_0^\infty \dot{\rho}_{ij}(t)e^{-Zt}\,dt\,, \tag{2.47}$$

assuming that at time $t=0$, the system is in thermal equilibrium so that $\rho_{ij}(0)=\rho_{ii}^{eq}\delta_{ij}$. The inverse Laplace transform is given by

$$\rho_{ij}(t)=\frac{1}{2\pi i}\int_{-i\infty+r}^{i\infty+r}e^{Zt}\rho_{ij}(Z)dZ\,. \tag{2.48}$$

3. Perturbation theory

In order to find the poles of the Laplace transformation, one must solve an nth-order equation in Z:

$$F(Z)=0\,. \tag{2.49}$$

For $n>2$, there is often no simple analytical solution of this equation and so one must resort to numerical solutions or to approximate zeroth-order solutions which can be improved by first- or second-order perturbation theory. We improve on the distinct zeroth-order solutions $Z_i^{(0)}$ by using the first-order solutions[16] (that is, solutions which are correct up to first order) obtained from the Taylor expansion

$$Z_i^{(1)}=Z_i^{(0)}-F(Z_i^{(0)})/F'(Z_i^{(0)}) \tag{2.50}$$

and on pairs of identical zeroth-order solutions $Z_{i,i+1}^{(0)}$ by using the second-order solutions derived from the Taylor expansion

$$Z_{i,i+1}^{(2)}=Z_i^{(0)}-F'(Z_i^{(0)})/F''(Z_i^{(0)}) \pm\{[Z_i^{(0)}+F'(Z_i^{(0)})/F''(Z_i^{(0)})]^2 -[2F(Z_i^{(0)})/F''(Z_i^{(0)})+Z_i^{(0)2}]\}^{1/2}\,. \tag{2.51}$$

In Eqs. (2.50) and (2.51), F' and F'' are the first and second derivatives of F with respect to Z. In all cases where these approximations were made, the results were compared with the numerical solution of Eq. (2.49).

III. PARTICULAR SOLUTIONS OF THE BLOCH EQUATIONS

A. Effective two-level system

The solutions of Eqs. (2.42)–(2.44), for pulses which are sufficiently short so that decay can be neglected, are well known[16,21]; ρ_{21}'' is given by

$$\rho_{21}''=2\Omega(\rho_{11}^{eq}-\rho_{22}^{eq})\left(\Delta\tilde{\omega}\frac{\sin^2[\frac{1}{2}(4\Omega^2+\Delta\tilde{\omega}^2)^{1/2}t]}{(4\Omega^2+\Delta\tilde{\omega}^2)}+\frac{i\sin[\frac{1}{2}(4\Omega^2+\Delta\tilde{\omega}^2)^{1/2}t]\cos[\frac{1}{2}(4\Omega^2+\Delta\tilde{\omega}^2)^{1/2}t]}{(4\Omega^2+\Delta\tilde{\omega}^2)^{1/2}}\right). \tag{3.1}$$

For systems prepared under steady-state conditions or after all the transients have decayed, the solutions of Eqs. (2.42)–(2.44) are obtained by setting all the time derivatives equal to zero. Thus we find that

$$\rho_{21}''^{ss}=\frac{\Omega(\rho_{22}^{eq}-\rho_{11}^{eq})}{[\Delta\tilde{\omega}+i(1/T_2)_{21}]}\,\frac{[\Delta\tilde{\omega}^2+(1/T_2)_{21}^2]}{[\Delta\tilde{\omega}^2+(1/T_2)_{21}^2+2\Omega^2 f]}, \quad (3.2)$$

where

$$f=\frac{[(1/T_1)_1+(1/T_1)_2-(1/T_1)_{21}](1/T_2)_{21}}{(1/T_1)_1(1/T_1)_2}. \quad (3.3)$$

For molecular systems in which $|1\rangle$ and $|2\rangle$ are vibrational-rotational states and collisional processes are significant, it is often true[16] that $(1/T_1)_{21}\ll(1/T_1)_1\simeq(1/T_1)_2\simeq(1/T_2)_{21}$, so that $f\simeq 2$. For excited-state atoms whose CARS spectra are of current experimental interest,[19(b)] $(1/T_1)_{21}<(1/T_1)_1\simeq(1/T_1)_2\neq(1/T_2)_{21}$, so that $f\simeq 2(1/T_2)_{21}/(1/T_1)_1$; a typical system might be $|1\rangle=\mathrm{Na}(3^2P_{1/2})$ and $|2\rangle=\mathrm{Na}(3^2P_{3/2})$. For atoms with a single $|2\rangle\to|1\rangle$ decay channel, $(1/T_1)_1=0$, $(1/T_1)_2=(1/T_1)_{21}$, and one can show using Eqs. (2.42)–(2.44) that $f=2(1/T_2)_{21}/(1/T_1)_{21}$.

We note that when $2\Omega^2 f\ll\Delta\tilde{\omega}^2+(1/T_2)_{21}^2$, Eq. (3.2) reduces to the expression obtained by trivially setting $\rho_{11}=\rho_{11}^{eq}$, $\rho_{22}=\rho_{22}^{eq}$, and $\Delta\tilde{\omega}=\Delta\omega$ in Eq. (2.44). When this expression is combined with Eqs. (2.31) and (2.39), Eq. (2.22) is obtained. We pointed out in Sec. II A that the traditional expression for the polarization of Raman-resonant CARS[3,7] can be derived by substituting Eq. (2.22) into Eq. (2.21). Substituting the expression for ρ_{21}^{ss} obtained from Eqs. (3.2), (2.31), and (2.39) into Eq. (2.21), we see that $\mathcal{P}_{\mathrm{CARS}}$ is proportional to $|\mathcal{E}_l|^2$ when the intensity of the ω_l pumping field is low, and independent of $|\mathcal{E}_l|$ when the intensity of the ω_l pumping field is so high that the $|1\rangle\to|2\rangle$ two-photon transition is completely saturated. However, as the intensity of the ω_s pumping field is raised, $\mathcal{P}_{\mathrm{CARS}}$ goes from being proportional to $|\mathcal{E}_s|$ at low intensities to being inversely proportional to $|\mathcal{E}_s|$ at high intensities.

B. Three-level system: $V_{13}\gg V_{23}$

In this section, we solve the three-level Bloch equations, Eqs. (2.24)–(2.29), for the case where the $|1\rangle\to|3\rangle$ transition is saturated by the field at frequency ω_l whereas the $|2\rangle\to|3\rangle$ transition is only weakly coupled to the field at frequency ω_s.[25] In addition, we assume for simplicity that the fastest decay process is the transfer of population from level $|3\rangle$ to the reservoir $|l\rangle$. This assumption is mainly true for molecular CARS at low pressures. When collisions are important, the steady state is quickly achieved [see Eq. (3.25) and the Appendix]. Thus

$$V_{13}\gg(1/T_1)_{3l},\ |\Delta_{31}|,\ |\Delta_{32}| \quad (3.4)$$

and

$$(1/T_1)_{3l}\gg V_{23},(1/T_1)_{21},(1/T_1)_{31},(1/T_1)_{32},(1/T_1)_{1l},(1/T_1)_{2l},(1/T_2^*)_{21},(1/T_2^*)_{31},(1/T_2^*)_{32}. \quad (3.5)$$

These assumptions allow us to solve Eqs. (2.24), (2.26), and (2.28) neglecting all terms that relate to level $|2\rangle$. Following Schenzle and Brewer's[16] treatment of the two-level system, we solve their Eq. (2.16) in the limit of Eq. (3.4) using the perturbation theory described in Sec. II C 3. We find that the time development of ρ_{11}, ρ_{33}, and ρ_{31}' is given by Eq. (2.46) with

$$\begin{aligned}
&Z_{1,2}^{(0)}=0,\\
&Z_{1,2}^{(2)}=-\tfrac{1}{2}(1/T_1)_{3l}[1\pm\Delta_{31}(4V_{13}^2+\Delta_{31}^2)^{-1/2}],\\
&Z_{3,4}^{(0)}=\pm i(4V_{13}^2+\Delta_{31}^2)^{1/2},\\
&Z_{3,4}^{(1)}=-\tfrac{1}{2}(1/T_1)_{3l}\pm i(4V_{13}^2+\Delta_{31}^2)^{1/2}\\
&\qquad\mp iV_{13}^2(1/T_1)_{3l}^2(4V_{13}^2+\Delta_{31}^2)^{-3/2}.
\end{aligned} \quad (3.6)$$

Thus, as expected for strong coupling, all the contributions to the density-matrix elements decay according to the fastest-decay rate, namely, $(1/T_1)_{3l}$. Thus for $t\gg(T_1)_{3l}$ we can safely assume that ρ_{11}, ρ_{33}, and ρ_{31}' have achieved their steady-state values

$$\rho_{11}^{ss}=\frac{\rho_{11}^{eq}(1/T_1)_1[x_{13}+(1/T_1)_3]+\rho_{33}^{eq}x_{13}[(1/T_1)_3-(1/T_1)_{31}]}{x_{13}[(1/T_1)_1+(1/T_1)_3-(1/T_1)_{31}]+(1/T_1)_1(1/T_1)_3}, \quad (3.7)$$

$$\rho_{33}^{ss}=\frac{x_{13}(1/T_1)_1\rho_{11}^{eq}+\rho_{33}^{eq}\{x_{13}[(1/T_1)_3-(1/T_1)_{31}]+(1/T_1)_1(1/T_1)_3\}}{x_{13}[(1/T_1)_1+(1/T_1)_3-(1/T_1)_{31}]+(1/T_1)_1(1/T_1)_3}, \quad (3.8)$$

$$\rho_{31}'^{ss}=\frac{V_{13}(1/T_1)_1(1/T_1)_3}{\Delta_{31}+i(1/T_2)_{31}}\left(\frac{\rho_{11}^{eq}-\rho_{33}^{eq}}{x_{13}[(1/T_1)_1+(1/T_1)_3-(1/T_1)_{31}]+(1/T_1)_1(1/T_1)_3}\right), \quad (3.9)$$

where the pumping rate for the $|1\rangle\to|3\rangle$ transition is given by

$$x_{13}=2V_{13}^2(1/T_2)_{31}/[\Delta_{31}^2+(1/T_2)_{31}^2]. \quad (3.10)$$

We now replace ρ_{11}, ρ_{33}, and ρ_{31}' by their steady-state values in Eqs. (2.25), (2.27), and (2.29) and solve for ρ_{21}''. No great simplification is obtained by assuming $\rho_{32}'=0$, thereby reducing the number of equations to be solved from five to three, and so we proceed with the solution of all five equations which we write in the form

$$\dot{P} = UP + V\,, \tag{3.11}$$

where

$$P = \begin{pmatrix} \rho_{22} \\ \rho''_{12} \\ \rho''_{21} \\ \rho'_{23} \\ \rho'_{32} \end{pmatrix}, \tag{3.12}$$

$$U = \begin{pmatrix} -(1/T_1)_2 & 0 & 0 & -iV_{23} & iV_{23} \\ 0 & -i\Delta\omega - (1/T_2)_{21} & 0 & 0 & iV_{13} \\ 0 & 0 & i\Delta\omega - (1/T_2)_{21} & -iV_{13} & 0 \\ -iV_{23} & 0 & -iV_{13} & i\Delta_{32} - (1/T_2)_{32} & 0 \\ iV_{23} & iV_{13} & 0 & 0 & -i\Delta_{32} - (1/T_2)_{32} \end{pmatrix}, \tag{3.13}$$

$$V = \begin{pmatrix} (1/T_1)_{32}(\rho_{33}^{ss} - \rho_{33}^{eq}) + (1/T_1)_2\rho_{22}^{eq} \\ -iV_{23}\rho_{13}^{\prime ss} \\ iV_{23}\rho_{31}^{\prime ss} \\ iV_{23}\rho_{33}^{ss} \\ -iV_{23}\rho_{33}^{ss} \end{pmatrix}. \tag{3.14}$$

Applying the Laplace transform of Eq. (2.47) to Eq. (3.11) we obtain

$$(Z - U)P(Z) = V'\,, \tag{3.15}$$

where

$$V' = V/Z + \delta_{1i}\rho_{22}^{eq}\,. \tag{3.16}$$

Thus,

$$\rho''_{21}(Z) \equiv P_3(Z) = \sum_i (Z - U)^{-1}_{3i} V'_i\,, \tag{3.17}$$

where

$$(Z - U)^{-1}_{3i} = \alpha_{i3}/\det(Z - U)\,. \tag{3.18}$$

The cofactors α_{i3} are given by

$$\alpha_{13} = -V_{13}V_{23}\{Z^2 + [(1/T_2)_{21} + (1/T_2)_{32} + i(\Delta\omega + \Delta_{32})] + V_{13}^2 + [(1/T_2)_{21} + i\Delta\omega][(1/T_2)_{32} + i\Delta_{32}]\}\,,$$

$$\alpha_{23} = V_{13}^2 V_{23}^2\,,$$

$$\begin{aligned} \alpha_{33} = {} & Z^4 + Z^3[(1/T_2)_{21} + 2(1/T_2)_{32} + (1/T_1)_2 + i\Delta\omega] \\ & + Z^2\{V_{13}^2 + 2V_{23}^2 + (1/T_2)_{32}^2 + [(1/T_1)_2 + 2(1/T_2)_{32}][(1/T_2)_{21} + i\Delta\omega] + 2(1/T_1)_2(1T_2)_{32}\} \\ & + Z([2V_{23}^2 + \Delta_{32}^2 + (1/T_2)_{32}^2][(1/T_2)_{21} + i\Delta\omega] + 2V_{23}^2(1/T_2)_{32} + V_{13}^2[(1/T_2)_{32} - i\Delta_{32}] \\ & \quad + (1/T_1)_2\{V_{13}^2 + (1/T_2)_{32}^2 + \Delta_{32}^2 + 2(1/T_2)_{32}[(1/T_2)_{21} + i\Delta\omega]\}) + V_{13}^2 V_{23}^2 \\ & + 2V_{23}^2(1/T_2)_{32}[(1/T_2)_{21} + i\Delta\omega] + (1/T_1)_2\{V_{1k}^2[(1/T_2)_{32} - i\Delta_{32}] + [(1/T_2)_{32}^2 + \Delta_{32}^2][(1/T_2)_{21} + i\Delta\omega]\}\,, \end{aligned} \tag{3.19}$$

$$\alpha_{43} = -iV_{1k}(Z^3 + Z^2[(1/T_2)_{32} + (1/T_2)_{21} + (1/T_1)_2 + i\Delta\omega + i\Delta_{32}] + Z\{V_{13}^2 + V_{23}^2 + (1/T_1)_2[(1/T_2)_{32} + (1/T_2)_{21} + i\Delta\omega + i\Delta_{32}] + [(1/T_2)_{32} + i\Delta_{32}][(1/T_2)_{21} + i\Delta\omega]\} + (1/T_1)_2\{V_{13}^2 + [(1/T_2)_{32} + i\Delta_{32}][(1/T_2)_{21} + i\Delta\omega] + V_{23}^2[(1/T_2)_{21} + i\Delta\omega]\}),$$

$$\alpha_{53} = -iV_{13}V_{23}^2[Z + (1/T_2)_{21} + i\Delta\omega],$$

and $\det(Z-U)$ can be written

$$\det(Z-U) = \sum_{i=0}^{n} c_i Z^i, \quad n=5 \tag{3.20}$$

with

$$\begin{aligned} c_5 &= 1, \\ c_4 &= (1/T_1)_2 + 2[(1/T_2)_{21} + (1/T_2)_{32}], \\ c_3 &= 2(V_{13}^2 + V_{23}^2) + \Delta\omega^2 + \Delta_{32}^2 + 2(1/T_1)_2[(1/T_2)_{21} + (1/T_2)_{32}] \\ &\quad + [(1/T_2)_{32}^2 + (1/T_2)_{21}^2 + 4(1/T_2)_{21}(1/T_2)_{32}], \\ c_2 &= (1/T_1)_2[\Delta\omega^2 + \Delta_{32}^2 + (1/T_2)_{32}^2 + (1/T_2)_{21}^2 + 4(1/T_1)_{21}(1/T_2)_{32} + 2V_{13}^2] \\ &\quad + 2\{\Delta\omega^2(1/T_2)_{32} + \Delta_{32}^2(1/T_2)_{21} + [(1/T_2)_{32} + (1/T_2)_{21}][(1/T_2)_{32}(1/T_2)_{21} + V_{13}^2] \\ &\quad + V_{23}^2[2(1/T_2)_{21} + (1/T_2)_{32}]\}, \\ c_1 &= 2(1/T_1)_2\{[(1/T_2)_{21} + (1/T_2)_{32}][V_{13}^2 + (1/T_2)_{21}(1/T_2)_{32}] + (1/T_2)_{32}\Delta\omega^2 + (1/T_2)_{21}\Delta_{32}^2\} \\ &\quad + [\Delta_{32}^2 + (1/T_2)_{32}^2][\Delta\omega^2 + (1/T_2)_{21}^2] + 2V_{13}^2[(1/T_2)_{21}(1/T_2)_{32} - \Delta\omega\Delta_{32}] + V_{13}^2(V_{13}^2 + 2V_{23}^2) \\ &\quad + 2V_{23}^2[2(1/T_2)_{21}(1/T_2)_{32} + (1/T_2)_{21}^2 + \Delta\omega^2], \\ c_0 &= (1/T_1)_2\{[\Delta_{32}^2 + (1/T_2)_{32}^2][\Delta\omega^2 + (1/T_2)_{21}^2] + 2V_{13}^2[(1/T_2)_{21}(1/T_2)_{32} - \Delta\omega\Delta_{32}] + V_{13}^4\} \\ &\quad + 2(1/T_2)_{32}V_{23}^2[\Delta\omega^2 + (1/T_2)_{21}^2] + 2(1/T_2)_{21}V_{13}^2V_{23}^2. \end{aligned} \tag{3.21}$$

The denominators of Eq. (3.17) are either of the form $Z\det(Z-U)$ or $\det(Z-U)$ and thus the poles of the transformation are given by the solutions of the equations $Z\det(Z-U)=0$ or $\det(Z-U)=0$. We see from the inverse Laplace transform of Eq. (2.48) that the terms in $\rho_{21}''(t)$ that derive from the pole at $Z=0$ give rise to $\rho_{21}''^{ss}$. Within the context of Eqs. (3.4) and (3.5), it can be shown that the other poles are given by

$$Z_1^{(0)} = 0, \quad Z_1^{(1)} = -c_0/c_1 \simeq (1/T_1)_2, \tag{3.22}$$

$$\begin{aligned} Z_{2,3}^{(0)} &= \tfrac{1}{4}c_4 + ic_1^{1/4} \simeq -\tfrac{1}{2}(1/T_2)_{32} + iV_{13}, \\ Z_{4,5}^{(0)} &= \tfrac{1}{4}c_4 - ic_1^{1/4} \simeq -\tfrac{1}{2}(1/T_2)_{32} - iV_{13}, \end{aligned} \tag{3.23}$$

with the first- and second-order corrections to $Z_{2,3,4,5}^{(0)}$ being much smaller than the leading terms given in Eq. (3.23). Since we are only interested in $t \gg (T_1)_{3l}$ we need only consider those contributions to ρ_{21}'' that decay according to the rate constant $(1/T_1)_2$ or that contribute to $\rho_{21}''^{ss}$. We note that since $\prod_{i=1}^{5} Z_i = -c_0$ and $|Z_{2,3,4,5}| \gg |Z_1|$ we can use the approximation

$$(Z_2 - Z_1)(Z_3 - Z_1)(Z_4 - Z_1)(Z_5 - Z_1) \simeq -c_0/Z_1 \simeq c_1 \tag{3.24}$$

in evaluating the inverse Laplace transform.

Combining Eqs. (2.48), (3.16)–(3.19), (3.21), (3.22), and (3.24) and considering only leading terms, we find that for $t \gg (T_1)_{3l}$:

$$\rho_{21}''(t) = f(\omega_l, \omega_s)\rho_{33}^{ss}\left(e^{-(1/T_1)_2 t} + \frac{[(1/T_1)_2 - (1/T_1)_{32}]}{(1/T_1)_2}(1 - e^{-(1/T_1)_2 t})\right), \tag{3.25}$$

where

$$f(\omega_l, \omega_s) = \frac{V_{13}V_{23}}{V_{13}^2 - [\Delta\omega + i(1/T_2)_{21}][\Delta_{32} + i(1/T_2)_{32}]}, \tag{3.26}$$

which on ignoring line-broadening effects reduces to

$$f(\omega_l,\omega_s) = -\frac{V_{13}V_{23}}{[\omega_s - \frac{1}{2}(\omega_{32}+\omega_l-\omega_{21}) + \frac{1}{2}(4V_{13}^2+\Delta_{31}^2)^{1/2}][\omega_s - \frac{1}{2}(\omega_{32}+\omega_l-\omega_{21}) - \frac{1}{2}(4V_{13}^2+\Delta_{31}^2)^{1/2}]}$$

$$\simeq -\frac{V_{13}V_{23}}{(\omega_s-\omega_{32}+V_{13})(\omega_s-\omega_{32}-V_{13})} \quad (\text{for } \omega_l \simeq \omega_{31}). \tag{3.27}$$

An analogous Stark splitting effect[25] should be obtained in the case where $V_{23} \gg V_{13}$: there we expect $|f(\omega_l,\omega_s)| \simeq |V_{13}V_{23}/[(\omega_l-\omega_{31}+V_{23})(\omega_l-\omega_{31}-V_{23})]|$ when $\omega_s \simeq \omega_{32}$.

Substituting the expression for $\rho_{21}'(t)$ obtained from Eqs. (2.31), (2.32), (3.8), and (3.25) into Eq. (2.21), we see that for very high intensities of the field at frequency ω_l, $\mathcal{P}_{\text{CARS}}$ is independent of $|\mathcal{E}_l|$ and proportional to $|\mathcal{E}_s|$ when $\omega_s \simeq \omega_{32}$. If, however, $\omega_s \simeq \omega_{32} \pm V_{13}$, we find that $\mathcal{P}_{\text{CARS}} \propto |\mathcal{E}_l||\mathcal{E}_s|$. Similarly, for the case $V_{23} \gg V_{13}$, we expect to obtain $\mathcal{P}_{\text{CARS}} \propto |\mathcal{E}_l|^2|\mathcal{E}_s|^{-1}$ when $\omega_l \simeq \omega_{31}$ and $\mathcal{P}_{\text{CARS}} \propto |\mathcal{E}_l|^2$ and independent of $|\mathcal{E}_s|$ when $\omega_l \simeq \omega_{31} \pm V_{23}$.

We note that the steady-state expression for ρ_{21}'' given in Eq. (3.25) is generally valid provided that the $|1\rangle \to |3\rangle$ transition is saturated by the ω_l field while the $|2\rangle \to |3\rangle$ transition is only weakly coupled to the ω_s field. Its validity does *not* depend on the relative magnitudes of the decay constants.

C. Three-level system: Wilcox-Lamb approximation

The rate equations obtained from Eqs. (2.24)–(2.29) by setting the time derivatives of the off-diagonal elements of the density matrix equal to zero can be expressed as in Eq. (3.11) of the previous section with

$$P = \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \end{pmatrix}, \tag{3.28}$$

$$U = \begin{pmatrix} B-(1/T_1)_1 & A+(1/T_1)_{21} & -(A+B)+(1/T_1)_{31} \\ A & C-(1/T_1)_2 & -(A+C)+(1/T_1)_{32} \\ -(A+B) & -(A+C) & 2A+B+C-(1/T_1)_3 \end{pmatrix}, \tag{3.29}$$

$$V = \begin{pmatrix} (1/T_1)_1\rho_{11}^{\text{eq}} - (1/T_1)_{21}\rho_{22}^{\text{eq}} - (1/T_1)_{31}\rho_{33}^{\text{eq}} \\ (1/T_1)_2\rho_{22}^{\text{eq}} - (1/T_1)_{32}\rho_{33}^{\text{eq}} \\ (1/T_1)_3\rho_{33}^{\text{eq}} \end{pmatrix}. \tag{3.30}$$

Here

$$A = \frac{2V_{13}^2V_{23}^2}{[\Delta\hat{\omega}^2+(1/\hat{T}_2)_{21}^2]}\left(\frac{\Delta\hat{\omega}[\Delta_{31}(1/T_2)_{32}-\Delta_{32}(1/T_2)_{31}]+(1/\hat{T}_2)_{21}[\Delta_{31}\Delta_{32}+(1/T_2)_{31}(1/T_2)_{32}]}{[\Delta_{31}^2+(1/T_2)_{31}^2][\Delta_{32}^2+(1/T_2)_{32}^2]}\right), \tag{3.31}$$

$$B = \frac{2V_{13}^2V_{23}^2}{[\Delta\hat{\omega}^2+(1/\hat{T}_2)_{21}^2]}\left(\frac{2\Delta\hat{\omega}\Delta_{31}(1/T_2)_{31}-(1/\hat{T}_2)_{21}[\Delta_{31}^2-(1/T_2)_{31}^2]}{[\Delta_{31}^2+(1/T_2)_{31}^2]^2}\right) - x_{13}, \tag{3.32}$$

$$C = -\frac{2V_{13}^2V_{23}^2}{\Delta\hat{\omega}^2+(1/\hat{T}_2)_{21}^2}\left(\frac{2\Delta\hat{\omega}\Delta_{32}(1/T_2)_{32}+(1/\hat{T}_2)_{21}[\Delta_{32}^2-(1/T_2)_{32}^2]}{[\Delta_{32}^2+(1/T_2)_{32}^2]^2}\right) - x_{23}, \tag{3.33}$$

with x_{23}, the pumping rate for the $|2\rangle \to |3\rangle$ transition defined analogously to x_{13} [Eq. (3.10)] and

$$(1/\hat{T}_2)_{21} = (1/T_2)_{21} + \frac{V_{23}^2(1/T_2)_{31}}{\Delta_{31}^2+(1/T_2)_{31}^2} + \frac{V_{13}^2(1/T_2)_{32}}{\Delta_{32}^2+(1/T_2)_{32}^2}, \tag{3.34}$$

$$\Delta\hat{\omega} = \Delta\omega + \frac{V_{23}^2\Delta_{31}}{\Delta_{31}^2+(1/T_2)_{31}^2} - \frac{V_{13}^2\Delta_{32}}{\Delta_{32}^2+(1/T_2)_{32}^2}. \tag{3.35}$$

Once ρ_{11}, ρ_{22}, and ρ_{33} are known one can calculate ρ_{21}'' using the following expression derived from Eqs. (2.24)–(2.29):

$$\rho_{21}'' = \frac{V_{13}V_{23}}{[\Delta\hat{\omega}+i(1/\hat{T}_2)_{21}]} \times \left(\frac{\rho_{22}-\rho_{33}}{\Delta_{32}+i(1/T_2)_{32}} - \frac{\rho_{11}-\rho_{33}}{\Delta_{31}-i(1/T_2)_{31}}\right). \tag{3.36}$$

In order for the Wilcox-Lamb approximation to be valid, we require (see the discussion in Sec. IIC 1)

$$x_{13},\, x_{23} \ll (1/T_2)_{31},\, (1/T_2)_{32}. \tag{3.37}$$

Of course, the steady-state solutions of the rate equations will still be valid even when Eq. (3.37) does not hold.

On examining the above rate equations, we first note that the term A contains only contributions from the $|1\rangle \to |3\rangle \to |2\rangle$ two-photon process whereas B and C contain contributions from both one- and two-photon processes. In Sec. III C 1 we shall consider the special case where the intensity is so low that direct two-photon processes can be disregarded and we can write

$$B \simeq -x_{13}, C \simeq -x_{23} \gg A . \tag{3.38}$$

We shall see that the usual assumption $\rho_{ii} = \rho_{ii}^{eq}$ is recovered when in addition x_{13} and x_{23} are small compared to the decay terms in the rate equations. When the intermediate level is either near resonance such that

$$|\Delta_{31}| \ll (1/T_2)_{31}, \quad |\Delta_{32}| \ll (1/T_2)_{32}, \tag{3.39}$$

or far from resonance such that

$$|\Delta_{31}| \simeq |\Delta_{32}| \gg |\Delta\omega|, (1/T_2)_{31}, (1/T_2)_{32}, \tag{3.40}$$

Eq. (3.38) can be rewritten as

$$\frac{V_{13}^2(1/\hat{T}_2)_{21}}{\Delta\hat{\omega}^2 + (1/\hat{T}_2)_{21}^2}, \frac{V_{23}^2(1/\hat{T}_2)_{21}}{\Delta\hat{\omega}^2 + (1/\hat{T}_2)_{21}^2} \ll (1/T_2)_{31}, \quad (1/T_2)_{32}, \tag{3.41}$$

respectively.

In Sec. III C 2 we shall consider the special case where the intermediate level is far from resonance [Eq. (3.40)] and the intensity is sufficiently high so that two-photon processes must be taken into account. If in addition, we assume that $(1/T_2)_{31} \simeq (1/T_2)_{32}$, we can write

$$A \simeq x_{12}, \quad B \simeq -x_{12} - x_{13}, \quad C \simeq -x_{12} - x_{23}, \tag{3.42}$$

where

$$x_{12} = \frac{2\Omega^2(1/\hat{T}_2)_{21}}{\Delta\hat{\omega}^2 + (1/\hat{T}_2)_{21}^2} \tag{3.43}$$

is the pumping rate of the $|1\rangle \to |2\rangle$ two-photon transition and Ω is defined by Eq. (2.41) with $k' = 3$. We shall show that the effective two-level expression for $\rho_{21}''^{ss}$ is recovered whenever x_{13} and x_{23} can be dropped from the rate equations, that is when

$$x_{12} \gg x_{13}, \ x_{23}. \tag{3.44}$$

Equations (3.40) and (3.44) together imply that

$$\frac{V_{13}^2(1/\hat{T}_2)_{21}}{\Delta\hat{\omega}^2 + (1/\hat{T}_2)_{21}^2}, \frac{V_{23}^2(1/\hat{T}_2)_{21}}{\Delta\hat{\omega}^2 + (1/\hat{T}_2)_{21}^2} \gg (1/T_2)_{31} \simeq (1/T_2)_{32}. \tag{3.45}$$

We note that this condition is consistent with the Wilcox-Lamb condition of Eq. (3.37).

In order to simplify the evaluation of the slow time development of $\rho_{21}''(t)$, we shall assume as in Sec. III B [Eq. (3.5)] that $(T_1)_{3l}$ is the shortest decay time in the system. When this assumption is invalid, we expect the steady state to be achieved rapidly (see the discussion in Sec. III B).

In Sec. III D, we discuss the steady-state solution of the rate equations for the case of saturating near-resonant fields, that is, where

$$\begin{aligned} &V_{13} \gg (1/T_2)_{31} \gg |\Delta_{31}|, \\ &V_{23} \gg (1/T_2)_{32} \gg |\Delta_{32}|. \end{aligned} \tag{3.46}$$

Here the intensity dependence of $\Delta\hat{\omega}$ and $(1/\hat{T}_2)_{21}$ becomes important and both the one- and two-photon contributions to A, B, and C must be taken into account.

In order to solve the rate equations, we apply the Laplace transform of Eq. (2.47) to Eq. (3.11) and obtain Eq. (3.15) with

$$V_i' = V_i/Z + \rho_{ii}^{eq}. \tag{3.47}$$

Thus,

$$\rho_{ii}(Z) \equiv P_i(Z) = \sum_j \frac{\alpha_{ji} V_j'}{\det(Z-U)}, \tag{3.48}$$

where the cofactors α_{ij} are given by

$$\begin{aligned}
\alpha_{11} &= Z^2 - Z[2A+B+C-(1/T_1)_2-(1/T_1)_3] + [2A+B+C-(1/T_1)_3][C-(1/T_1)_2] - (A+C)[A+C-(1/T_1)_{32}], \\
\alpha_{12} &= ZA - A[2A+B+C-(1/T_1)_3] + (A+B)[A+C-(1/T_1)_{32}], \\
\alpha_{13} &= -Z(A+B) + (A+B)[C-(1/T_1)_2] - A(A+C), \\
\alpha_{21} &= Z[A+(1/T_1)_{21}] - [A+(1/T_1)_{21}][2A+B+C-(1/T_1)_3] + (A+C)[A+B-(1/T_1)_{31}], \\
\alpha_{22} &= Z^2 - Z[2A+2B+C-(1/T_1)_1-(1/T_1)_3] + [B-(1/T_1)_1][2A+B+C-(1/T_1)_3] \\
&\quad - (A+B)[A+B-(1/T_1)_{31}], \\
\alpha_{23} &= -Z(A+C) - (A+C)[B-(1/T_1)_1] - (A+B)[A+(1/T_1)_{21}], \\
\alpha_{31} &= -Z[A+B-(1/T_1)_{31}] + [A+B-(1/T_1)_{31}][C-(1/T_1)_2] \\
&\quad - [A+(1/T_1)_{21}][A+C-(1/T_1)_{32}], \\
\alpha_{32} &= -Z[A+C-(1/T_1)_{32}] + [A+C-(1/T_1)_{32}][B-(1/T_1)_1] - A[A+B-(1/T_1)_{31}], \\
\alpha_{33} &= Z^2 - Z[B+C-(1/T_1)_1-(1/T_1)_2] + [B-(1/T_1)_1][C-(1/T_1)_2] - A[A+(1/T_1)_{21}],
\end{aligned} \tag{3.49}$$

and $\det(Z-U)$ is expanded as in Eq. (3.20) with $n=3$ and

$$\begin{aligned} c_3&=1\,,\\ c_2&=-[2(A+B+C)-(1/T_1)_1-(1/T_1)_2-(1/T_1)_3]\,,\\ c_1&=[2A+B+C-(1/T_1)_3][B+C-(1/T_1)_1-(1/T_1)_2]+[B-(1/T_1)_1][C-(1/T_1)_2]-A[A+(1/T_1)_{21}]\\ &\quad-(A+C)[A+C-(1/T_1)_{32}]-(A+B)[A+B-(1/T_1)_{31}]\,,\\ c_0&=[2A+B+C-(1/T_1)_3]\{A[A+(1/T_1)_{21}]-[B-(1/T_1)_1][C-(1/T_1)_2]\}\\ &\quad+(A+C)\{[B-(1/T_1)_1][A+C-(1/T_1)_{32}]-A[A+B-(1/T_1)_{31}]\}\\ &\quad-(A+B)\{[A+(1/T_1)_{21}][A+C-(1/T_1)_{32}]-[C-(1/T_1)_2][A+B-(1/T_1)_{31}]\}\,. \end{aligned} \tag{3.50}$$

1. Very low intensity: two-photon processes negligible

When the substitutions of Eq. (3.38) are made in Eq. (3.50) and it is assumed that $(1/T_1)_{3l}$ is the largest decay rate, we obtain the following poles of the Laplace transform:

$$\begin{aligned} &Z_1^{(0)}=-(1/T_1)_3\,,\\ &Z_1^{(1)}=-(1/T_1)_3-(1/T_1)_1-(1/T_1)_2-x_{13}-x_{23}\,,\\ &Z_2^{(0)}=0\,,\quad Z_2^{(2)}=-(1/T_1)_1-x_{13}\,,\\ &Z_3^{(0)}=0\,,\quad Z_3^{(2)}=-(1/T_1)_2-x_{23}\,. \end{aligned} \tag{3.51}$$

In keeping with the discussion of Sec. II C 1, we consider only those poles that give the slowest decaying terms of ρ_{ll}. We therefore conclude from Eqs. (2.48), (3.38), (3.48), and (3.51) that for $t\gg(T_1)_{3l}$:

$$\begin{aligned} \rho_{ll}-\rho_{33}=&\frac{1}{(Z_2^{(2)}-Z_3^{(2)})}\left(a_l e^{Z_2^{(2)}t}-b_l e^{Z_3^{(2)}t}\right)\\ &+f_l\left(\frac{e^{Z_2^{(2)}t}}{(Z_2^{(2)}-Z_3^{(2)})Z_2^{(2)}}-\frac{e^{Z_3^{(2)}t}}{(Z_2^{(2)}-Z_3^{(2)})Z_3^{(2)}}\right.\\ &\left.+\frac{1}{Z_2^{(2)}Z_3^{(2)}}\right),\quad i=1,2 \end{aligned} \tag{3.52}$$

$$\begin{aligned} a_1&=[x_{23}-x_{13}+(1/T_1)_2](\rho_{11}^{eq}-\rho_{33}^{eq})\\ &\quad-(1/T_1)_{2l}\rho_{22}^{eq}\,,\\ b_1&=(1/T_1)_1(\rho_{11}^{eq}-\rho_{33}^{eq})-(1/T_1)_{2l}\rho_{22}^{eq}\,,\\ f_1&=(1/T_1)_1[x_{23}+(1/T_1)_2](\rho_{11}^{eq}-\rho_{33}^{eq})\\ &\quad-x_{23}(1/T_1)_{21}(\rho_{22}^{eq}-\rho_{33}^{eq})\,,\\ a_2&=(1/T_1)_2(\rho_{22}^{eq}-\rho_{33}^{eq})\,, \end{aligned} \tag{3.53}$$

$$\begin{aligned} b_2&=[x_{13}-x_{23}+(1/T_1)_1](\rho_{22}^{eq}-\rho_{33}^{eq})\,,\\ f_2&=(1/T_1)_2[x_{13}+(1/T_1)_1](\rho_{22}^{eq}-\rho_{33}^{eq})\,. \end{aligned} \tag{3.54}$$

It is interesting to note that if

$$(T_1)_{3l}\ll t\ll[x_{13}+(1/T_1)_1]^{-1}\,,\ [x_{23}+(1/T_1)_2]^{-1}\,, \tag{3.55}$$

then

$$\rho_{ll}-\rho_{33}=\rho_{ll}^{eq}-\rho_{33}^{eq} \tag{3.56}$$

and if

$$t\gg[x_{13}+(1/T_1)_1]^{-1}\,,\quad[x_{23}+(1/T_1)_2]^{-1}\,, \tag{3.57}$$

which is the case in many CARS experiments

$$\begin{aligned} \rho_{ll}-\rho_{33}&=\rho_{ll}^{ss}-\rho_{33}^{ss}=f_l/Z_2^{(2)}Z_3^{(2)}\\ &=\rho_{ll}^{eq}-\rho_{33}^{eq}\,, \end{aligned} \tag{3.58}$$

provided the intensity is so low that terms containing x_{13} and x_{23} can be neglected. That this conclusion is quite general and does not depend on the relative magnitude of the decay rates can be checked by substituting $A=B=C=0$ in Eqs. (A2), (A4), and (A5) of the Appendix. Similarly a more general expression of $\rho_{ll}^{ss}-\rho_{33}^{ss}$ at low intensities can be found by substituting Eq. (3.38) into Eqs. (A2), (A4), and (A5).

The usual steady-state formula for $\mathcal{P}_{\rm CARS}$ (Refs. 3 and 7) for the case where the pump fields are weak and ω_l is nearly resonant with an electronic transition can be obtained by replacing $\rho_{ll}-\rho_{33}$ by $\rho_{ll}^{eq}-\rho_{33}^{eq}$ in Eqs. (3.36) and substituting the resulting expression for ρ_{21}' in Eq. (2.21). The above discussion shows that even for weak fields this expression may require modification.

2. Intermediate level far from resonance: inclusion of two-photon terms

When the substitutions of Eq. (3.42) are made in Eq. (3.50) and it is assumed that $(T_1)_{3l}$ is the fastest decay time, we find that simple (similar) analytical expressions can be found for the poles of the transformation for the two extreme cases

$$x_{12}\gg(1/T_1)_3\gg x_{13},\ x_{23} \tag{3.59}$$

$$(1/T_1)_3\gg x_{12}\gg x_{13},\ x_{23}\,. \tag{3.60}$$

When Eq. (3.59) holds,

$$\begin{aligned}
&Z_1^{(0)}=0,\quad Z_1^{(1)}=-\tfrac{1}{2}[(1/T_1)_1+(1/T_1)_{2l}+x_{13}+x_{23}]+O((1/T_1)_3^{-1}),\\
&Z_2^{(0)}=-(1/T_1)_3-\tfrac{1}{2}[(1/T_1)_1+(1/T_1)_{2l}+3x_{13}+3x_{23}],\quad Z_2^{(1)}=-(1/T_1)_3-x_{13}-x_{23}+O((1/T_1)_3^{-1},\\
&Z_3^{(0)}=-2x_{12}-\tfrac{1}{2}[(1/T_1)_1+(1/T_1)_{2l}+x_{13}+x_{23}],\quad Z_3^{(1)}=Z_3^{(0)}+O(1/x_{12}),
\end{aligned} \tag{3.61}$$

and when Eq. (3.60) holds,

$$\begin{aligned}
&Z_1^{(0)}=0,\quad Z_1^{(2)}=-\tfrac{1}{2}[(1/T_1)_1+(1/T_1)_{2l}+x_{13}+x_{23}]+O(1/x_{12}),\\
&Z_2^{(0)}=0,\quad Z_2^{(2)}=-2x_{12}-\tfrac{1}{2}[(1/T_1)_1+(1/T_1)_{2l}+x_{13}+x_{23}]+O(1/x_{12}),\\
&Z_3^{(0)}=-(1/T_1)_3,\quad Z_3^{(1)}=-(1/T_1)_3-[2x_{12}+x_{13}+x_{23}+(1/T_1)_1+(1/T_1)_2]+O((1/T_1)_3^{-1}).
\end{aligned} \tag{3.62}$$

Thus in both cases, the slowest decay time is $|Z_1|$ and we find that for $t\gg(1/T_1)_3$, $(1/x_{12})$ the leading terms are given by

$$\rho''_{21}=\frac{\Omega}{[\Delta\hat{\omega}+i(1/\hat{T}_2)_{21}]}e^{-Z_1t}\left((\rho_{22}^{eq}-\rho_{11}^{eq})\frac{[(1/T_1)_1+(1/T_1)_2+(1/T_1)_{21}]}{4x_{12}}-\rho_{22}^{eq}\frac{(1/T_1)_2}{2(1/T_1)_3}+(\rho_{11}^{eq}+\rho_{22}^{eq})\frac{(x_{13}-x_{23})}{4x_{12}}\right)+(1-e^{-Z_1t})\rho_{21}''^{ss}, \tag{3.63}$$

where

$$\begin{aligned}
\rho_{21}''^{ss}=&\frac{\Omega}{[\Delta\hat{\omega}+i(1/\hat{T}_2)_{21}]}\{[\rho_{22}^{eq}(1/T_1)_{21}-\rho_{11}^{eq}(1/T_1)_1][x_{23}+(1/T_1)_2]+\rho_{22}^{eq}(1/T_1)_2[x_{13}+(1/T_1)_1-(1/T_1)_{21}]\}\\
&\times\left(x_{12}[x_{13}+x_{23}+(1/T_1)_1+(1/T_1)_2-(1/T_1)_{21}]-x_{12}x_{23}\frac{[x_{13}+x_{23}+(1/T_1)_{31}+(1/T_1)_{32}]}{[x_{13}+x_{23}+(1/T_1)_3]}\right.\\
&\left.+[x_{13}+(1/T_1)_1][x_{23}+(1/T_1)_2]\right)^{-1}.
\end{aligned} \tag{3.64}$$

The above steady-state expression reduces to that of the effective two-level system [Eq. (3.2)] when terms containing x_{13} and x_{23} can be neglected. This conclusion is valid even when $(1/T_1)_{3l}$ is not the largest-decay rate as can be checked by substituting $A=-B=-C=x_{12}$ in Eqs. (A2), (A4), and (A5) and the resulting expressions in Eq. (3.36). We note that $\Delta\hat{\omega}\to\Delta\bar{\omega}$ and $(1/\hat{T}_2)_2\to(1/T_2)_{21}$ for the case where $k'=3$ and level $|3\rangle$ is not too far from resonance with ω_l.

D. Both fields strong and near resonance

We now consider the case where both transitions are saturated by near-resonant fields,[26] that is, where Eq. (3.46) holds. In this regime, the Wilcox-Lamb approximation is invalid and $\rho''_{21}(t)$ can only be obtained by solving the Bloch equations numerically. However, in this strong-coupling situation, we expect the steady state to be achieved at a rate determined by the fastest decay rate. Thus the steady-state solution should be valid for low-pressure ground-state CARS at times $t\gg(T_1)_3$, for low-pressure excited-state CARS at times $t\gg(T_1)_1\simeq(T_1)_2\simeq(T_1)_3$, and for high-pressure CARS at times $t\gg(T_2)_{21}\simeq(T_2)_{31}\simeq(T_2)_{32}$.

An expression for $\rho_{21}''^{ss}$ for the present case can be obtained from Eqs. (3.36), (A2), (A4), and (A5) by noting that when Eq. (3.46) holds,

$$A\simeq 2V_{13}^2V_{23}^2/(1/\hat{T}_2)_{21}(1/T_2)_{31}(1/T_2)_{32}, \tag{3.65}$$

$$B\simeq-\frac{2V_{13}^2}{(1/\hat{T}_2)_{21}(1/T_2)_{31}}[(1/T_2)_{21}+V_{13}^2/(1/T_2)_{32}], \tag{3.66}$$

$$C\simeq-\frac{2V_{23}^2}{(1/\hat{T}_2)_{21}(1/T_2)_{32}}[(1/T_2)_{21}+V_{23}^2/(1/T_2)_{31}], \tag{3.67}$$

$$A^2-BC\simeq-2A(1/T_2)_{21}. \tag{3.68}$$

We shall consider three limiting cases: (i) $V_{13}\gg V_{23}$, (ii) $V_{23}\gg V_{13}$, and (iii) $V_{13}\simeq V_{23}\simeq V$. For case (i), we find on combining Eqs. (3.34)–(3.36), (3.65)–(3.68), and (A2)–(A5) that the leading term of $\rho_{21}''^{ss}$ is given by

$$\rho_{21}''^{ss}=\frac{V_{13}V_{23}}{\{V_{13}^2-[\Delta\omega+i(1/T_2)_{21}][\Delta_{32}+i(1/T_2)_{32}]\}}\frac{(1/T_1)_1\rho_{11}^{eq}[(1/T_1)_2-(1/T_1)_{32}]}{\{[(1/T_1)_1+(1/T_1)_3-(1/T_1)_{31}]-[(1/T_1)_{21}(1/T_1)_{32}/(1/T_1)_2]\}}, \tag{3.69}$$

which is identical to the expression of Eq. (3.25) provided $[(1/T_1)_{21}(1/T_1)_{32}/(1/T_1)_2] \ll [(1/T_1)_1+(1/T_1)_3 - (1/T_1)_{31}]$ which is usually the case. Similarly, for case (ii), we find that

$$\rho_{21}^{\prime\prime ss} \simeq -\frac{V_{13}V_{23}\rho_{11}^{eq}}{\{V_{23}^2+[\Delta\omega+i(1/T_2)_{21}][\Delta_{31}-i(1/T_2)_{31}]\}}, \tag{3.70}$$

which on ignoring line-broadening effects reduces to the result predicted in Sec. IIIC 2.

For case (iii) we obtain

$$\rho_{21}^{\prime\prime ss} = f(\omega_l,\omega_s)\frac{\rho_{11}^{eq}(1/T_1)_1[(1/T_1)_2+(1/T_1)_3-(1/T_1)_{32}]}{\{[(1/T_1)_3+2(1/T_2)_{21}][(1/T_1)_1+(1/T_1)_{21}]+2(1/T_2)_{21}(1/T_1)_{31}\}}, \tag{3.71}$$

where

$$f(\omega_l,\omega_s) = \frac{V^2[\Delta\omega+i(1/T_2)_{31}+i(1/T_2)_{32}]}{\{[\Delta\omega+i(1/T_2)_{21}][\Delta_{31}-i(1/T_2)_{31}][\Delta_{32}+i(1/T_2)_{32}]+V^2[\Delta\omega+i(1/T_2)_{31}+i(1/T_2)_{32}]\}}, \tag{3.72}$$

which on ignoring line-broadening effects reduces to

$$\begin{aligned} f(\omega_l,\omega_s) &= \frac{V^2}{V^2+\Delta_{31}\Delta_{32}} \\ &= 8V^2[4(\omega_l-\omega_{31})(\omega_s-\omega_{32})+(\omega_l-\omega_{31}-V)(\omega_s-\omega_{32}-2V)+(\omega_l-\omega_{31}+V)(\omega_s-\omega_{32}+2V) \\ &\quad +(\omega_l-\omega_{31}-2V)(\omega_s-\omega_{32}-V)+(\omega_l-\omega_{31}+2V)(\omega_s-\omega_{32}+V)]^{-1}. \end{aligned} \tag{3.73}$$

Thus we expect to obtain five Stark split peaks in the CARS spectrum at the frequencies $\omega_l=\omega_{31}$, $\omega_{31}\pm V$, and $\omega_{31}\pm 2V$ with relative intensities of 1; $V^2/(V\pm\Delta_{32})^2$; $V^2/(V\pm 2\Delta_{32})^2$ if ω_s is kept constant, and five peaks at the frequencies $\omega_s=\omega_{32}$, $\omega_{32}\pm V$, and $\omega_{32}\pm 2V$ with relative intensities of 1; $V^2/(V\pm\Delta_{31})^2$; $V^2/(V\pm 2\Delta_{31})^2$ if ω_l is kept constant. Similar effects have been analyzed in the absorption and fluorescence spectra of two simultaneously saturated transitions using a dressed-atom[26(b)] or quasilevel approach.[26(d)] On substituting the expression for $\rho_{21}'(t)$ obtained from Eqs. (2.31), (3.71) and (3.72) into Eq. (2.21), we find that $\mathcal{P}_{CARS} \propto |\mathcal{E}_l|$ and independent of $|\mathcal{E}_s|$.

IV. DISCUSSION

We have discussed saturation in CARS spectroscopy, limiting ourselves to Raman-resonant CARS ($\omega_l-\omega_s\simeq\omega_{21}$) with the possible addition of the one-photon resonance $\omega_l\simeq\omega_{31}$ (see Fig. 1). We have derived a general expression for the CARS polarization $\mathcal{P}_{CARS}$ for these cases which shows that $\mathcal{P}_{CARS}$ is proportional to the off-diagonal element of the density matrix ρ_{21}. For the case where the Raman resonance is the only resonance, ρ_{21} can be determined by solving the Bloch equations for the effective two-level system formed by the levels $|1\rangle$ and $|2\rangle$. However, when the one-photon resonance is also present, the three-level Bloch equations must be solved. In both the two- and three-level Bloch equations, we have included terms describing decay both to the lower levels of the system and to a set of levels $|\{l\}\rangle$ whose populations are assumed to remain in thermal equilibrium.

The Bloch equations, and the rate equations derived from the three-level Bloch equations by means of the Wilcox-Lamb approximation, were solved using Laplace transform techniques. In order to obtain simple analytical solutions, the poles of the transforms were determined using first- and second-order perturbation theory. The general approach was to neglect fast decaying contributions to ρ_{21} and to consider only slowly decaying contributions (where they exist) and the steady state. Such slowly decaying contributions are of great importance in the low-pressure regime when at least one pumping field is weak. However, when the pressure is high, collisions ensure that the steady state is rapidly achieved and when both fields are intense, all the states are strongly coupled and, therefore, decay at the rate of the fastest decaying state.

When the effective two-level model is appropriate, that is, when sequential one-photon processes can be neglected in favor of the direct two-photon process and the fields are weak, we have reproduced the usual expression for $\mathcal{P}_{CARS}$ in which $\mathcal{P}_{CARS} \propto P_l P_s^{1/2}$ where $P_{l,s}$ are the powers of the pump fields at frequencies ω_l, ω_s. However, when the two-level system is saturated, we found that $\mathcal{P}_{CARS}$ is independent of P_l and inversely proportional to $P_s^{1/2}$.

Several special cases of the three-level model have been treated. We found that when the $|1\rangle\to|3\rangle$ ($|2\rangle\to|3\rangle$) transition is strongly coupled to the ω_l (ω_s) field, while the other one-photon transition is only weakly coupled to the ω_s (ω_l)

field, $\mathcal{P}_{CARS}$ and, hence, the CARS excitations spectrum is split into two Stark split (or shifted) peaks. When ω_s is the weak (probe) field, $\mathcal{P}_{CARS} \propto P_l^0 P_s^{1/2}$ for $\omega_s \simeq \omega_{32}$ whereas $\mathcal{P}_{CARS} \simeq P_l^{1/2} P_s^{1/2}$ when the probe field is tuned to one of the components of the Stark split level $|3\rangle$, that is, $\omega_s \simeq \omega_{32} \pm V_{13}$ where V_{13} is the one-photon Rabi frequency for the $|1\rangle \rightarrow |3\rangle$ transition. On the other hand, when ω_l is the weak field, $\mathcal{P}_{CARS} \propto P_l P_s^{-1/2}$ for $\omega_l \simeq \omega_{31}$ and $\mathcal{P}_{CARS} \propto P_l P_s^0$ for $\omega_l \simeq \omega_{31} \pm V_{23}$.

The Wilcox-Lamb approximation was employed in order to reduce the three-level Bloch equations to rate equations which contain terms which derive from both one- and two-photon processes. We showed that when the intensity is so low so that both one- and two-photon processes are small compared to the decay terms in the rate equations, we can reproduce the usual expression for one-photon resonant $\mathcal{P}_{CARS}$. Expressions were also derived for $\mathcal{P}_{CARS}$ when the one-photon terms are significant. When the one-photon terms can be neglected in favor of the two-photon terms, we showed that the expressions for the effective two-level system could be obtained.

Finally, we discussed the case where both fields are saturating and near resonance. Here both one- and two-photon processes must be considered on the same footing and only the steady-state solution need be considered since strong coupling will ensure that it is rapidly achieved. We discussed three special cases: $V_{13} \gg V_{23}$, $V_{23} \gg V_{13}$, and $V_{13} \simeq V_{23} \simeq V$. In the first two cases, the results were essentially the same as those obtained for the case of one strong and one weak field. When, however, both fields are of comparable strengths, we found that the CARS spectrum splits into five Stark split components at $\omega_l \simeq \omega_{31}$, $\omega_l \simeq \omega_{31} \pm V$, and $\omega_{31} \pm 2V$ if ω_s is held constant, and at $\omega_s \simeq \omega_{32}$, $\omega_{32} \pm V$, and $\omega_{32} \pm 2V$ if ω_l is held constant. When $\omega_l \simeq \omega_{31}$ and $\omega_s \simeq \omega_{32}$ we found that $\mathcal{P}_{CARS} \propto P_l^{1/2} P_s^0$.

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APPENDIX: GENERAL EXPRESSION FOR $\rho_{21}^{\prime\prime ss}$

Using Eqs. (2.48), (3.47), and (3.48), we find that

$$\rho_{ii}^{ss} = \sum_j \alpha_{ji}(Z=0)\frac{V_i}{c_0}, \tag{A1}$$

where V_i, α_{ji}, and c_0 are given by Eqs. (3.47), (3.49), and (3.50), respectively. The expression for c_0 can be rewritten

$$c_0 = (BC - A^2)[(1/T_1)_1 + (1/T_1)_{2l} + (1/T_1)_{3l}] + d_1 A + d_2 B + d_3 C + (1/T_1)_1(1/T_1)_2(1/T_1)_3\,, \tag{A2}$$

with

$$\begin{aligned}
d_1 &= (1/T_1)_2(1/T_1)_{31} + (1/T_1)_{21}(1/T_1)_{32} + (1/T_1)_1(1/T_1)_{32} - (1/T_1)_{21}(1/T_1)_3 - 2(1/T_1)_1(1/T_1)_2\,,\\
d_2 &= -(1/T_1)_2[(1/T_1)_1 + (1/T_1)_3 - (1/T_1)_{31}] + (1/T_1)_{21}(1/T_1)_{32}\,,\\
d_3 &= (1/T_1)_1[(1/T_1)_{32} - (1/T_1)_3 - (1/T_1)_2]\,.
\end{aligned} \tag{A3}$$

From Eq. (A1) we find that

$$\begin{aligned}
c_0(\rho_{11}^{ss} - \rho_{33}^{ss}) = {} & [(1/T_1)\rho_{11}^{eq} - (1/T_1)_{21}\rho_{22}^{eq} - (1/T_1)_{31}\rho_{33}^{eq}]\{(A+C)[(1/T_1)_{32} - (1/T_1)_2] - C(1/T_1)_3 + (1/T_1)_2(1/T_1)_3\}\\
& + [(1/T_1)_2\rho_{22}^{eq} - (1/T_1)_{32}\rho_{33}^{eq}]\{(A+C)[(1/T_1)_1 - (1/T_1)_{21} - (1/T_1)_{31}] + A(1/T_1)_3 + (1/T_1)_{21}(1/T_1)_3\}\\
& + (1/T_1)_3\rho_{33}^{eq}\{[(1/T_1)_{32} - (1/T_1)_2]A + [(1/T_1)_1 - (1/T_1)_{21} - (1/T_1)_{31}]C\\
& \qquad + (1/T_1)_{21}(1/T_1)_{32} + (1/T_1)_2(1/T_1)_{31} - (1/T_1)_1(1/T_1)_2\}\,,
\end{aligned} \tag{A4}$$

$$\begin{aligned}
c_0(\rho_{22}^{ss} - \rho_{33}^{ss}) = {} & [(1/T_1)_1\rho_{11}^{eq} - (1/T_1)_{21}\rho_{22}^{eq} - (1/T_1)_{31}\rho_{33}^{eq}]\{-(A+B)[(1/T_1)_{32} - (1/T_1)_2] + A(1/T_1)_3\}\\
& + [(1/T_1)_2\rho_{22}^{eq} - (1/T_1)_{32}\rho_{33}^{eq}]\{-(A+B)[(1/T_1)_1 - (1/T_1)_{21} - (1/T_2)_{31}] - B(1/T_1)_3 + (1/T_1)_1(1/T_1)_3\}\\
& + (1/T_1)_3\rho_{33}^{eq}\{-[(1/T_1)_{32} - (1/T_1)_2]B - [(1/T_1)_1 - (1/T_1)_{21} - (1/T_1)_{31}]A\\
& \qquad + (1/T_1)_1(1/T_1)_{32} - (1/T_1)_1(1/T_1)_2\}\,.
\end{aligned} \tag{A5}$$

A general expression for $\rho_{21}^{\prime\prime ss}$ can now be obtained by inserting Eqs. (A4) and (A5) into Eq. (3.36).

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