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Optical triple resonance

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A semiclassical treatment is given for the serial, near-resonant interaction of three waves in seven equivalent four-level atomic or molecular systems. Explicit equations are presented for the complex susceptibilties for the three waves, valid for $t \gg T_2$, which contain implicit ac Stark-shift and -splitting information, and can be separated into one-, two-, and three-photon contributions. For the case of a weak third or terminal wave, equations for the degree of ac Stark shifting and splitting are found and indicate that the three-photon or triple-resonance contribution is immune to the optical Stark effect if the remaining two waves are tuned to at least two-photon resonance conditions. The conditions for Doppler-free triple resonance are outlined, and it is shown that an equivalent ac Stark broadening may exist but may also be minimized by an appropriate choice of field intensities.

I. INTRODUCTION

Multiple-wave or multiphoton interactions in atomic and molecular systems are of continual interest from the standpoint of linear and nonlinear spectroscopic applications, energy transfer studies, laser induced reactions, and coherent source generation. Two-wave interactions in two- and three-level systems have been intensively studied, both theoretically and experimentally, during the past decade leading to new insights and applications. For example, saturation or Lamb dip spectroscopy, Doppler-free two-photon absorption spectroscopy, near resonant stimulated Raman emission, optically pumped lasers, line and mode coupling in lasers, and double resonance effects are all characterized by at least two waves interacting with a medium in a naturally occurring or constructed situation.[1,2]

Similarly, three-wave interactions exist under varying conditions and configurations, some of which are graphed in Fig. 1. In Fig. 1(a) is shown a three-photon absorption event, which has also been observed under Doppler-free conditions,[3] and could illustrate a three-photon or cascade emission which might exist in, for example, multiline CO lasers and exists in optically pumped far-infrared (FIR) lasers.[4] Figures 1(b)–1(d) show two-photon pumping, including hyper-Raman, which has been used in alkali metal vapors and CO_2 laser-pumped ir and FIR lasers.[5-7] Figures 1(e) and 1(f) illustrate cases of normal one-photon pumping with a laser or stimulated Raman emission followed by a cascade transition, observed in optically pumped D_2O and HCl and forming three of the four steps in the four-wave parametric mixing schemes in the alkali vapors used to generate tunable near infrared radiation.[8-10] Figure 1(g) illustrates another variation of one-photon pumping, a situation which exists in optically pumped FIR lasers, ir-microwave-microwave triple resonance, and could exist in He-Ne lasers if the 1.15-μm, 6328-Å, and 3.39-μm lines interacted simultaneously.[11-13] Situations involving nonserial or sequential transitions and parametric interactions also exist but will not be discussed.

It is the objective of this paper to develop and discuss the analytical solution of the three-wave four-level system problem, with particular emphasis placed on field coupling coefficients and ac Stark shifts and splittings which may easily occur under the conditions of strong field interactions. Previous treatments of these interactions were based on a simple one-photon rate equation

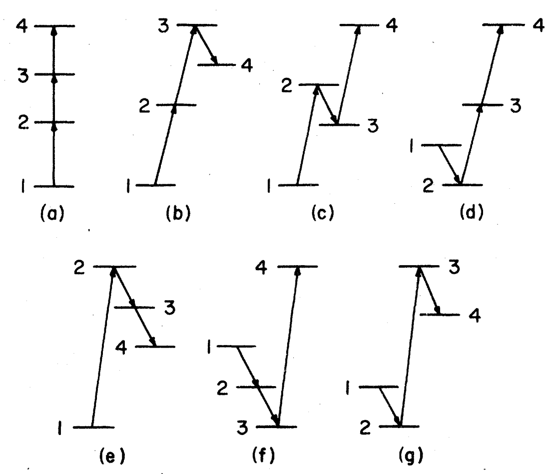

FIG. 1. Seven possible configurations involving the sequential interaction of three photons or waves.

analysis or a perturbation treatment of a three-wave interaction, the latter of which could only yield the ac Stark shifts to lowest order. Alternate treatments which do contain the ac Stark shifts and splittings have been presented, but were restricted to full resonance.[14] In contrast, soluable situations exist for the semiclassical approach which have the capability of yielding field coupling coefficients and Stark shifts valid for higher-order interactions. In Sec. II, the basic equations, assumptions and solutions appropriate to the three-wave four-level system in Fig. 1(g) are outlined. In Sec. III, the transformation of these solutions appropriate to the other configurations in Fig. 1 is discussed along with optical-polarization effects. Section IV contains a discussion of the solution presented in Sec. II, followed by a summary and conclusions of the treatment and major results.

II. DENSITY-MATRIX TREATMENT

The energy-level structure and wave interactions to be treated are shown in Fig. 2(a) along with the state, frequency, and field labels used below. It is clear from this diagram that there may exist three one-wave interactions or transitions ($|1\rangle \to |2\rangle$, $|2\rangle \to |3\rangle$ and $|3\rangle \to |4\rangle$), two two-wave interactions ($|1\rangle \to |3\rangle$ and $|2\rangle \to |4\rangle$) and one three-wave interaction ($|1\rangle \to |4\rangle$), all of which may be important simultaneously.

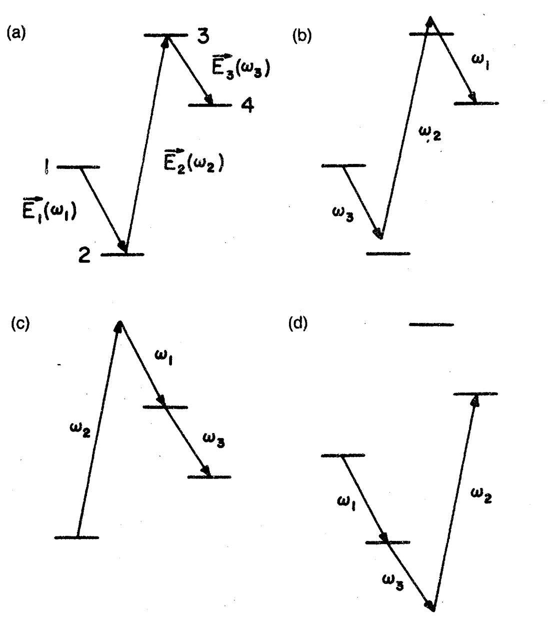

FIG. 2. (a) Energy-level notation and field labels for the configurations under consideration. (b)–(d) are alternate interaction orderings involving the same fields. Levels are assumed nondegenerate.

The density matrix ρ for this system contains 16 elements, four population or diagonal elements and 12 off-diagonal elements of which only six need be considered because of the Hermiticity of ρ.[15] Using the electric-dipole approximation with nonzero transition-dipole moments $\vec{\mu}_{12}$, $\vec{\mu}_{23}$, and $\vec{\mu}_{34}$, the equations of motion for the off-diagonal elements appropriate to Fig. 2(a) are, from Schrödinger's equation $\partial\rho/\partial t = [H, \rho]/i\hbar$:

$$\frac{\partial\rho_{12}}{\partial t} = -\left(i\Omega_{12} + \frac{1}{T_{12}}\right)\rho_{12} + \frac{\vec{\mu}_{12}\cdot\vec{E}(\rho_{11}-\rho_{22}) + \vec{\mu}_{32}\cdot\vec{E}\rho_{13}}{i\hbar}, \tag{1}$$

$$\frac{\partial\rho_{13}}{\partial t} = -\left(i\Omega_{13} + \frac{1}{T_{13}}\right)\rho_{13} + \frac{\vec{\mu}_{23}\cdot\vec{E}\rho_{12} + \vec{\mu}_{43}\cdot\vec{E}\rho_{14} - \vec{\mu}_{12}\cdot\vec{E}\rho_{23}}{i\hbar}, \tag{2}$$

$$\frac{\partial\rho_{14}}{\partial t} = -\left(i\Omega_{14} + \frac{1}{T_{14}}\right)\rho_{14} + \frac{\vec{\mu}_{34}\cdot\vec{E}\rho_{13} - \vec{\mu}_{12}\cdot\vec{E}\rho_{24}}{i\hbar}, \tag{3}$$

$$\frac{\partial\rho_{23}}{\partial t} = -\left(i\Omega_{23} + \frac{1}{T_{23}}\right)\rho_{23} + \frac{\vec{\mu}_{23}\cdot\vec{E}(\rho_{22}-\rho_{33}) + \vec{\mu}_{43}\cdot\vec{E}\rho_{24} - \vec{\mu}_{21}\cdot\vec{E}\rho_{13}}{i\hbar}, \tag{4}$$

$$\frac{\partial\rho_{24}}{\partial t} = -\left(i\Omega_{24} + \frac{1}{T_{24}}\right)\rho_{24} + \frac{\vec{\mu}_{34}\cdot\vec{E}\rho_{23} - \vec{\mu}_{21}\cdot\vec{E}\rho_{14} - \vec{\mu}_{23}\cdot\vec{E}\rho_{34}}{i\hbar}, \tag{5}$$

$$\frac{\partial\rho_{34}}{\partial t} = -\left(i\Omega_{34} + \frac{1}{T_{34}}\right)\rho_{34} + \frac{\vec{\mu}_{34}\cdot\vec{E}(\rho_{33}-\rho_{44}) - \vec{\mu}_{32}\cdot\vec{E}\rho_{24}}{i\hbar}, \tag{6}$$

where the phenomenological T_2 dephasing times are labeled as T_{ij} and the transition frequency is defined in terms of the eigenenergies E_i as $\Omega_{ij} = (E_i - E_j)/\hbar$ and has sign dependence.

Similarly, the equations of evolution for the diagonal elements are found to be

$$\frac{\partial\rho_{11}}{\partial t} = -\frac{\rho_{11}-\rho_{11}^e}{T_{11}} + \frac{\vec{\mu}_{12}\cdot\vec{E}(\rho_{12}-\rho_{21})}{i\hbar}, \tag{7}$$

$$\frac{\partial\rho_{22}}{\partial t} = -\frac{\rho_{22}-\rho_{22}^e}{T_{22}} + \frac{\vec{\mu}_{12}\cdot\vec{E}(\rho_{21}-\rho_{12}) - \vec{\mu}_{23}\cdot\vec{E}(\rho_{32}-\rho_{23})}{i\hbar}, \tag{8}$$

$$\frac{\partial\rho_{33}}{\partial t} = -\frac{\rho_{33}-\rho_{33}^e}{T_{33}} + \frac{\vec{\mu}_{23}\cdot\vec{E}(\rho_{32}-\rho_{23}) - \vec{\mu}_{34}\cdot\vec{E}(\rho_{43}-\rho_{34})}{i\hbar}, \tag{9}$$

$$\frac{\partial\rho_{44}}{\partial t} = -\frac{\rho_{44}-\rho_{44}^e}{T_{44}} + \frac{\vec{\mu}_{34}\cdot\vec{E}(\rho_{43}-\rho_{34})}{i\hbar}, \tag{10}$$

where the phenomenological T_1 decay times are labeled as T_{ii} with equilibrium diagonal elements ρ^e_{ii}.

The solution of these coupled equations is made tractable by introducing certain assumptions. First, we seek solutions on a time scale which is long compared to the T_2 values which mean transient nutation effects will be ignored. Second, since we are interested specifically in near resonant interactions, the rotating-wave approximation will be assumed along with a near resonant approximation, the effect of which is to ignore the alternate absorption/emission sequences, examples of which are shown as graphs in Figs. 2(b)–2(d). The driving field is chosen to be of the form $\vec{E} = \vec{E}_1 \cos\omega_1 t + \vec{E}_2 \cos\omega_2 t + \vec{E}_3 \cos\omega_3 t$ with amplitudes $\vec{E}_i$ varying, at most, slowly on a T_2 time scale. With these approximations and assumptions, inspection of Eqs. (1)–(6) results in the identification of the dominant Fourier coefficients as $\rho_{12} \cong \tilde{\rho}_{12} e^{-i\omega_1 t}$, $\rho_{13} \cong \tilde{\rho}_{13} e^{i(\omega_2-\omega_1)t}$, $\rho_{14} \cong \tilde{\rho}_{14} e^{i(\omega_2-\omega_1-\omega_3)t}$, $\rho_{23} \cong \tilde{\rho}_{23} e^{i\omega_2 t}$, $\rho_{24} \cong \tilde{\rho}_{24} e^{i(\omega_2-\omega_3)t}$, and $\rho_{34} \cong \tilde{\rho}_{34} e^{-i\omega_3 t}$, where $\tilde{\rho}_{ij}$ is an assumed steady state (in an adiabatic sense) complex amplitude.[15] Equations (1)–(6) are reduced to a set of algebraic equations by substituting the assumed Fourier coefficients into these equations, multiplying through by the conjugate of the phase factor of ρ_{ij} and performing a short time average on the right-hand side to eliminate rapidly oscillating terms. The subsequent solution of these algebraic equations is tedious but straightforward.

The resulting solutions will be presented as complex susceptibilities χ_i for the ith wave. These are identified and extracted from the driving terms in Eqs. (7)–(10) by noting that those terms should be of the form $\alpha_i I_i$ where the "Beer's" coefficient is given by $\alpha_i = k_i \,\mathrm{Im}(\chi_i)$ and the flux is $I_i = c\epsilon_0 |\vec{E}_i|^2/2\hbar\omega_i$. Thus, for example,

$$\chi_3 = -\frac{2}{|\vec{E}_3|^2}\left(\frac{\vec{\mu}_{34}\cdot\vec{E}_3}{\epsilon_0}\right)\tilde{\rho}_{34}.$$

In terms of the solutions of Eqs. (1)–(6), the susceptibility can be written in the form

$$\chi_3 = [(\vec{\mu}_{34}\cdot\hat{\epsilon}_3)^2/\hbar\epsilon_0][S_1^{(3)}(\rho_{33}-\rho_{44}) + S_2^{(3)}(\rho_{22}-\rho_{44}) + S_3^{(3)}(\rho_{11}-\rho_{44})], \quad (11)$$

where $\hat{\epsilon}_i$ is the polarization unit vector of the ith wave and $S_n^{(i)}$ are complex frequency response functions for the ith wave and nth photon interaction. Thus $S_2^{(3)}$ is a two-photon or stimulated Raman interaction and $S_3^{(3)}$ is a three-photon interaction, both affecting the propagation of wave 3.

With the wave Rabi frequencies defined as $\Lambda_1 = \vec{\mu}_{12}\cdot\vec{E}_1/2\hbar$, $\Lambda_2 = \vec{\mu}_{23}\cdot\vec{E}_2/2\hbar$ and $\Lambda_3 = \vec{\mu}_{34}\cdot\vec{E}_3/2\hbar$ and complex detuning functions defined as

one photon or laser
$$L_1 = \Omega_{12} - \omega_1 - i/T_{12}, \quad (12)$$
$$L_2 = \Omega_{23} + \omega_2 - i/T_{23}, \quad (13)$$
$$L_3 = \Omega_{34} - \omega_3 - i/T_{34}; \quad (14)$$

two photon or Raman
$$R_{13} = \Omega_{13} - (\omega_1 - \omega_2) - i/T_{13}, \quad (15)$$
$$R_{24} = \Omega_{24} - (\omega_3 - \omega_2) - i/T_{24}; \quad (16)$$

three photon
$$T = \Omega_{14} - (\omega_3 + \omega_1 - \omega_2) - i/T_{14}; \quad (17)$$

the $S_n^{(3)}$ can be expressed as follows:

$$S_1^{(3)} = \frac{1}{L_3}\left\{1 + \frac{\Lambda_2^2}{R_{24}D}\left[(1-F_3)\left(\frac{1}{L_3}+\frac{1}{L_2}\right) + \frac{\Lambda_1^2}{L_2R_{13}}\left(\frac{1}{T}+\frac{1}{L_2}\right)\right]\right\}, \quad (18)$$

$$S_2^{(3)} = -\frac{\Lambda_2^2}{L_3R_{24}D}\left[\frac{1-F_3}{L_2} + \frac{\Lambda_1^2}{R_{13}} \times\left(\frac{1}{T}+\frac{1}{L_2}\right)\left(\frac{1}{L_1}+\frac{1}{L_2}\right)\right], \quad (19)$$

$$S_3^{(3)} = \frac{\Lambda_2^2\Lambda_1^2}{L_3L_1R_{13}R_{24}D}\left(\frac{1}{T}+\frac{1}{L_2}\right), \quad (20)$$

where

$$F_3 = \frac{1}{R_{13}}\left(\frac{\Lambda_2^2}{L_1}+\frac{\Lambda_1^2}{L_2}+\frac{\Lambda_3^2}{T}\right), \quad (21)$$

$$F_1 = \frac{1}{R_{24}}\left(\frac{\Lambda_3^2}{L_2}+\frac{\Lambda_2^2}{L_3}+\frac{\Lambda_1^2}{T}\right), \quad (22)$$

and

$$D = (1-F_1)(1-F_3) - \frac{\Lambda_1^2\Lambda_3^2}{R_{13}R_{24}}\left(\frac{1}{T}+\frac{1}{L_2}\right)^2. \quad (23)$$

These results, while somewhat nontransparent, are general in the sense that possible ac Stark contributions due to all waves in all orders of interaction are explicitly contained in the $S_n^{(i)}$ functions. The remaining susceptibilities and $S_n^{(i)}$ functions are listed in Appendix A. The next stage of the calculation entails the solution for the individual population values which can then be used to evaluate a particular χ_i for specified field and equilibrium populations. Examples will be given in Sec. IV.

III. OTHER CONFIGURATIONS AND LEVEL DEGENERACY

Although the solutions outlined in Sec. II were specifically for the case of the nondegenerate level configuration in Fig. 1(g), the results can be generalized to be applicable to the other configurations in Fig. 1 and can be modified to include level degeneracy.

A. Other configurations

The major distinguishing features between the configurations shown in Fig. 1 entails whether a particular wave is absorbed or emitted and are formally manifested in the sign of the frequencies in $e^{\pm i\omega_l t}$ or in $\Omega_{ij}\pm\omega_l$. Thus the functional form of the $S_n^{(i)}$ and χ_i will be the same for all configurations in Fig. 1, differing at most by changes in sign and detuning definitions. The complex detunings can be written in a generalized form as

$$L_1=\Omega_{12}-a_1\omega_1-i/T_{12},$$
$$L_2=\Omega_{23}-a_2\omega_2-i/T_{23},$$
$$L_3=\Omega_{34}-a_3\omega_3-i/T_{34},$$
$$R_{13}=\Omega_{13}-(a_1\omega_1+a_2\omega_2)-i/T_{13},$$
$$R_{24}=\Omega_{24}-(a_2\omega_2+a_3\omega_3)-i/T_{24},$$
$$T=\Omega_{14}-(a_1\omega_1+a_2\omega_2+a_3\omega_3)-i/T_{14},$$

which are to be used in the $S_n^{(i)}$ functions along with replacing α_i by $a_i\alpha_i$. The constants a_i have a value of ±1, the signs of which have been determined and are listed in Table I for the seven configurations shown in Fig. 1.

TABLE I. a_i multipliers.

Fig. 1	(a)	(b)	(c)	(d)	(e)	(f)	(g)
a_1	−	−	−	+	−	+	+
a_2	−	−	+	−	+	+	−
a_3	−	+	−	−	+	−	+

B. Level degeneracy

As is well known, the inclusion of level degeneracy may lead to a tensorial population distribution, optical polarization dependence and to degeneracy-sublevel-dependent ac Stark shifts or splittings.[16] If all these features are thought present, then Eqs. (7)–(11), (A3), and (A4) have to be solved simultaneously for all sublevels, a task best suited to machine computations. For the specialized case of weak Stark shifts or splittings and rapid cross relaxation between the degenerate sublevels, a simple orientational average of Eq. (11) can be performed which will yield the polarization dependent coupling of the waves.

It is clear from the form of Eq. (11), that each term should be summed over the degenerate sublevels in $|1\rangle$, $|2\rangle$, and $|3\rangle$ which connect to some sublevel in $|4\rangle$, the results then being summed over all the sublevels in $|4\rangle$. In terms of averaged emission transition moments $\overline{\mu}_{ij}^2$ and total populations $\rho_i=g_i\rho_{ii}$, Eq. (11) can be rewritten, in the above limit, as

$$\chi_3\cong\frac{\overline{\mu}_{34}^2}{3\hbar\epsilon_0}\left[\frac{1}{L_3}\left(\rho_3-\frac{g_3}{g_4}\rho_4\right)-\frac{b_2(\hat{\epsilon}_2,\hat{\epsilon}_3)\overline{\Lambda}_2^2}{L_2L_3R_{24}}\left(\frac{\rho_2}{g_2}-\frac{\rho_4}{g_4}\right)+\frac{b_3(\hat{\epsilon}_1,\hat{\epsilon}_2,\hat{\epsilon}_3)\overline{\Lambda}_2^2\overline{\Lambda}_1^2}{L_1L_3R_{13}R_{24}}\left(\frac{1}{T}+\frac{1}{L_2}\right)\left(\frac{\rho_1}{g_1}-\frac{\rho_4}{g_4}\right)\right],$$

with $\overline{\Lambda}_1^2=\overline{\mu}_{12}^2E_1^2/4\hbar^2$, $\overline{\Lambda}_2^2=\overline{\mu}_{32}^2E_2^2/4\hbar^2$, and the two- and three-wave coupling coefficients are defined as

$$b_2(\hat{\epsilon}_2,\hat{\epsilon}_3)=\frac{3\sum_j\sum_k\sum_l|\langle 3,k|\vec{\mu}\cdot\hat{\epsilon}_3|4,l\rangle|^2|\langle 2,j|\vec{\mu}\cdot\hat{\epsilon}_2|3,k\rangle|^2}{\overline{\mu}_{34}^2\overline{\mu}_{32}^2}$$

and

$$b_3(\hat{\epsilon}_1,\hat{\epsilon}_2,\hat{\epsilon}_3)=\frac{3\sum_i\sum_j\sum_k\sum_l|\langle 3,k|\vec{\mu}\cdot\hat{\epsilon}_3|4,l\rangle|^2|\langle 2,j|\vec{\mu}\cdot\hat{\epsilon}_2|3,k\rangle|^2|\langle 1,i|\vec{\mu}\cdot\hat{\epsilon}_1|2,j\rangle|^2}{\overline{\mu}_{34}^2\overline{\mu}_{32}^2\overline{\mu}_{12}^2},$$

with i, j, k, and l the labels for the sublevels in states $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$.[17] The matrix elements can be reduced with the aid of the Wigner-Eckart theorem leaving sums over angular elements.[18] For the case of linearly polarized radiation and M degeneracy associated with rotational quantum number J, the b values tend to constants in the high-J limit. This limit is convenient in estimating the optimum polarizations for molecular situations. Table II contains the b_2 elements for various transitions and polarizations in this limit while Table III contains the corresponding b_3 elements for various transitions, polarizations and directions of propagation. The normalizations of the b's are such that for unpolarized waves 1 and 2, $b_2\overline{\Lambda}_2^2\to\frac{1}{3}\overline{\Lambda}_2^2$ and $b_3\overline{\Lambda}_2^2\overline{\Lambda}_1^2\to\frac{1}{9}\overline{\Lambda}_2^2\overline{\Lambda}_1^2$, the classically averaged results. The relative b_3 coefficients are consistent with the relative b_2 coef-

TABLE II. $b_2(\hat{\epsilon}_2, \hat{\epsilon}_3)$ coefficients in the high-J limit.

Transition branches[a]		$\hat{\epsilon}_i\hat{\epsilon}_j$[b] zz	zx, zy	Optimum polarization[c]
Q	Q	$\frac{3}{5}$	$\frac{1}{5}$	$\parallel$
R	Q	$\frac{1}{5}$	$\frac{2}{5}$	$\perp$
P	Q			
R	R			
R	P	$\frac{2}{5}$	$\frac{3}{10}$	$\parallel$
P	P			

[a] P, Q, R stand for $\Delta J = -1, 0, +1$. The b_2 elements are invariant with respect to the branch ordering.
[b] Polarization direction, invariant with respect to order.
[c] Polarization of one wave relative to the other for a maximum b_2 coefficient.

ficients for $\vec{E}_1$ and $\vec{E}_2$, and $\vec{E}_2$ and $\vec{E}_3$ taken separately.

IV. DISCUSSION OF SOLUTION

The solutions given by Eqs. (18)–(20) can best be appreciated by first treating selected weak field limits before considering stronger field cases. Since these solutions revert to the solutions for the usual two-wave interaction in the limit that either $\vec{E}_1$ or $\vec{E}_3$ tends to zero, then the discussion to follow will be directed at the influence of arbitrary $\vec{E}_1$ and $\vec{E}_2$ on the third wave $\vec{E}_3$.[2,11,19,20]

TABLE III. $b_3(\hat{\epsilon}_1, \hat{\epsilon}_2, \hat{\epsilon}_3)$ coefficients in the high-J limit.

Transition branches[a]			$\hat{\epsilon}_i\hat{\epsilon}_j\hat{\epsilon}_k$[b] zzz	zzx	zxx	zxy[c]	Optimum polarization[d]
Q	Q	Q	$\frac{15}{105}$	$\frac{3}{105}$	$\frac{3}{105}$	$\frac{1}{105}$	$\parallel,\parallel$
P	P	P	$\frac{6}{105}$	$\frac{4}{105}$	$\frac{4}{105}$	$\frac{1}{42}$	$\parallel,\parallel$
R	R	R					
P	Q	Q	$\frac{3}{35}$	$\frac{2}{105}$	$\frac{9}{105}$	$\frac{3}{105}$	$\perp,\perp$
R	Q	Q					
Q	P	P					
Q	R	R	$\frac{2}{105}$	$\frac{1}{42}$	$\frac{6}{105}$	$\frac{11}{210}$	$\parallel,\perp$
Q	R	P					

[a] P, Q, R stand for $\Delta J = -1, 0, +1$. The b_3 elements are invariant with respect to the branching order.
[b] Polarization directions, invariant with respect to order.
[c] This case requires noncollinear propagation.
[d] Polarization of two waves relative to the third for a maximum b_3 coefficient.

A. Weak-field limit

In the limit of very weak fields such that $D \to 1$, the leading contribution to $S_n^{(3)}$ are

$$S_1^{(3)} \cong \frac{1}{L_3} = \frac{(\Omega_{34} - \omega_3 + i/T_{34})}{(\Omega_{34} - \omega_3)^2 + 1/T_{34}^2},$$

$$S_2^{(3)} \cong -\Lambda_2^2/L_2L_3R_{24},$$

$$S_3^{(3)} \cong (\Lambda_1^2\Lambda_2^2/L_1L_3R_{13}R_{24})(1/T + 1/L_2).$$

The $S_1^{(3)}$ term can thus be recognized as a complex Lorentzian response function, the imaginary part of which yields the usual homogeneously broadened line shape. The $S_2^{(3)}$ term is of the form of a standard two-wave or stimulated Raman emission result driven by $\vec{E}_2$ since $S_2^{(3)}$ has a maximum imaginary part when $\Omega_{42} = \omega_2 - \omega_3$, the Raman resonance condition.[11] The presence of the complex terms L_2 and L_3 is a manifestation of the near-resonant interaction and yields the detuning conditions (of ω_1 and ω_2) for resonant enhancement. For this case, the enhanced requirement is simply $\omega_2 = \Omega_{32}$.

The new term $S_3^{(3)}$ represents a three-photon or three-wave interaction since it depends on the product of the intensities of waves 1 and 2. The form of $S_3^{(3)}$ is interesting in that it yields two conditions for a maximum imaginary part. For $|\Omega_{32} - \omega_3| \gg 1/T_{23}$ such that $1/L_2 \sim 0$, maxima will occur when the triple resonance condition is satisfied, $\Omega_{41} = \omega_2 - \omega_1 - \omega_3$, and when either $\omega_3 = \omega_2 - \Omega_{42}$ for $\omega_1 = \Omega_{12}$ or $\omega_3 = \Omega_{34}$ for $\omega_1 = \omega_2 - \Omega_{31}$. That is, for fixed ω_2, a maximum interaction will occur when ω_3 is on one photon resonance with ω_1 at two-photon resonance or when ω_3 is on two-photon resonance with ω_1 on one-photon resonance. This is again a consequence of resonant enhancement as reflected by the presence of the L's and R's in the denominator of $S_3^{(3)}$.

B. ac Stark shifts

For stronger fields, shifting and splittings may occur, the description of which must be contained in the full form of Eqs. (18)–(20), each term of which can be manipulated to extract the degree of shifting or splitting. However, there is a much simpler functional form which can be derived which contains all the desired spectroscopic information. This is obtained by noting that the susceptibility in Eq. (11) is a linear function of the diagonal elements, each of which may be a nonlinear function of the fields. Because of this linear dependence, we may use superposition to simplify χ_3 by setting $\rho_{11}=\rho_{22}=\rho_{33}=0$ leaving what might be termed a reduced χ_3 which is responsible for the inverse of the one-, two-, and three-photon "gain" processes. This reduced χ_3 is thus proportional to $S_1^{(3)}+S_2^{(3)}+S_3^{(3)}$ which will be labeled as $S_{\rm net}^{(3)}$ and equated to $1/L_{\rm net}$. Hence

$$S_{\rm net}^{(3)}=\frac{1}{L_{\rm net}}=S_1^{(3)}+S_2^{(3)}+S_3^{(3)}$$
$$=\frac{1}{L_3}\left(1+\frac{\Lambda_2^2(1-F_3)}{L_3R_{24}D}\right). \qquad (24)$$

To implement this equation, we merely seek the roots of the $\mathrm{Re}(L_{\rm net})=0$ which must contain the one-, two-, and three-photon resonance conditions.

As a specific result, we take the case where $\vec{E}_3$ is a weak tunable probe wave such that $\Lambda_3\simeq 0$. For this limit, from Eq. (23), $D\cong(1-F_3)(1-F_1)$, which allows Eq. (24) to be written in a very compact form as

$$L_{\rm net}=L_3-\frac{\Lambda_2^2}{R_{24}(1-\Lambda_1^2/R_{24}T)}, \qquad (25)$$

which clearly contains the one-, two-, and three-photon complex detunings. Without loss in generality, the roots may be obtained in the sharp line limit by setting the i/T_2 terms to zero, simplifying the root equation to a real equation

$$0=L_3R_{24}T-\Lambda_1^2L_3-\Lambda_2^2T$$

or

$$(\Omega_{34}-\omega_3)(\Omega_{24}-\omega_3+\omega_2)(\Omega_{14}-\omega_3-\omega_1+\omega_2)$$
$$=(\Omega_{34}-\omega_3)[(\Omega_{34}-\omega_3)-(\Omega_{32}-\omega_2)]$$
$$\times[(\Omega_{34}-\omega_3)+(\Omega_{12}-\omega_1)-(\Omega_{32}-\omega_2)]$$
$$=(\Omega_{34}-\omega_3)\Lambda_1^2+[(\Omega_{34}-\omega_3)+(\Omega_{12}-\omega_1)-(\Omega_{32}-\omega_2)]\Lambda_2^2, \qquad (26)$$

which is an equation cubic in $\Omega_{34}-\omega_3$. The left-hand side of this equation clearly specifies the zero-field one-, two-, and three-photon resonance conditions, while the right-hand side must then be responsible for shifting and splitting. Because Eq. (26) is a simplification of Eq. (24), the right-hand side of Eq. (26) is understood to be zero if $\Lambda_2=0$.

A very important result may be obtained by setting ω_3 to the zero-field triple resonance ($\omega_3=\Omega_{14}-\omega_1+\omega_2$) for which the root equation is identically satisfied if additionally $\omega_3=\Omega_{34}$ which also requires $\Omega_{12}-\omega_1=\Omega_{32}-\omega_2$. Thus the triple resonance is not shifted when ω_1 and ω_2 are at least on two-photon resonance ($\omega_2-\omega_1=\Omega_{31}$). In fact, for this condition the solutions to Eq. (26) are simple to obtain and are

$$(\Omega_{34}-\omega_3)=0, \qquad (27)$$

$$(\Omega_{34}-\omega_3)=\tfrac{1}{2}\{(\Omega_{32}-\omega_2)+[(\Omega_{32}-\omega_2)^2+4(\Lambda_1^2+\Lambda_2^2)]^{1/2}\}, \qquad (28)$$

$$(\Omega_{34}-\omega_3)=\tfrac{1}{2}\{(\Omega_{32}-\omega_2)-[(\Omega_{32}-\omega_2)^2+4(\Lambda_1^2+\Lambda_2^2)]^{1/2}\}. \qquad (29)$$

Equation (28) can easily be recognized as the ac Stark shifted two-photon or Raman condition while Eq. (29) can be identified with an ac Stark shifted one-photon interaction. For the special case of $\Omega_{32}-\omega_2=\Omega_{12}-\omega_1=0$, the normally degenerate one-, two-, and three-photon interactions are split into a triplet, one component at line center which is the triple resonance and two components at $\Omega_{34}-\omega_3=\pm(\Lambda_1^2+\Lambda_2^2)^{1/2}$, the two-photon analog of Autler-Townes splitting.[21] These results and identifications are in complete agreement with recent calculations using dressing transformations of the atom plus field eigenstates, with numerical solutions of the QED equations of motion of three levels coupled by two strong fields, and with the previously mentioned resonant three-wave case.[14,22,23]

Next we consider the shift in the triple resonance when $\Omega_{32}-\omega_2\neq\Omega_{12}-\omega_1$. Considering small shifts only, the approximate resonance obtained from Eq. (26) is given by

$$(\Omega_{34}-\omega_3)\cong-[(\Omega_{12}-\omega_1)-(\Omega_{32}-\omega_2)]\left(1+\frac{\Lambda_1^2}{(\Omega_{12}-\omega_1)[(\Omega_{12}-\omega_1)-(\Omega_{32}-\omega_2)]-\Lambda_2^2}\right), \qquad (30)$$

which does yield an ac Stark shift for $(\Omega_{12}-\omega_1)\neq(\Omega_{32}-\omega_2)$, and which indicates a shift primarily dependent on Λ_1. Hence only under the conditions of at least two-photon resonance is the triple resonance ac Stark free. Finally, the effect of $\Lambda_3\neq 0$ may be treated perturbatively, an approach which has the result of adding a term proportional to $\Lambda_3^2(\Omega_{14}-\omega_3-\omega_1+\omega_2)$ to the right-hand side of the root equation, Eq. (26). This term is clearly zero on triple resonance indicating an additional lack of ac Stark shift contribution, in this case from $\Lambda_3\neq 0$. Other cases may be handled from the general results in Eq. (24).

C. Strong-field solutions

The shifts and splittings can be further illustrated with numerical evaluations of Eqs. (7)–(11)

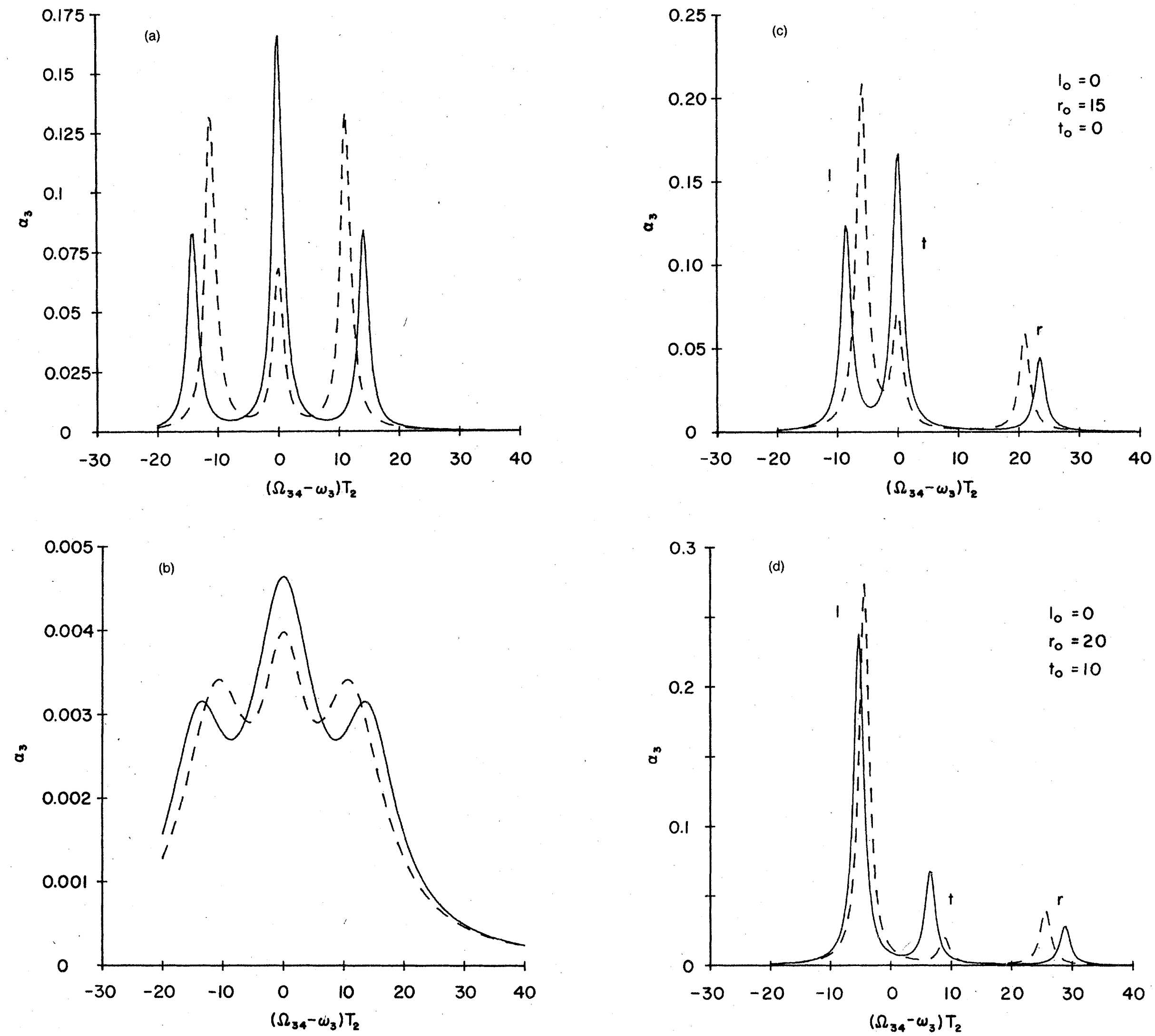

FIG. 3. Calculated Beer's coefficient α_3 for Fig. 1(g) from Eq. (11) vs detuning $T_2(\Omega_{34}-\omega_3)$. For these calculations all T_2 and T_1 values were set equal and $\rho_{11}^e=\rho_{22}^e=\rho_{33}^e=\frac{1}{3}$. α_3 is in units of $k_3(\vec{\mu}_{34}\cdot\hat{\epsilon}_3)^2N/\hbar\epsilon_0$, where N is the total number density in the four states. Except where noted, $\Lambda_3T_2=0.001$, $\Lambda_2T_2=10$, $\Lambda_1T_2=10$ (solid line) and 5 (dashed line). (a) $(\Omega_{12}-\omega_1)T_2=(\Omega_{32}-\omega_2)T_2=0$, full resonance showing Autler-Townes doublet. (b) Same as (a) except $\Lambda_3T_2=5$, showing saturation and power broadening. (c) $(\Omega_{12}-\omega_1)T_2=(\Omega_{32}-\omega_2)T_2=15$, two photon resonance. Labels l, r, and t are the one-, two-, and three-photon contribution with zero field values indicated as l_0, r_0, and t_0. (d) $(\Omega_{12}-\omega_1)T_2=10$, $(\Omega_{32}-\omega_2)T_2=20$ showing ac Stark shifts for all contributions.

and (18)–(20) for selected cases. For purposes of illustration, all T_2 values will be set equal with Rabi frequencies and detunings measured in units of $1/T_2$. The graphs will be the normalized Beer's coefficient of wave 3 versus detuning $(\Omega_{34}-\omega_3)$ for fixed $\omega_1, \omega_2, \Lambda_2, \Lambda_3$ and for two values of Λ_1. The first example is given in Fig. 3(a) for full resonance illustrating the triple resonance contribution at line center and the Autler-Townes doublet. The doublet spacing calculated from Eqs. (28) and (29), ±11.2 and ±14.1, is in agreement with Fig. 3(a), for both values of Λ_1. Figure 3(b) is the same as Fig. 3(a) except for a strong Λ_3 illustrating saturation and power broadening. Figure 3(c) is the same as Fig. 3(a) except that ω_1 and ω_2 are set to two-photon resonance. Labels l, r, and t refer to the one-, two-, and three-photon contributions with the zero field locations indicated by a subscript zero. The one-photon resonances from Eq. (29)

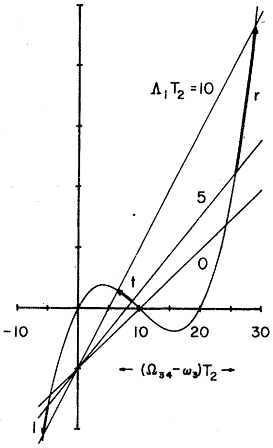

FIG. 4. Graphical solution of Eq. (26) for the case of Fig. 3(d). The S-shaped curve is the left-hand side of Eq. (26) with the highlighted sections showing the magnitude and direction of the ac Stark shift as $\Lambda_1 T_2$ increases from 5 to 10.

are at −6 and −8.5 while the two-photon or Raman resonances from Eq. (28) are at 21 and 23.5, again in agreement with Fig. 3(c). Figure 3(d) represents the case where ω_1 and ω_2 are not on separate one- or two-photon resonances. The ac Stark shift of the triple resonance is evident, is in direct contrast to the unshifted cases in Figs. 3(a) and 3(c), and is qualitatively described by Eq. (30). A simple graphical solution of Eq. (26), shown in Fig. 4, yields one-photon resonances at −5 and −5.4, two-photon resonances at 25.6 and 28.6, and three-photon resonances at 9 and 6.5 in accord with Fig. 3(d).

V. SUMMARY

In this paper, the analytical description of three waves interacting serially and near-resonantly in a four-level system has been presented for the first time. The solution was shown to be applicable to seven different configurations. The weak-field optical polarization coefficients were also derived for the high-J limit, appropriate to molecular interactions. With the availability of these solutions, it is now possible to treat selected interactions which are known to occur. Examples of these will be given later for infrared interactions in D_2O and NH_3.[24]

Aside from the explicit equations for the Beer's coefficients, one additional outcome of this study was in the development of a very simple equation, Eq. (25), the roots of which yielded ac Stark shifts and splittings. The form of this equation manifestly contains multiphoton interactions and their respective contribution to the shifts and are documented in Eq. (27)–(30) and Figs. 3 and 4. Since the assumptions needed to derive this equation ($\rho_{44}=1, \Lambda_3 \sim 0$) place no restrictions on Λ_2 or Λ_1, then Eq. (25) may be considered exact to all orders in these fields.[25] Of course, there is additionally the nonresonantly enhanced quadratic Stark shift contributions associated with each state which has not been included because of the number of levels treated. These can be added by setting $E_i = E_i + \Delta E_i(\vec{E}_1, \vec{E}_2, \vec{E}_3)$, where ΔE_i represents the combined Stark shift due to all waves and depends on coupling to all states excluded from the configurations in Fig. 1.

One very interesting outcome of this study was the lack of Stark shift of the triple resonance under certain conditions, suggesting possible spectroscopic applications which can be explored further. The generalized condition for Doppler-free triple resonance can be stated as $a_1\vec{k}_1 + a_2\vec{k}_2 + a_3\vec{k}_3 = 0$ and may require noncollinear propagation to be satisfied.[3] Because of the various detuning contributions to the $S_n^{(3)}$ terms in Eqs. (18)–(20), the Doppler-free triple resonance may be superimposed on a Doppler broadened background.[26] In addition, because of velocity-subgroup detuning dependence, there may exist an equivalent Stark broadening of the Doppler-free triple resonance. This can be treated using Eq. (30) by replacing $\omega_i \rightarrow \omega_i + \vec{k}_i \cdot \vec{v}$ and assuming Doppler-free triple resonance $(\vec{k}_1 + \vec{k}_3 = \vec{k}_2)$. One interesting limit occurs for at least two-photon resonance and for large Λ_2. For this case, the equivalent Stark broadening of the triple resonance is approximately given by $\Delta\omega_{D,3}\Lambda_1^2/\Lambda_2^2$, where $\Delta\omega_{D,3}$ is the Doppler width of the $|3\rangle \rightarrow |4\rangle$ transition. Thus if $\Lambda_2^2 \gg \Lambda_1^2$, the Stark broadening of the Doppler-free triple resonance may be minimized. This requirement is a consequence of the fact that the dominant Stark shift of the triple resonance is due to Λ_1, as indicated by Eq. (30) and further illustrated in the case of Fig. 4. This leads us to the conclusion that resonantly enhanced triple resonance can be made Doppler-free but may suffer from an equivalent Stark broadening which might be minimized.

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APPENDIX

The remaining susceptibilities identified from Eqs. (7)–(10) are

$$\chi_1 = -\frac{2}{|\vec{E}_1|^2}\left(\frac{\vec{\mu}_{12}\cdot\vec{E}_1}{\epsilon_0}\right)\tilde{\rho}_{12} \quad \text{(A1)}$$

and

$$\chi_2 = \frac{2}{|\vec{E}_2|^2}\left(\frac{\vec{\mu}_{23}\cdot\vec{E}_2}{\epsilon_0}\right)\tilde{\rho}_{23} \tag{A2}$$

and are decomposed as

$$\chi_1 = [(\vec{\mu}_{12}\cdot\hat{\epsilon}_1)^2/\hbar\epsilon_0][S_1^{(1)}(\rho_{11}-\rho_{22}) + S_2^{(1)}(\rho_{11}-\rho_{33}) + S_3^{(1)}(\rho_{11}-\rho_{44})] \tag{A3}$$

and

$$\chi_2 = [(\vec{\mu}_{23}\cdot\hat{\epsilon}_2)^2/\hbar\epsilon_0][S_a^{(2)}(\rho_{22}-\rho_{33}) + S_b^{(2)}(\rho_{11}-\rho_{33}) + S_c^{(2)}(\rho_{22}-\rho_{44})]. \tag{A4}$$

In these equations,

$$S_1^{(1)} = \frac{1}{L_1}\left\{1 + \frac{\Lambda_2^2}{R_{13}D}\left[(1-F_1)\left(\frac{1}{L_1}+\frac{1}{L_2}\right) + \frac{\Lambda_3^2}{L_2R_{24}}\left(\frac{1}{T}+\frac{1}{L_2}\right)\right]\right\}, \tag{A5}$$

$$S_2^{(1)} = -\frac{\Lambda_2^2}{L_1R_{13}D}\left[\frac{1-F_1}{L_2} + \frac{\Lambda_3^2}{R_{24}} \times\left(\frac{1}{L_2}+\frac{1}{T}\right)\left(\frac{1}{L_2}+\frac{1}{L_3}\right)\right], \tag{A6}$$

$$S_3^{(1)} = \frac{\Lambda_2^2\Lambda_3^2}{L_1L_3R_{13}R_{24}D}\left(\frac{1}{L_2}+\frac{1}{T}\right), \tag{A7}$$

$$S_a^{(2)} = \frac{1}{L_2}\left[1 + \frac{\Lambda_1^2}{R_{13}D}\left(\frac{1}{L_1}+\frac{1}{L_2}\right)\left(1 - \frac{\Lambda_2^2}{L_3R_{24}} + \frac{\Lambda_3^2-\Lambda_1^2}{TR_{24}}\right) + \frac{\Lambda_3^2}{R_{24}D}\left(\frac{1}{L_3}+\frac{1}{L_2}\right)\left(1 - \frac{\Lambda_2^2}{L_1R_{13}} + \frac{\Lambda_1^2-\Lambda_3^2}{TR_{13}}\right)\right], \tag{A8}$$

$$S_b^{(2)} = -\frac{\Lambda_1^2}{L_1L_2R_{13}D}\left(1 - \frac{\Lambda_2^2}{L_3R_{24}} + \frac{\Lambda_3^2-\Lambda_1^2}{TR_{24}}\right), \tag{A9}$$

$$S_c^{(2)} = -\frac{\Lambda_3^2}{L_2L_3R_{24}D}\left(1 - \frac{\Lambda_2^2}{L_1R_{13}} + \frac{\Lambda_1^2-\Lambda_3^2}{TR_{13}}\right). \tag{A10}$$

In these results, the $S_x^{(2)}$ terms cannot be separated into identifiable one-, two-, and three-photon terms as was done for waves one and three.

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