Today, 25, No. 8, 93 (1972); J. M. Wessner, D. K. Anderson, and R. T. Robiscoe, Phys. Rev. Lett. 29, 1126 (1972); F. R. Nash and J. P. Gordon (unpublished). The present experiment has the advantage of being the experiment suggested by Jaynes; it also demonstrates the validity of QED in a new regime.

[4]We find

$$\Gamma_{J'M'_J} \propto |(J'M'_J|\mathcal{O}|JM_J)|^2 \propto |(J'\|\mathcal{O}\|J)|^2 \begin{pmatrix} J' & k & J \\ -M'_J & q & M_J \end{pmatrix}^2$$

$$\propto \begin{Bmatrix} l' & J' & s \\ J & l & k \end{Bmatrix}^2 |(l'\|\mathcal{O}\|l)|^2 \begin{pmatrix} J' & k & J \\ -M'_J & q & M_J \end{pmatrix}^2 ,$$

where $\mathcal{O} = e^{-i\mathbf{k}\cdot\mathbf{r}}\nabla$. But for $J = J' = 1/2$, $l = 0$, $l' = 1$, $s = 1/2$ the $6-j$ symbol is zero for $k \neq 1$, so that only the rank-1 tensorial component, i.e., vector component, of $\mathcal{O}$ contributes. The ratio of $3-j$ symbols then yields $\Gamma_{ab} = 2\Gamma_{ac}$.

[5]R. E. Slusher and H. M. Gibbs, Phys. Rev. A 5, 1634 (1972); Phys. Rev. A 6, 1255 (1972).

[6]For the three input areas of that Fig., the NCT output area is larger than the QED area but not by more than 4%. The maximum difference in the NCT and QED values of $\mathcal{S}$ is less than 4% for the two larger areas and about 10% for the smallest area. Even for DS = 100 MHz the 2.46π simulation output area is only about 10% too high to reproduce the experimental output. That is, the NCT simulation has a small secondary maximum at 17 nsec indicating the onset of breakup.

[7]O. S. Heavens, J. Opt. Soc. Am. 51, 1058 (1961). See Ref. 11(b) for further discussion of nuclear-spin-dependent lifetimes.

[8]Phys. Today 25, No. 10, 17 (1972).

[9]C. R. Stroud, Jr. (private communication).

[10]Computer simulations for this case do not differ greatly from the simulation presented here. The predicted lifetimes are longer, since as complete inversion is approached τ goes to infinity rather than to τ_{ac}.

[11]J. M. Wessner *et al.*, in Ref. 3; and H. M. Gibbs, G. G. Churchill, and G. J. Salamo, Bull. Am. Phys. Soc. 17, 1128 (1972); and Phys. Rev. A 7, 1766 (1973). The latter find contradictions in the fluorescence ratios from weakly excited Pb vapor initially almost purely in the ground state.

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Coherent Raman Beats

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The phenomenon of coherent Raman beats observed recently by Shoemaker and Brewer is analyzed through solutions of the coupled Maxwell-Schrödinger equations. The effect arises in coherently prepared molecular samples where the level degeneracy is suddenly removed by Stark-pulse switching. The problem divides into two parts: (a) a steady-state preparative regime whereby the initially degenerate quantum levels are placed in superposition by a resonant laser field, and (b) a transient regime in which coherent forward Raman scattering decays in the presence of the same laser field during a nonresonant condition. The laser and Raman light thus propagate together and produce at a detector a coherent beat with a frequency that corresponds to the level splitting between initial and final states. The beat signal possesses the remarkable property of being entirely independent of longitudinal molecular velocity in the case of a plane-wave laser beam and of being almost so for milliradian divergence. It follows that relaxation involving velocity-changing collisions and that Doppler dephasing effects are absent in coherent Raman beats, in agreement with experimental measurements of the decay rate. The effect of off-resonance excitation on the dephasing time and on the period of the beat signal is also discussed, and the possibility of a small rotation of the plane of polarization of the scattered light is included. The subject presents a new aspect of Raman scattering which can now yield precise radio-frequency splittings directly and offers a selective way of examining relaxation phenomena.

I. INTRODUCTION

Raman scattering which exhibits coherent beats was reported recently by Shoemaker and Brewer.[1] This is one of a class of coherent transient phenomena, similar in nature to photon echoes,[2] optical nutation,[2] and free-induction decay,[3] which have now been observed in molecular gases by the technique of Stark-pulse switching. The effect appears when a cw laser beam excites a molecular sample where the level degeneracy is suddenly removed by a Stark field (see Fig. 1). The coherent Raman emission that follows is not only directional and intense but produces with the laser beam a heterodyne beat at a frequency which corresponds to the level splitting between initial and final states.

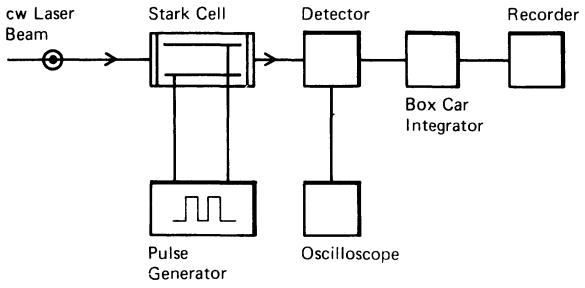

FIG. 1. Monitoring technique for observing coherent Raman beats following a step-function Stark field or a Stark pulse (from Brewer and Shoemaker, Ref. 2).

Furthermore, the decay of the beat signal (Fig. 2) is independent of molecular velocity; this follows from the behavior of two-photon forward scattering in coherently prepared molecular samples.[4] As a consequence, the beat displays the unusual characteristics of being insensitive to velocity-changing collisions and to Doppler dephasing. The method thus provides a new aspect of Raman scattering which yields precise radio-frequency splittings directly and offers a selective way of examining relaxation phenomena.

While many of the features of Raman beats were explained previously by Shoemaker and Brewer,[1] a more detailed derivation of these effects is presented here.

II. EQUATIONS OF MOTION

The coherent Raman forward scattering effect can be described in terms of a three-quantum-level system subjected to the resonance and off-resonance perturbation of a laser beam. Level structures with a higher degeneracy are expected to behave similarly. The effect is brought about in two stages. First, there is a preparative stage in which the quantum levels are placed in quantum-mechanical superposition by the laser beam. The second stage begins when the quantum levels are shifted away from resonance by the sudden application of a dc electric field, because of the Stark effect. The laser beam remains on as a steady beam in the experiment reported here. The dipole moments which have been set up during the preparative stage begin to radiate coherently in the direction of the laser beam during the second stage. The laser light is essential in two ways. First, it serves to prepare the system, but it must be present continuously during the second stage in order to stimulate the coherent Raman emission, when the system is in the off-resonance condition. As has already been noted, the observable is not just the Raman light itself but rather the heterodyne beat signal which it produces with the laser beam at the detector.

Our discussion assumes, for simplicity, the molecular three-level structure given in Fig. 3. Initially, levels 1 and 2 are degenerate and connect with level 3 by excitation with cw laser radiation. As a result, all levels are put into some degree of superposition. The off-diagonal density matrix element ρ_{12} therefore exists under steady-state conditions during the time interval $t \leq 0$, which we designate as the preparative stage. Sudden application of a Stark field at $t = 0$ switches the transitions $1 \leftrightarrow 3$ and $2 \leftrightarrow 3$ out of resonance with the laser frequency, and the two-photon Raman transient occurs for $t \geq 0$.

In terms of the Raman effect, the Stokes ($3 \leftrightarrow 2$) and anti-Stokes ($1 \leftrightarrow 3$) transitions occur periodically during $t > 0$. Small fractions of the level populations, represented by on-diagonal elements ρ_{11}, ρ_{22}, and ρ_{33}, oscillate at the difference frequency ω_{12}, corresponding to the Stark-shifted level separation of states 1 and 2. In the experiment, the presence of this oscillation manifests

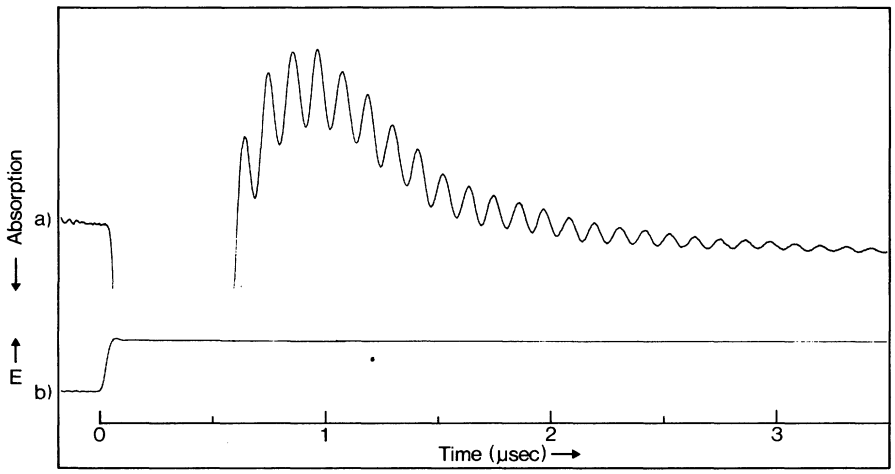

FIG. 2. (a) Coherent Raman beat signal in $C^{13}H_3F$ at 3.25 mTorr pressure following (b) a step-function Stark pulse (0–46 V/cm). Two beats are actually present, whose intensity ratio (~10 here) depends on the CO_2 laser intensity. The strong downward spike and slowly varying background is one-half of an optical nutation cycle. The transition is the ν_3 band line $(J,K) = (4,3) \leftrightarrow (5,3)$ (from Shoemaker and Brewer, Ref. 1).

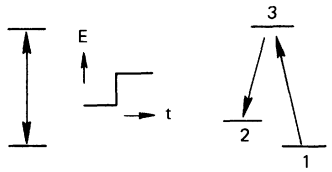

FIG. 3. Energy-level diagram for a degenerate two-level system (a) before and (b) after a step-function Stark field.

itself by the beats contained in the emitted dipole radiation. These beats appear in the analysis of the off-diagonal matrix elements ρ_{13} and ρ_{23} that describe the dipole sources in the gas sample. We focus our attention on the off-diagonal elements in the analysis of the experiment since the variations in population occur in higher order.

The time dependence of the density matrix ρ is expressed by

$$i\hbar\dot{\rho} = [H, \rho] - i\hbar\rho/T_2 , \tag{1}$$

where the phenomenological incoherent damping time constant T_2 is introduced. In the Hamiltonian

$$H = H_0 - \vec{\mu}\cdot\vec{\mathrm{E}}(z, t), \tag{2}$$

H_0 specifies the level eigenenergies, and $\vec{\mu}\cdot\vec{\mathrm{E}}(z, t)$ is a small dipole perturbation energy, where $E(z, t)$ is chosen as the applied laser field, linearly polarized along the x axis, and propagating in the z direction. The dipole moment operator connects two states, allowing quantum-number changes $\Delta m = \pm 1$ in angular momentum.

A rigorous semiclassical calculation would require $E(z, t)$ to be a self-consistent field, simultaneously satisfying Eq. (1) and the Maxwell wave equation

$$\frac{\partial^2\vec{\mathrm{E}}(z, t)}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2\vec{\mathrm{E}}(z, t)}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2\vec{\mathrm{P}}(z, t)}{\partial t^2}, \tag{3}$$

where P is the macroscopic induced polarization. The extremely small optical densities in the present experiments, corresponding to a very small fraction of an absorption length, permits $E(z,t)$ in (2) to be expressed as the laser driving field,

$$E_x(z,t) = \tfrac{1}{2}\epsilon_0(e^{i(\omega' t - kz)} + \text{c.c.}). \tag{4}$$

Experimental conditions do not exist for the occurrence of measurable coherent radiation damping or propagation effects such as self-induced transparency. Perturbation solutions for ρ will be obtained from (1) in order to evaluate the polarization

$$P = N\,\mathrm{Tr}\{\rho\mu\} \tag{5}$$

for N molecules/cm^3. Using P as a source term in (3), a new total field $E(z,t)$ is then calculated from (3) in the approximation of the slowly varying wave envelope, which yields small coherent radiation fields ΔE radiated from the dipole sources, where $\Delta E << E_x$. The combination of radiated and driving fields shows up as intensity beats measured at the detector in the experiment.

It will be convenient to solve for off-diagonal elements of ρ in the frame of reference of an observer at position z_0 moving with the molecule at its particular velocity component along the z direction v_z, where $z = z_0 + v_z t$. In the moving frame, therefore, the laser field is

$$E_x(z_0, t) = \tfrac{1}{2}\epsilon_0(e^{i(\omega t - kz_0)} + \text{c.c.}), \tag{6}$$

where $\omega = \omega'(1 - v_z/c)$, and ω' is the laboratory laser frequency.

Because of the distribution in Doppler frequency shifts due to a spread in molecular velocities, it will be necessary later to average the radiated field over the emitted frequencies as interpreted by an observer at position z in the laboratory frame of reference. This is carried out by applying the inverse transformation

$$z_0 \to z - v_z t, \tag{7}$$

and then averaging v_z over the molecular velocity distribution.

The perturbation term in (2), using (6), is written as

$$\vec{\mu}\cdot\vec{\mathrm{E}}(z,t) = \tfrac{1}{2}(\mu_+ + \mu_-)\,E_x(z,t),$$

with $\mu_\pm = \mu_x \pm i\mu_y$ expressing the usual raising and lowering dipole operator form. The following definitions will be adopted:

$$\tfrac{1}{2}\langle\mu_\pm\rangle = \langle\mu_{ij}\rangle ,$$

$$\omega_{ij} = (E_i - E_j)/\hbar ,$$

$$\Delta\rho_{ij} = \rho_{ii} - \rho_{jj} ,$$

$$\alpha = \langle\mu_{13}\rangle\,\epsilon_0/2\hbar ,$$

$$\beta = \langle\mu_{23}\rangle\,\epsilon_0/2\hbar .$$

The sign of ω_{ij} is determined by the convention $E_1 < E_2 < E_3$.

The equations of motion for the off-diagonal elements take the specific form

$$\left(\frac{d}{dt} + i\omega_{13} + \frac{1}{T_2}\right)\rho_{13} = \frac{i\langle\mu_{13}\rangle E_x(z,t)}{\hbar}(\rho_{33} - \rho_{11}) - \frac{i\langle\mu_{23}\rangle E_x(z,t)}{\hbar}\rho_{12} , \tag{8}$$

$$\left(\frac{d}{dt} + i\omega_{23} + \frac{1}{T_2}\right)\rho_{23} = \frac{i\langle\mu_{23}\rangle E_x(z,t)}{\hbar}(\rho_{33} - \rho_{22}) - \frac{i\langle\mu_{13}\rangle E_x(z,t)}{\hbar}\rho_{21} , \tag{9}$$

$$\left(\frac{d}{dt}+i\omega_{12}+\frac{1}{\tau_2}\right)\rho_{12}=\frac{i\langle\mu_{13}\rangle E_x(z,t)}{\hbar}\rho_{32}-\frac{i\langle\mu_{32}\rangle E_x(z,t)}{\hbar}\rho_{13}. \tag{10}$$

Note that the dephasing time T_2 in (8) and (9) may approximate the Raman dephasing time τ_2 in (10), but the two relaxation times are not necessarily equal. By a perturbation-series expansion, we define

$$\rho(z_0,t,\omega)=\rho(\omega)e^{i(\omega t-kz_0)}+\text{c.c.},$$

where

$$\rho(\omega)=\rho^{(0)}(\omega)+\rho^{(1)}(\omega)+\rho^{(2)}(\omega)+\cdots$$

is the Fourier component of the density matrix at the laser frequency ω. It is understood that $\rho(\omega)$ is a slowly varying function of z_0 and t, and that $\rho_{ij}(\omega)=\rho_{ji}^{*}(\omega)$.

III. STEADY-STATE PREPARATION

First-order solutions of ρ_{13} and ρ_{23} are easily obtained in the steady state from Eqs. (8) and (9), written as

$$\left(\frac{d}{dt}+i\omega_{13}+\frac{1}{T_2}\right)\rho_{13}^{(1)}=\frac{i\langle\mu_{13}\rangle E_x(z,t)}{\hbar}\Delta\rho_{31}^{(0)}, \tag{11}$$

$$\left(\frac{d}{dt}+i\omega_{23}+\frac{1}{T_2}\right)\rho_{23}^{(1)}=\frac{i\langle\mu_{23}\rangle E_x(z,t)}{\hbar}\Delta\rho_{32}^{(0)}. \tag{12}$$

The ρ_{12} term may be neglected, since it appears in second order. During $t\leq 0$, the preparative stage, the steady-state solutions of (11) and (12) are obtained for levels 1 and 2 degenerate, namely, $\omega_{13}=\omega_{23}=-\omega_0$ $\omega_{12}=0$ and $\Delta\rho_{32}^{(0)}=\Delta\rho_{31}^{(0)}=\Delta\rho^{(0)}$;

$$\rho_{13}^{(1)}(t)=\frac{i\alpha\Delta\rho^{(0)}e^{i(\omega t-kz_0)}}{i(\omega-\omega_0)+1/T_2}=\rho_{31}^{(1)*}(t), \tag{13}$$

$$\rho_{23}^{(1)}(t)=\frac{i\beta\Delta\rho^{(0)}e^{i(\omega t-kz_0)}}{i(\omega-\omega_0)+1/T_2}=\rho_{32}^{(1)*}(t). \tag{14}$$

By virtue of (13) and (14) introduced as ρ_{13} and ρ_{23} in (10), the steady-state expression for ρ_{12} is found to be

$$\rho_{12}=\frac{2(\tau_2/T_2)\alpha\beta\Delta\rho^{(0)}}{(\omega-\omega_0)^2+1/T_2^2}. \tag{15}$$

This quantity represents the preparative step, since the initial amplitude of Raman beats observed during the second state ($t\geq 0$) is proportional to ρ_{12} above. How the beat envelope decays will be determined by a transient solution for ρ_{12}, which will be evaluated for $t\geq 0$. The absence of any dependence of ρ_{12} on laser beam phase is connected with the symmetry and consequent phase cancellation involving the presence of both quantum-number changes $\Delta m=1$ and $\Delta m=-1$.

IV. TRANSIENT RESPONSE

A. Illustrative Case

Equations (8)–(10) are now solved again, but in the transient regime for $t\geq 0$, where the initial conditions at $t=0$ have been established by steady-state solutions (13)–(15) during the preparative stage $t\leq 0$. The appearance of a Stark field at $t=0$ terminates the preparative stage by switching molecules out of resonance with the laser frequency, and the degeneracy of levels 1 and 2 is thereby removed.

The solution for ρ_{13} also provides the solution for ρ_{23} by application of index interchanges $ij=13\rightarrow 23$, and $\rho_{12}\rightarrow\rho_{21}$ from inspection of Eqs. (8) and (9). First-order transient solutions are obtain by letting

$$\Delta\rho_{ij}(t)=\Delta\rho_{ij}(0)=\Delta\rho^{(0)}.$$

This assumes, for simplicity, that $\Delta\rho_{13}(0)=\Delta\rho_{23}(0)$. Consider Eq. (8) first, which becomes

$$\left(\frac{d}{dt}-i|\omega_{13}|+\frac{1}{T_2}\right)\rho_{13}=i\alpha\Delta\rho^{(0)}e^{i(\omega t-kz_0)}-i\beta e^{i(\omega t-kz_0)}\rho_{12}(t\geq 0). \tag{16}$$

The solution for ρ_{12} during $t\geq 0$ may be expressed as

$$\rho_{12}(t)=\rho_{12}(0)e^{i|\omega_{12}|t-t/\tau_2}, \tag{17}$$

where $\rho_{12}(0)$ is given by (15). This is valid if the off-resonance effect of the laser field which perturbs the superposition of states 1 and 2 is neglected, so that terms on the right side of (10) may be dropped. This is allowed for a laser field sufficiently weak so that $\alpha\ll|\omega-|\omega_{23}||$ and $\beta\ll|\omega-|\omega_{13}||$. The transient solution of (16) for the case where (17) applies will be given first, since it is relatively simple, and the inclusion of off-resonant driving effects will be deferred until Sec. IV B. The result for $\rho_{13}(t\geq 0)$ is

$$\rho_{13}(t)=\rho_{13}(0)e^{+i|\omega_{13}|t-t/T_2}+\frac{i\alpha\Delta\rho^{(0)}e^{-ikz_0}(e^{i\omega t}-e^{i|\omega_{13}|t-t/T_2})}{i(\omega-|\omega_{13}|)+1/T_2}-\frac{i\beta\rho_{12}(0)e^{-ikz_0}(e^{i(\omega+|\omega_{12}|)t-t/\tau_2}-e^{+i|\omega_{13}|t-t/T_2})}{i(\omega-|\omega_{23}|)+(1/T_2-1/\tau_2)}. \tag{18}$$

The first term in (18) corresponds to optical free-

induction decay[3] for the level pair superposition of states 1 and 3. The second term represents the driven, off-resonance effect involving states 1 and 3, which would supply a steady-state remnant term in the limit $t \to \infty$. The third term, containing ω_{12}, which is of interest here, gives rise to the Raman beat. This term appears similarly in $\rho_{23}(t)$. Expressing these beat terms separately,

$$\rho_{13}^{b}(t) = \frac{-i\beta\rho_{12}(0)\, e^{-ikz_0}\, e^{i(\omega+|\omega_{12}|)t - t/\tau_2}}{i(\omega - |\omega_{23}|) + (1/T_2 - 1/\tau_2)},$$
$$\rho_{23}^{b}(t) = \frac{-i\alpha\rho_{21}(0)\, e^{-ikz_0}\, e^{i(\omega-|\omega_{12}|)t - t/\tau_2}}{i(\omega - |\omega_{13}|) + (1/T_2 - 1/\tau_2)}. \quad (19)$$

B. Off-Resonant Driving Effect

To include effects of the off-resonant driving laser field on the Raman beat oscillation, suitable solutions for ρ_{32} and ρ_{13} must be inserted into Eq. (10). It is valid to insert steady-state solutions for ρ_{32} and ρ_{13} into (10), if expressed in terms of ρ_{12}, where ρ_{12} is a slowly varying term. In (8) and (9), a slowly varying ρ_{12} satisfies the steady-state condition, whereas we look upon the transient solution for ρ_{12} in (10) as a slowly decaying transient. The pertinent steady-state solutions for ρ_{13} and ρ_{32} are similar to those given in (13) and (14), but are now to be expressed in terms of ρ_{13} and ρ_{32} for $t \geq 0$, which have Fourier amplitudes which follow the slow decay in magnitude of ρ_{12}. Considering the ρ_{12} terms only, these solutions are

$$\rho_{13} = \frac{-i\beta\rho_{12}\, e^{i(\omega t - kz_0)}}{i(\omega - |\omega_{13}|) + 1/T_2},$$
$$\rho_{23} = \frac{-i\alpha\rho_{21}\, e^{i(\omega t - kz_0)}}{i(\omega - |\omega_{23}|) + 1/T_2}. \quad (20)$$

Note that (20) satisfies the high-frequency variations in (10), since ρ_{12} oscillates at ω_{12} and therefore ρ_{13} and ρ_{32} vary intrinsically at frequencies $\omega \pm |\omega_{12}|$ after the Stark field is suddenly applied. After inserting (20) into (10), the solution of (10) gives

$$\rho_{12}(t \geq 0) = \rho_{12}(0)\, e^{-(t/T_2^{\text{eff}} + i|\omega_{12}+\nu|t)}, \quad (21)$$

where we choose for simplicity $|\omega - |\omega_{13}|| = |\omega - |\omega_{23}|| = \frac{1}{2}|\omega_{12}| = \Delta\omega_f$, so that

$$\frac{1}{T_2^{\text{eff}}} \cong \frac{1}{\tau_2} + \frac{1}{T_2}\left[\frac{\alpha^2+\beta^2}{\Delta\omega_f^2 + 1/T_2^2}\right]. \quad (22)$$

The extra damping term involving $1/T_2$ becomes important for α^2 and β^2 sufficiently large. However, this is valid only for the factor of $1/T_2$ remaining somewhat less than unity. The imaginary terms of (21) introduce a small frequency shift in the Raman beat frequency, away from ω_{12}, of magnitude

$$\nu = \Delta\omega_f \frac{\beta^2+\alpha^2}{(\Delta\omega_f)^2 + 1/T_2^2}. \quad (23)$$

For the case where $\omega - |\omega_{13}| \neq \omega - |\omega_{23}|$ and both of these frequency-difference terms are of the same sign, the β^2 and α^2 terms in (23) will be of opposite sign, making the shift ν smaller yet, while the signs in (22) will be unaltered.

These characteristics have been confirmed qualitatively in recent experiments[5] with $C^{13}H_3F$. Increasing the laser power, for example, or reducing the Stark shift produces a shortening of the observed lifetime T_2^{eff} consistent with (22). The observed dependence of relaxation time on laser power P for $C^{13}H_3F$ is given by $1/T_2^{\text{eff}} = 1/T_2[1 + 0.076P\ (\text{W/cm}^2)]$, where it is observed that $T_2 = \tau_2$ and thus direct measurements of τ_2 are possible by simply reducing the laser power.[5] No evidence for a frequency shift was detected at a power of 6 W/cm^2, probably because of the near canceling of β^2 and α^2 terms, apropos of the experimental level structure. A quantitative comparison with (22) or (23) is not immediately evident, because this $R(4)$ transition[2] $(v_3, J, K) = (0, 4, 3) \rightarrow (1, 5, 3)$ is highly degenerate and is not a simple three-level problem.

V. WAVE PROPAGATION

The off-diagonal elements of the density matrix calculated in the particular case of a three-level system suggest that for arbitrary types of excitation, not only is a Raman intensity beat predicted, but the polarization generated in the sample also could give rise to an output beam of slightly different electric field polarization and phase relative to the driving laser beam. Let us consider, therefore, the radiation which could be developed from an arbitrarily excited system of polarized atoms.

In the laboratory distance frame of reference, the superposition of macroscopic polarization P_j from N atoms/cm^3 is given by

$$P_T = N\,\text{Tr}\{\mu_+\rho(t)\} = \sum_j P_j\, e^{i(\omega_j t - k_j z)}$$
$$= P_x(z,t) + iP_y(z,t). \quad (24)$$

Here $\rho(t)$ is an arbitrary density matrix for any system of quantum levels, which leads to the definition of polarizations P_x and P_y in the laboratory frame. An initial plane wave is considered, traveling in the z direction, which induces polarization Fourier components P_j at frequencies ω_j and propagation vector k_j, not necessarily the same

as ω' and k of the incident wave in the laboratory frame.

Correspondingly, the x and y components of the net electric field are expressed in terms of

$$E_T = E_x + iE_y = \sum_j \epsilon_j(z,t)\, e^{i(\omega_j t - k_j z)}. \tag{25}$$

The field and polarization moduli ϵ_j and P_j are slowly varying, relative to the rates given by ω_j, and may be complex quantities.

Substitution of E_T from (25) and P_T from (24) in the Maxwell wave equation

$$\frac{\partial^2 E_T}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 E_T}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2 P_T}{\partial t^2} \tag{26}$$

is carried out, and higher-order terms are dropped, using the slowly varying envelope approximation,

$$\frac{\partial \epsilon}{\partial z}, \frac{\partial P}{\partial z} << k\epsilon, kP, \quad \frac{\partial \epsilon}{\partial t}, \frac{\partial P}{\partial t} << \omega\epsilon, \omega P.$$

With separation of real and imaginary terms, using the retarded time frame $t \to t - z/c$, the resulting relations are

$$\frac{\partial \mathrm{Re}\{\epsilon_j\}}{\partial z} = \frac{2\pi\omega_j}{c}\,\mathrm{Im}\{P_j\}, \tag{27}$$

$$\frac{\partial \mathrm{Im}\{\epsilon_j\}}{\partial z} = -\frac{2\pi\omega_j}{c}\,\mathrm{Re}\{P_j\}. \tag{28}$$

In this particular three-level problem, we evaluate P_j and ϵ_j as Fourier components of the laser beam frequency and propagation vector $\pm\omega'$ and $\pm k$ as they pertain to the Raman beat effect. The polarization giving rise to the beat is obtained by inserting the density-matrix elements of (19) into (24). According to the operator rules of $\mu_\pm$, the example chosen takes $m_J = +1$ for level 2, $m_J = -1$ for level 1, and $m_J = 0$ for level 3. Also $\rho_{12}(0) = \rho_{21}(0)$ is real from (15). Therefore,

$$P_T^b = 2N(\mu_{31}\rho_{13}^b + \mu_{23}\rho_{32}^b)$$
$$= -2N\rho_{12}(0)\, e^{-t/\tau_2}\, e^{i|\omega_{12}|t}\left(\frac{\beta\mu_{31}[\Delta_{23} + i(1/T_2 - 1/\tau_2)]\, e^{i(\omega' t - kz)}}{\Delta_{23}^2 + (1/T_2 - 1/\tau_2)^2} + \frac{\alpha\mu_{23}[\Delta_{13} - i(1/T_2 - 1/\tau_2)]\, e^{-i(\omega' t - kz)}}{\Delta_{13}^2 + (1/T_2 - 1/\tau_2)^2}\right), \tag{29}$$

where $\Delta_{13} = \omega - |\omega_{13}|$ and $\Delta_{23} = \omega - |\omega_{23}|$. Equation (29) is expressed in the laboratory distance frame, noting that $\omega t - k_0 z \to \omega' t - kz$.

The moduli of (29), when inserted into (27) and (28), yield electric fields which beat with the laser field and give rather directly the final expression (36) for the beat amplitude when $T_2 = \tau_2$. The procedure given below is cast in a somewhat more detailed and general form than this, however.

The Fourier coefficients of $e^{+i(\omega' t - kz)}$ are

$$\mathrm{Re}\{P_j\} = P_{+r} = \frac{-2N\rho_{12}(0)e^{-t/\tau_2}\mu_{31}\beta[\Delta_{23}\cos|\omega_{12}|t - (1/T_2 - 1/\tau_2)\sin|\omega_{12}|t]}{\Delta_{23}^2 + (1/T_2 - 1/\tau_2)^2},$$
$$\mathrm{Im}\{P_j\} = P_{+i} = \frac{-2N\rho_{12}(0)e^{-t/\tau_2}\mu_{31}\beta[\Delta_{23}\sin|\omega_{12}|t + (1/T_2 - 1/\tau_2)\cos|\omega_{12}|t]}{\Delta_{23}^2 + (1/T_2 - 1/\tau_2)^2}. \tag{30}$$

The Fourier coefficients of $e^{-i(\omega' t - kz)}$ are

$$\mathrm{Re}\{P_{-j}\} = P_{-r} = \frac{-2N\rho_{12}(0)e^{-t/\tau_2}\mu_{23}\alpha[\Delta_{13}\cos|\omega_{12}|t + (1/T_2 - 1/\tau_2)\sin|\omega_{12}|t]}{\Delta_{13}^2 + (1/T_2 - 1/\tau_2)^2},$$
$$\mathrm{Im}\{P_{-j}\} = P_{-i} = \frac{-2N\rho_{12}(0)e^{-t/\tau_2}\mu_{23}\alpha[\Delta_{13}\sin|\omega_{12}|t - (1/T_2 - 1/\tau_2)\cos|\omega_{12}|t]}{\Delta_{13}^2 + (1/T_2 - 1/\tau_2)^2}. \tag{31}$$

The electric fields given by (27) and (28) then become

$$\mathrm{Re}\{\epsilon_j\} = \epsilon_{+r}(z = L, t) = \epsilon_{+r}(0,0) + (2\pi\omega' L/c)\, P_{+i},$$
$$\mathrm{Re}\{\epsilon_{-j}\} = \epsilon_{-r}(z = L, t) = \epsilon_{-r}(0,0) + (2\pi\omega' L/c)\, P_{-i},$$
$$\mathrm{Im}\{\epsilon_j\} = \epsilon_{+i}(z = L, t) = (-2\pi\omega' L/c)\, P_{+r}, \tag{32}$$
$$\mathrm{Im}\{\epsilon_{-j}\} = \epsilon_{-i}(z = L, t) = (-2\pi\omega' L/c)\, P_{-r},$$

where all quantities are defined now in the laboratory frame z. The sample is of length L. We neglect the time $z/c = L/c$ compared to observation times t contained in P_j. The initial conditions at $z = 0$, $t = 0$ specify from Eq. (6) that $\epsilon_{+r}(0,0) = \epsilon_{-r}(0,0) = \frac{1}{2}\epsilon_0$ and $\epsilon_{+i}(0,0) = \epsilon_{-i}(0,0) = 0$.

In terms of the field components given by Eqs. (32) the total output field $E_T(L)$ at $z = L$, defined by Eq. (25), is

$$E_T(L) = [\epsilon_{+r}(L) + i\epsilon_{+i}(L)]e^{+i(\omega' t - kL)} + [\epsilon_{-r}(L) + i\epsilon_{-i}(L)]e^{-i(\omega' t - kL)}. \quad (33)$$

The time-average electric field intensity over many laser frequency cycles is

$$E_T E_T^* = \epsilon_{+r}^2(L) + \epsilon_{-r}^2(L) + \epsilon_{+i}^2(L) + \epsilon_{-i}^2(L). \quad (34)$$

Equation (34) is now to be expressed in terms of basic quantities given by Eqs. (30)–(32), and is expanded to include only cross terms to first order in P_j. Terms in P_j^2 are dropped as negligibly small. Therefore,

$$E_T E_T^* \approx \frac{\epsilon_0^2}{2} - \frac{4\pi\omega' LN\epsilon_0\rho_{12}(0)\, e^{-t/\tau_2}}{c} \times\left(\frac{\mu_{31}\beta[\Delta_{23}\sin|\omega_{12}|t + (1/T_2 - 1/\tau_2)\cos|\omega_{12}|t]}{\Delta_{23}^2 + (1/T_2 - 1/\tau_2)^2} + \frac{\mu_{23}\alpha[\Delta_{13}\sin|\omega_{12}|t - (1/T_2 - 1/\tau_2)\cos|\omega_{12}|t]}{\Delta_{13}^2 + (1/T_2 - 1/\tau_2)^2}\right). \quad (35)$$

For weak laser intensities, the experimental results[5] show that $1/T_2 \cong 1/\tau_2$. Applying this condition to (35), and substituting for $\rho_{12}(0)$ from (15), the cross term gives the following expression for the power in the Raman beat output:

$$\left|\frac{c(E_T E_T^*)^b}{8\pi}\right| = 2NL(\hbar\omega')(\alpha\beta)^2\,\Delta\rho^{(0)} \times \frac{\sin(|\omega_{12}|t)e^{-t/\tau_2}}{(\omega - \omega_0)^2 + 1/\tau_2^2}\left(\frac{1}{\Delta_{23}} + \frac{1}{\Delta_{13}}\right), \quad (36)$$

which is valid in the limit of large Δ_{ij}; for small Δ_{ij} both terms in ρ_{12} of (18) must be retained to avoid divergence. This is the final result, which contains all of the characteristics that were observed by Shoemaker and Brewer and will be discussed further in Sec. VI. Most important, (36) predicts a beat signal at frequency $|\omega_{12}|$ which decays with a time constant τ_2, independent of molecular velocity, and which requires the preparation $\rho_{12}(0)$.

In general, (36) is valid for asymmetric excitation of the three-level system, namely, for $\omega - |\omega_{13}| \neq \omega - |\omega_{32}|$. According to Eq. (33), the output radiation is then described in terms of the superposition of left and right circularly polarized waves, each with its own phase shift θ_+ and θ_-, as follows:

$$E_T(L) = (\epsilon_{+r}^2 + \epsilon_{+i}^2)^{\frac{1}{2}} e^{+i(\omega' t - kL + \theta_+)} + (\epsilon_{-r}^2 + \epsilon_{-i}^2)^{\frac{1}{2}} e^{-i(\omega' t - kL + \theta_-)}, \quad (37)$$

where $\theta_+ \equiv \tan^{-1}(2\epsilon_{+i}^{(L)}/\epsilon_0)$, $\theta_- \equiv \tan^{-1}(-2\epsilon_{-i}^{(L)}/\epsilon_0)$.

Therefore, the rotatory power of such a system, defined as optically active, is given by $(\theta_+ - \theta_-)/L$, where $\theta_+ - \theta_-$ is the angle through which the plane of polarization of the laser beam has been turned at $z = L$. For symmetric excitation $\omega - |\omega_{13}| = -(\omega - |\omega_{23}|)$, and $P_{+r} = -P_{-r}$ from (30) and (31). From (32) we see that $\theta_+ - \theta_- = 0$, and the optical activity disappears. However, the plane-polarized beam undergoes a small oscillatory phase shift, which is negligibly small.

In addition, we suggested in Sec. II that the diagonal elements ρ_{ii} yield higher-order solutions which oscillate at ω_{12} as can be seen by inspecting the corresponding equations of motion and by using the transient solutions for ρ_{ij} given in Sec. IV. Oscillation in the diagonal elements indicates that there exists a small degree of oscillatory energy exchange between the propagating field and the three-level system. It would appear that the Raman beat phenomenon is purely an interference effect, but also involved inextricably in this process is amplitude modulation at the same frequency.

VI. TWO-PHOTON DOPPLER SHIFT

It remains to average the Raman beat (36) over a Gaussian velocity distribution. However, we note the curious result that the oscillatory part of (36) is entirely independent of velocity, and hence the averaged quantity is (36) itself. The point must be made that a small Doppler shift actually occurs in the scattered light but it is absent in the heterodyne beat. To see this more clearly, note that the electric field of the scattered light, in the moving frame, exhibits a time and space dependence of the form expressed by (19); for example,

$$e^{i(\omega + |\omega_{12}|)t - i\vec{k}\cdot\vec{z}_0}, \quad (38)$$

where $\vec{k}$ and $\vec{z}_0$ are no longer collinear. In the laboratory frame, this becomes

$$e^{i(\omega' + |\omega_{12}|)t - i\vec{k}\cdot\vec{z}}, \quad (39)$$

where we recall that the laser frequency is $\omega' = kc$ and the frequency of the scattered light is $\omega' + |\omega_{12}| = k'c$. Since the scattered light must propagate with vector $\vec{k}'$, (39) may be written as

$$e^{i(\omega' + |\omega_{12}|)t - i\vec{k}'\cdot\vec{z}} e^{i(\vec{k}' - \vec{k})\cdot\vec{z}}. \quad (40)$$

The first exponential properly relates frequency and propagation vector, and the second exponential demonstrates a slow spatial modulation along the propagation direction and, accounts furthermore, for the Doppler shift, which we shall return to shortly. It is evident that the laser field

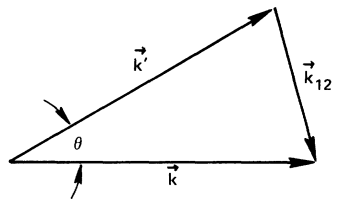

FIG. 4. Raman scattering $\vec{k}$ vector diagram.

$e^{i(\omega' t - \vec{k}\cdot\vec{z})}$ produces with (39) or (40) a beat in the intensity of the form

$$e^{i|\omega_{12}|t} \tag{41}$$

which, in this plane-wave treatment, contains no Doppler shift whatsoever. Connected with this property is the fact that (17) or (21) expresses ρ_{12} with no phase dependence on z. This is a result of spatial phase cancellation effects of simultaneous $\Delta m = \pm 1$ transitions. Since the beat is the observable, this aspect of Raman scattering is unique and follows directly from the coherent preparation.

Let us return to the Doppler shift in the scattered light wave that arises through the term $e^{i(\vec{k}'-\vec{k})\cdot\vec{z}}$ in (40). In general, $\vec{k}$ and $\vec{k}'$ are not collinear (Fig. 4) and scattering may occur at various angles θ where we continue to assume that the exciting light beam is a plane wave and the direction of observation is along $\vec{k}'$.

Referring to Fig. 4, energy and momentum conservation requires

$$\omega_{12} = \omega - \omega', \quad \vec{k}_{12} = \vec{k} - \vec{k}', \qquad k_{12}^2 = (k')^2 - k^2 - 2kk'\cos\theta . \tag{42}$$

The Doppler frequency shift for this two-photon process is $\delta = \vec{k}_{12}\cdot\vec{v}$, where the velocity component $\vec{v}$ is along the direction of observation (along $\vec{k}'$) and corresponds to the narrow velocity band which was initially prepared by the laser beam:

$$\delta = (v/c)[4(\omega^2 - \omega|\omega_{12}|)\sin^2\tfrac{1}{2}\theta + \omega_{12}^2]^{1/2} . \tag{43}$$

We have for $1 >> \theta >> \omega_{12}/\omega$

$$\delta = (v/c)\omega\theta , \tag{44}$$

and for $\omega_{12}/\omega >> \theta$

$$\delta = (v/c)\omega_{12} . \tag{45}$$

Estimates of δ may be made using the experimental conditions of Shoemaker and Brewer[1]: $\omega_{12} \sim 10^7$Hz, $\omega \sim 3\times 10^{13}$Hz, and $\theta \sim 1$ mrad. Here, θ corresponds to the divergence angle of the laser beam, since the beat measurements are restricted to scattered light which falls within this angle. These numbers suggest, using (44), that the spread in Doppler shift for the scattered wave can be no greater than ~40 kHz, while the minimum value, predicted by (45), is ~10 Hz for the exact forward direction. We emphasize again, according to (36) and (41), that the selective heterodyne beat between the forward scattered wave and the laser beam removes this two-photon Doppler shift when the excitation is in the form of a plane wave. This is essentially the experimental observation.

A still more rigorous treatment of the Doppler shift would include the small divergence of the laser beam and its effect on the Raman beat. Transverse molecular motion exposes molecules to slightly varying laser $\vec{k}$ vectors which do not completely cancel the $\vec{k}$ vectors involved in the preparative step. These are higher-order time-dependent effects which in any event will not exceed (44) and should be significantly less than 40 kHz.

An interesting consequence of these ideas is that the decay rate τ_2 in (36) does not include velocity-changing collisions. Molecules which are coherently prepared will continue to exhibit Raman beats even if their velocity is altered by collisions. Instead, τ_2 reflects all other dephasing and lifetime-limiting processes. This feature is particularly appealing, since other coherent transient effects, such as the photon echo, are highly sensitive to velocity-changing collisions[5] and a comparison of these methods now allows a clear separation of the various collisional mechanisms.[6] Finally, it should be noted that Raman echoes[7] are not expected in molecular gases by Stark switching, because of the absence of inhomogeneous dephasing by the Doppler effect.

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[2]R. G. Brewer and R. L. Shoemaker, Phys. Rev. Lett. **27**, 631 (1971).

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[4]Note that the transient Raman beats described here, in which the macroscopic sample requires a preparative step and scatters coherently, differs from previous discussions. For example, the possibility of observing much weaker Raman beats without preparation and under steady-state conditions was considered by C. H. Townes, in *Advances in Quantum*

Electronics (Columbia U.P., New York, 1961), pp. 3–11. In the former, the phase of the scattered wave is preserved throughout the sample, but in the latter it is not.

[5]J. Schmidt and R. G. Brewer (unpublished). The evidence that $T_2 \cong \tau_2$ follows from the observed decay rates being nearly equal in coherent Raman beats (a τ_2 measurement) and in multiple-pulse photon echoes (a T_2 measurement). Both methods are insensitive to velocity-changing collisions. Note that multiple-pulse echoes are the optical analog of the Carr-Purcell NMR technique [H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954)]. The two-pulse photon echo, on the other hand, gives different results as it is sensitive to velocity-changing collisions and will be discussed elsewhere.

[6]F. A. Hopf, M. O. Scully, and R. F. Shea Phys. Rev. A (to be published) review certain aspects of coherent transients, including a preliminary treatment of Raman beats.

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Revised Scaling Equation of State at the Liquid-Vapor Critical Point*

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By a simple change of variables, the scaling hypothesis of Widom is extended to apply not only to those liquid-vapor models for which it was originally designed, but also to those recently discovered models that violate the law of rectilinear diameters. "Corrections to scaling," i.e., additional terms in the equation of state beyond the homogeneous one, are shown in general not to make contributions to the singularities characteristic of these models, comparable to those coming from the change in scaling variables. Therefore, these models cannot be regarded as evidence in support of such proposed correction schemes. A more elaborate revision of the scaling hypothesis proposed by Widom and Stillinger, is shown to be implied by the simple one proposed here.

I. INTRODUCTION

The homogeneous (or scaling) equation of state proposed by Widom[1] to hold near a liquid-vapor critical point has since been applied to a variety of phase transitions and has become a fundamental heuristic tool in the general theory of the critical point.[2] There are now indications that, at least in the magnetic case, renormalization-group techniques may succeed in giving the scaling equation of state a sound theoretical derivation.[3,4]

Recently, however, some difficulties with the equation have emerged in the particular case for which it was originally designed, the liquid-vapor transition. Widom's equation of state incorporates a symmetry in the μ-T plane which corresponds to the trivial symmetry under reversal of field direction in the analogous magnetic system, and appears as the rather less natural "particle-hole symmetry" in the ordinary lattice gas.[5] This symmetry has several implications, perhaps the most notable being the "law of rectilinear diameters,"[6] which is a direct consequence of Widom's equation of state. Widom himself, however, has invented a continuum model in which this "law" is violated,[7] and one of us has found several lattice models with the same kind of diameter singularity.[8,9]

This paper is addressed to the question of how drastically the original Widom scaling equation of state must be modified in order to account for the new singular structure revealed by the models of Refs. 7–9 (hereafter referred to as "asymmetric models"). We find that this can be achieved by a very simple revision (which we shall call "revised scaling") in which the homogeneous form is retained, but in a different set of variables.[10] We note, however, that the new singularities of the asymmetric models can also be produced by adding additional terms to the homogeneous equation of state, thereby destroying the homogeneous form (which we shall refer to as "corrections to scaling"), or by a combination of both types of modification.[11,12] We argue that in the asymmetric-lattice models of Refs. 8 and 9, as well as the penetrable-sphere model of Ref. 7 and its generalizations (hereafter referred to as "the asymmetric-continuum models") there is considerable evidence that corrections to scaling do not contribute in leading order to the new types of singularities which appear to be fully described by revised scaling alone.

The paper is organized as follows. In Sec. II we review Widom's equation of state for the liquid-vapor transition and show why it is unsatisfactory for asymmetric systems.

In Sec. III we assume that Widom's equation of state does give a satisfactory description of the critical region of the ordinary symmetric-lattice gas. Given this, we deduce a scaling form for the