Effects of Mixing Collisions on Photon Echoes in Gases

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(Received 30 July 1969; revised manuscript received 22 September 1969)

Effects of electric dipole reorienting collisions on photon echoes are investigated. In an extension of the author's earlier work, a general expression is derived, including terms from binary collisions, for the photon-echo dipole moment amplitude. The explicit results are worked out for simple cases such as $j_1=\frac{1}{2}\leftrightarrow j_2=\frac{1}{2}$, $j_1=1\leftrightarrow j_2=0$, $j_1=1\leftrightarrow j_2=1$, and $j_1=\frac{3}{2}\leftrightarrow j_2=\frac{1}{2}$ transitions. While it is shown that echoes resulting from the above simple transitions will not be depolarized by atomic collisions, photon echoes induced by any other transitions are necessarily depolarized by collisions. In addition, it is possible to show that the general expression for the echo dipole moment can be written as a sum of multipole moments. Only the odd moments contribute to the echoes. The importance of this picture is that collision-induced relaxation of each moment is described by a single time constant—as in the model commonly used for Hanle-effect experiments. As a result, for an echo arising from a $j_1\leftrightarrow j_2$ transition ($j_1\geq j_2$), there must be $\frac{1}{2}j_1(j_1+1)$ time constants to describe the collision damping of the echo intensity, j_1 being an integer. The corresponding formula for the half-integer case is $\frac{1}{2}(j_2+\frac{1}{2})(j_2+\frac{3}{2})$.

I. INTRODUCTION

THE properties of photon echoes observed in SF_6 [1] (a gas system) differ considerably from those observed in ruby.[2] Using as excitation two separate and linearly polarized laser pulses propagating along the same direction, one finds that the echo produced in SF_6 is polarized along the second pulse, and that the echo intensity varies as $\cos^2\psi$, where ψ is the angle between the electric field vectors of the two laser pulses. By contrast, one finds that the echo produced in ruby is polarized at an angle 2ψ with respect to the first pulse (or at ψ with respect to the second pulse) and that the echo intensity is independent of ψ. A recent analysis[3] has demonstrated that those properties are inherent to the angular momenta of the states involved in the echo production. For example, in any inhomogenously broadened atomic system (we shall use the word "atomic" throughout the paper, although the context might refer to a molecular system), an echo induced from a $j_1=1\leftrightarrow j_2=1$ or a $j_1=1\leftrightarrow j_2=0$ transition has the same behavior as that observed in SF_6, while an echo induced from a $j_1=\frac{1}{2}\leftrightarrow j_2=\frac{1}{2}$ transition has the same properties as those observed in ruby. Echoes resulting from transitions of other angular momentum states have a somewhat more complicated but unique ψ dependence.[3]

The theoretical analysis reported in Ref. 3 did not include relaxation effects such as spontaneous emission and atomic collisions. Spontaneous emission and atomic collisions that remove atoms from the states involved in the echo formation cannot change the ψ-dependent properties of photon echoes, although those processes will attenuate the echo intensity. But the type of collisions that cause mixing of various dipole moments can change the ψ-dependent echo properties; this is so because the strength of interaction between laser pulses and electric dipole moments depends on their respective orientations. Collisions, which reorient dipole moments and can thus modify the interaction. As a result, the study of the photon echo provides information of reorientation collision processes in a way analogous to what one obtains from Hanle-effect experiments.[4] There are differences, however. The depolarization effect observed from Hanle-effect experiments is caused by reorientation of the angular momentum vector of an ensemble of excited atoms, whereas the depolarization of the echo, as we shall see in Sec. II, is caused by reorientation of an ensemble of electric dipole moments induced by laser pulses.

This paper presents an investigation of the effects of mixing collisions on the photon echo. In Sec. II an expression is derived for the mean echo dipole moment amplitude (MEDMA), including terms that result from binary collisions. In Sec. III an explicit calculation is carried out for a few simple cases such as $j_1=\frac{1}{2}\leftrightarrow j_2=\frac{1}{2}$, $j_1=1\leftrightarrow j_2=0$, $j_1=1\leftrightarrow j_2=1$, and $j_1=\frac{3}{2}\leftrightarrow j_2=\frac{1}{2}$ transitions. The calculations show that in these cases atomic collisions cannot affect the ψ dependence of photon echo. In the general case, the expression for the MEDMA has been rewritten as a sum of multipole moments resulting from different pairs of Zeeman sublevels between the upper and the lower states. In this picture, collisions that induce relaxation of each multipole moment can be described by a single rate constant. Since different multipole moments are associated with different relaxation rate constants, the implication then is that, except for the simple cases indicated above, the echo polarization angle is generally a function of gas pressure. The case corresponding to a $j_1=2\leftrightarrow j_2=1$ transition is worked out as an example to show the presence of collision-induced depolarization. A summary is given in Sec. IV.

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[3] J. P. Gordon, C. H. Wang, C. K. N. Patel, R. E. Slusher, and W. J. Tomlinson, Phys. Rev. **179**, 294 (1969).
[4] W. Happer and E. B. Saloman, Phys. Rev. **160**, 23 (1967).

II. DERIVATIONS

The model and the assumptions to be used for deriving the MEDMA expression are similar to those used in Ref. 3. Namely, we will consider the interaction of a thin, inhomogenously broadened optical medium with linearly polarized optical frequency laser pulses described by

$$\mathbf{E}(t)=\boldsymbol{\varepsilon}(t)\cos\omega t,$$

where $\boldsymbol{\varepsilon}(t)$ is a slowly time-varying amplitude. In addition, it will be assumed that the laser frequency ω coincides with the atomic line center frequency and that the difference between the field and atomic frequency is small such that $\Delta\ll\mathbf{P}\cdot\boldsymbol{\varepsilon}(\hbar=1)$, where Δ is the Doppler frequency shift.

Because only the case of thin optical medium will be considered, the echo-propagation effect will be neglected in the present paper. As a result, the present calculation cannot give accurate information regarding the echo pulse shape for an optically thick medium. However, since the polarization angle associating with the echo will not vary as the pulse propagates through a nondichroic and nonbirefringent medium, one expects that the echo polarization angle formula, as well as the ψ dependence of echo properties, should be accurate for both thin and thick media. As was discussed in Ref. 3, it is convenient to apply the rotating wave approximation at the beginning of calculation so that the rapid optical frequency variation is removed. We will then consider the upper state $|A\rangle$ having energy Δ with a total angular moment j_1, and the lower state $|B\rangle$ having zero energy with a total angular momentum j_2. The selection rule for the electric dipole radiation thus requires $|j_1-j_2|=0$, 1. For notation, Latin letters a, b, c, etc., will be used for specifying magnetic sublevels of the upper state, and Greek letters α, β, γ, etc., for specifying magnetic sublevels of the lower state. This rule, however, will be relaxed in situations where no ambiguity occurs.

In a typical photon-echo experiment, the pulse duration t_c is short, compared with the pulse separation τ. Furthermore, if the condition

$$\Delta t_c\gg\int_0^{t_c}V(t')dt'$$

is satisfied, where t_c is the pulse duration and $V(t')$ is the interaction potential between colliding atoms in the interaction representation, we can neglect, in the calculation atomic collisions during periods when the pulses are applied and consider only collisions occurring between pulses. Moreover, as previously pointed out, the processes of spontaneous decay and inelastic collisions can only attenuate the echo amplitude by removing atoms from the considered states to other states without causing depolarization of the echo; to simplify the calculations we only include the spontaneous-decay process phenomenologically at the end of calculation.

The model to be considered is an ensemble of active atoms initially prepared in the lower state, which is described by a Maxwellian distribution $f(\nu)$.[5] The first laser pulse interacts with the atomic system for a time t_c, inducing an off-diagonal matrix element $\rho_{a\mu}(1)$ between a magnetic sublevel of the upper state $|a\rangle$ and a magnetic sublevel of the lower state $|\mu\rangle$. The quantity $\rho_{a\mu}(1)$ is proportional to the pulse-induced dipole moment.

It has been shown in Ref. 3 that, if the reaction of the induced polarization back on the field can be neglected, then, at the end of the first pulse, $\rho_{a\mu}(1)$ is given by (in the rotating frame)

$$\rho_{a\mu}(1)=\langle a|\sin2(\mathbf{A}_1\cdot\mathbf{p})|\mu\rangle, \tag{1}$$

where $\mathbf{A}_i$ is given by

$$\mathbf{A}_i=\int_{\text{(pulse duration)}}\boldsymbol{\varepsilon}_i(t)dt,$$

$i=1$ and 2 for the first pulse and the second pulse, respectively. Equation (1) is correct only when the distance traveled by the atom during the pulse is small (i.e., $\Delta t_c\ll1$), so that the atom will not see a different field $\epsilon_i(t)$ due to its motion.

In order to simplify the notation, quantum numbers will not be written out, except those enumerating the magnetic sublevels, unless the contrary is explicitly stated.

At the end of the pulse, $\rho_{a\mu}(1)$ is left alone for evolution. If no collision takes place up to a time δt, the free evolution simply shifts the phase of $\rho_{a\mu}(1)$ to $\theta_1=\Delta\delta t_1$, $(\delta t_1<\tau)$. Suppose that a collision has occurred from δt_1 to $\delta t_1+\tau_c$, where τ_c is the duration of collision. Then, at the end of the collision, the phase and the amplitude of the dipole moment are modified. The type of collision by which the atoms originally in the $|A\rangle$ or in the $|B\rangle$ states are removed to other states will annihilate the echo dipole moment. Therefore, in order to obtain an expression for the density matrix to describe the echo, we must have the density matrix $\rho_{b\nu}$, where b and ν describe the magnetic sublevels within the same angular momentum manifolds as a and μ, respectively. The effect of the collision on the motion of $\rho_{a\mu}(1,\delta t_1)$ can generally be described by

$$\rho_{b\nu}(1,\,\delta t_1+\tau_c)=D(b\nu|a\mu,\tau_c)\rho_{a\mu}(1,\delta t_1), \tag{2}$$

where

$$\rho_{a\mu}(1,\delta t_1)\equiv\rho_{a\mu}(1)e^{-i\Delta\delta t_1}.$$

Unless specifically written out to avoid confusion, the convention will be used throughout the paper that the repeated indices stand for summation. Therefore, in

[5] The analysis can also be applied in considering the case in which initially prepared active atoms are in the upper state. However, no advantages will be obtained in studying atomic processes by inducing photon echoes from atoms initially prepared in the upper state.

Eq. (2), summations over magnetic sublevels $|a\rangle$ and $|\mu\rangle$ are implied.

Assuming binary collisions and classical relative translational motion, one can show that, for $t>\tau_c$ under the impact approximation (i.e., $t\gg\tau_c$), the four-indexed matrix $D(b\nu|a\mu,\tau_c)$ is given by[6,7]

$$D(b\nu|a\mu,\tau_c)=\delta_{ba}\delta_{\nu\mu}-\eta\Gamma(b\nu|a\mu,\tau_c)\,, \tag{3}$$

where

$$\Gamma(b\nu|a\mu,\tau_c)=t\int bdbd\Omega d^3v|\mathbf{v}|F(\mathbf{v})\times\{\delta_{ba}\delta_{\nu\mu}-\langle b|S|a\rangle\langle\mu|S^\dagger|\nu\rangle\}\,, \tag{4}$$

with $d\Omega=\sin\theta d\theta d\phi d\Phi$, where η is the number density of perturbing atoms, θ and ϕ are the polar angles of the relative velocity vector $\mathbf{v}$ with respect to the quantization axis, and Φ is the azimuth angle of the impact parameter vector $\mathbf{b}$ in a plane perpendicular to $\mathbf{v}$. The $F(\mathbf{v})$ is the distribution of relative velocity, and finally $\langle b|S|a\rangle$ and $\langle\mu|S^\dagger|\nu\rangle$ are collision S matrices describing the reorientation.[8]

The angular integration over Ω can be carried out if one rotates the quantization axis to the $\mathbf{v}$ axis in the $(\mathbf{b},\mathbf{v})$ plane and evaluates the S matrix in that new coordinate system. This can readily be done with the help of rotation matrices and the formula of the Clebsch-Gordan series.[9] When this has been done, we can obtain from Eq. (4) a compact expression for $\Gamma(b\nu|a\mu,\tau_c)$ as

$$\Gamma(b\nu|a\mu,\tau_c)=2\pi t\int bdbd^3v|\mathbf{v}|F(\mathbf{v})\sum_{Jm}G(J)\times\begin{pmatrix}j_1 & j_2 & J\\ b & \nu & m\end{pmatrix}\begin{pmatrix}j_1 & j_2 & J\\ a & \mu & m\end{pmatrix}. \tag{5}$$

Here the $G(J)$ functions contain all the collision dynamics and are given by[10]

$$G(J)=(2J+1)\begin{pmatrix}j_1 & j_2 & J\\ c & \epsilon & n\end{pmatrix}\begin{pmatrix}j_1 & j_2 & J\\ c' & \epsilon' & n\end{pmatrix}\times[\delta_{cc'}\langle\epsilon|T^\dagger|\epsilon'\rangle+\delta_{\epsilon\epsilon'}\langle c|T|c'\rangle-\langle c|T|c'\rangle\langle\epsilon|T^\dagger|\epsilon'\rangle]\,, \tag{6}$$

where it is emphasized that the repeated indices imply summations, and that the T matrix is related to the S matrix by $S_{lm}=\delta_{lm}-T_{lm}$. The three j symbols in Eq. (6) specify selection rules for the mixing collisions.

To excite a photon echo, one applies a second pulse at the time $\delta t_1=\tau$ after the first pulse. As also shown in Ref. 3, after the second pulse, the part of the density matrix responsible for the echo is related to $\rho_{b\nu}(1,\tau+\tau_c)$ by

$$\rho_{\alpha f}(2)=\langle\alpha|\sin(\mathbf{A}_2\cdot\mathbf{P})|b\rangle\rho_{b\nu}(1,\tau+\tau_c)\times\langle\nu|\sin(\mathbf{A}_2\cdot\mathbf{P})|f\rangle. \tag{7}$$

Since the echo polarization radiates most strongly at time of order τ after the second pulse, many collisions can occur during this interval of time. Again assuming that the reorienting collisions have taken place at δt_2 (free evolution before δt_2), we can relate the echo density matrices before and after the collision by

$$\rho_{\beta g}(2,\Delta t_2+\tau_c)=D(\beta g|\alpha f,\tau_c)\rho_{\alpha f}(2,\delta t_2)\,, \tag{8}$$

where

$$\rho_{\alpha f}(2,\delta t_2)\equiv\rho_{\alpha f}(2)e^{-i\Delta\delta t_2}\,,$$

and where the D matrix is defined similarly to Eq. (5), changing b to β, ν to g, a to α, and μ to f, and interchanging j_1 with j_2, T with $T^\dagger$ in Eqs. (5) and (6), respectively. The mean echo dipole moment amplitude at the time τ after the second pulse is then given by[3]

$$\langle\mathbf{P}\rangle_{\text{echo}}=\langle g|P|\beta\rangle\rho_{\beta g}(2,\tau+\tau_c)\,, \tag{9}$$

which, when written out explicitly by the substitution of Eqs. (1)–(8) into Eq. (9) is

$$\langle\mathbf{P}\rangle_{\text{echo}}=\langle\mathbf{P}\rangle_0-\eta\tau\langle\mathbf{A}\rangle-\eta\tau\langle B\rangle\,, \tag{10}$$

where only terms up to linear in number density are included. Here $\langle\mathbf{P}\rangle_0$ is the same as that given in Eq. (5.1) of Ref. 3, namely,

$$\begin{aligned}\langle\mathbf{P}\rangle_0&=\mathrm{Tr}_a[\sin(\mathbf{A}_2\cdot\mathbf{P})\sin(2\mathbf{A}_1\cdot\mathbf{P})\sin(\mathbf{A}_2\cdot\mathbf{P})\mathbf{P}]\\&=\langle a|\mathbf{P}|\alpha\rangle\langle\alpha|\sin(\mathbf{A}_2\cdot\mathbf{P})|b\rangle\langle b|\sin(2\mathbf{A}_1\cdot\mathbf{P})|\beta\rangle\times\langle\beta|\sin(\mathbf{A}_2\cdot\mathbf{P})|a\rangle.\end{aligned} \tag{11}$$

The parts due to atomic collisions during the time between the first and the second pulse and during the time between the second pulse and the echo are, respectively, $\langle\mathbf{A}\rangle$ and $\langle\mathbf{B}\rangle$, which are given by

$$\langle\mathbf{A}\rangle=2\pi\int bdbd^3v|\mathbf{v}|F(\mathbf{v})\times\Big[\sum_{Jm}G(J)\begin{pmatrix}j_1 & j_2 & J\\ b & \mu & m\end{pmatrix}\begin{pmatrix}j_1 & j_2 & J\\ b' & \mu' & m\end{pmatrix}\times\langle a|\sin(\mathbf{A}_2\cdot\mathbf{P})|\mu\rangle\langle\mu'|\sin2(\mathbf{A}_1\cdot\mathbf{P})|b\rangle\times\langle b'|\sin(\mathbf{A}_2\cdot\mathbf{P})|\nu\rangle\langle\nu|\mathbf{P}|a\rangle\Big] \tag{12}$$

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[6] The derivations of Eqs. (3) and (4) can be obtained from the same arguments used by Zwanzig in his calculation of self-diffusion coefficients. See the derivation of Eq. (A12) in Phys. Rev. **129**, 486 (1963).

[7] The time t considered does not result from τ_c, the duration of the collision. According to Zwanzig, it is a result of classical linear-path approximation, so that one can replace the relative distance traveled by the atoms after a collision by $|v|t$, provided that $t\gg\tau_c$. An alternative approach can be found, for example, in the paper by Gerstein and Foley [Phys. Rev. **182**, 24 (1969)] or in Ref. 8.

[8] C. H. Wang and W. J. Tomlinson, Phys. Rev. **181**, 115 (1969).

[9] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1960), Chaps. 4 and 5.

[10] The steps needed to derive Eq. (5) are similar to the derivations of Eqs. (7) and (8) of Ref. 8, in which one considers the reorientation of the angular momentum of an atom.

and

$$\langle B\rangle=2\pi\int bdbd^3v|\mathbf{v}|F(\mathbf{v})$$
$$\times\Big[\sum_{Jm}G^*(J)\begin{pmatrix}j_1 & j_2 & J\\ a & \nu & m\end{pmatrix}\begin{pmatrix}j_1 & j_2 & J\\ a' & \nu' & m\end{pmatrix}$$
$$\times\langle a'|\sin(\mathbf{A}_2\cdot\mathbf{P})|\mu\rangle\langle\mu|\sin2(\mathbf{A}_1\cdot\mathbf{P})|b\rangle$$
$$\times\langle b|\sin(\mathbf{A}_2\cdot\mathbf{P})|\nu\rangle\langle\nu'|\mathbf{P}|a\rangle\Big].\quad(13)$$

The expressions given in Eqs. (11)–(13) are the basic result. As we can see from these equations, the collision dynamics are separated out and appear only in the $G(J)$ functions; it is, therefore, possible to evaluate Eq. (11) by considering the functions $G(J)$ as parameters. To be sure, the $G(J)$ can be calculated if the interatomic force acting during collision is known. $G(J)$ will not be calculated in the present paper.

III. EVALUATIONS

The crux of the evaluation of $\langle\mathbf{P}\rangle_0$, $\langle\mathbf{A}\rangle$, and $\langle\mathbf{B}\rangle$ lies in the calculation of the matrix elements of the operator $\sin(\mathbf{A}_i\cdot\mathbf{P})$ between two states involved in the transitions. In Ref. 3, we suggested two methods for finding the matrix elements. One of these requires the calculations of rotation matrices, which is quite suitable for machine computation. The other method requires the use of the Sylvester theorem[11] and needs only straightforward matrix multiplication. The explicit analytical calculations for the simple transition cases will be carried out by the second method. In investigating the cases corresponding to high j transitions, the two methods will be combined to obtain general results and to show clearly terms from which the echo depolarization will originate.

Because the operator $(\mathbf{A}_i\cdot\mathbf{P})$ causes a transition from the lower level to the upper level and vice versa, the operator D_i, defined by

$$D_i=[\mathbf{A}_i\cdot\mathbf{P}]^2,\quad(14)$$

connects only states of the same level. Therefore, D_i can be represented as a square matrix. If we make a power-series expansion of $\sin(\mathbf{A}_i\cdot\mathbf{P})$ in the form

$$\sin\mathbf{A}_i\cdot\mathbf{P}=\sum_n\frac{(-1)^n}{(2n+1)!}D_i^n(\mathbf{A}_i\cdot\mathbf{P})$$
$$=\sum_n\frac{(-1)^n}{(2n+1)!}(\mathbf{A}_i\cdot\mathbf{P})D_i^n,\quad(15)$$

[11] R. A. Frazer, W. J. Duncan, and A. R. Collar, *Elementary Matrices* (Cambridge University Press, London, 1946), Chap. 3.

then the D_i^n operator can be reduced, by means of the reduced Hamilton-Cayley theorem,[11] as follows:

$$D_i^n=\sum_\alpha\left(\frac{1}{2}\theta_{i\alpha}\right)^{2n}z_\alpha(i),\quad(16)$$

where $\frac{1}{2}\theta_{i\alpha}$ (commonly referred as the rotation angles by the ith pulse) are eigenvalues of D_i, given by

$$\theta_{i\alpha}=2(A_i\mathcal{P})\begin{pmatrix}j_1 & 1 & j_2\\ -\alpha & 0 & \alpha\end{pmatrix},\quad(17)$$

where $\mathcal{P}=(|\langle j_1\|P\|j_2\rangle|^2)^{1/2}$. The reduced dipole matrix element is defined according to the convention of Edmonds.[9] The operator $z_\alpha(i)$ is given by

$$z_\alpha(i)=\prod_{m\neq\alpha}\frac{(\theta_{im}^2I-4D_i)}{(\theta_{im}^2-\theta_{i\alpha}^2)}.\quad(18)$$

Here the sum and the continuous product only go over the distinct eigenvalues. It is simple to show that $z_\alpha(i)$ are projectors, satisfying the orthogonalization property

$$z_\alpha z_\beta=z_\alpha\delta_{\alpha\beta}.\quad(19)$$

Substituting Eq. (16) into Eq. (15), we have

$$\sin(\mathbf{A}_i\cdot\mathbf{P})=\sum_\alpha(\mathbf{A}_i\cdot\mathbf{P})z_\alpha(i)\frac{\sin(\frac{1}{2}\theta_{i\alpha})}{\frac{1}{2}\theta_{i\alpha}}$$
$$=\sum_\alpha z_\alpha(i)(\mathbf{A}_i\cdot\mathbf{P})\frac{\sin(\frac{1}{2}\theta_{i\alpha})}{\frac{1}{2}\theta_{i\alpha}}.\quad(20)$$

As one sees clearly from Eq. (17), the field-induced "nutation angle" of the dipole moment depends, in general, upon the magnetic quantum number (i.e., the orientation of the dipole moment). For a given applied laser pulse, differently orienting dipole moments are, therefore, nutated by different angles. Except for simple transitions such as $j_1=\frac{1}{2}\leftrightarrow j_2=\frac{1}{2}$, $j_1=1\leftrightarrow j_2=0$, $j_1=1\leftrightarrow j_2=1$, and $j_1=\frac{1}{2}\leftrightarrow j_2=\frac{3}{2}$, it becomes impossible to state uniquely that a given pulse corresponds to a π pulse or any other angle pulse, without referring to the particular pair of sublevels. This complication is demonstrated by the different arguments present in the sine functions given in Eq. (20).

The substitution of Eq. (19) into Eqs. (11), (12), and (14) yields

$$\langle\mathbf{P}\rangle_0=\sum_{l,k,n}\frac{8}{\theta_{1n}\theta_{2l}\theta_{2k}}\sin(\tfrac{1}{2}\theta_{2k})\sin(\tfrac{1}{2}\theta_{2l})\sin(\theta_{1n})$$
$$\times\langle a|\mathbf{P}|\alpha\rangle\langle\alpha|(\mathbf{A}_2\cdot\mathbf{P})z_k(2)|b\rangle\langle b|(\mathbf{A}_1\cdot\mathbf{P})z_n(1)|\beta\rangle$$
$$\times\langle\beta|(\mathbf{A}_2\cdot\mathbf{P}_1)z_l(2)|a\rangle,\quad(21)$$

$$\langle \mathbf{A}\rangle = \sum_{Jm} [G(J)]_{\rm av} \sum_{l,k,n} \begin{pmatrix} j_1 & j_2 & J \\ b & \mu & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J \\ b' & \mu' & m \end{pmatrix} \times \frac{8}{\theta_{2l}\theta_{2k}\theta_{1n}} \sin(\tfrac{1}{2}\theta_{2l}) \sin(\tfrac{1}{2}\theta_{2k}) \sin(\theta_{1n}) \times\langle a|(\mathbf{A}_2\cdot\mathbf{P})z_l(2)|\mu\rangle\langle\mu'|z_n(1)(\mathbf{A}_1\cdot\mathbf{P})|b\rangle \times\langle b'|z_k(2)(\mathbf{A}_2\cdot\mathbf{P})|\nu\rangle\langle\nu|\mathbf{P}|a\rangle, \quad (22)$$

$$\langle \mathbf{B}\rangle = \sum_{Jm} [G(J)]_{\rm av} \sum_{l,k,n} \begin{pmatrix} j_1 & j_2 & J \\ a & \nu & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J \\ a' & \nu' & m \end{pmatrix} \times \frac{8}{\theta_{2l}\theta_{2k}\theta_{1n}} \sin(\tfrac{1}{2}\theta_{2l}) \sin(\tfrac{1}{2}\theta_{2k}) \sin(\theta_{1n}) \times\langle a'|(\mathbf{A}_2\cdot\mathbf{P})z_l(2)|\mu\rangle\langle\mu|(\mathbf{A}_1\cdot\mathbf{P})z_n(1)|b\rangle \times\langle b|(\mathbf{A}_2\cdot\mathbf{P})z_k(2)|\nu\rangle\langle\nu'|\mathbf{P}|a\rangle, \quad (23)$$

where the subscript av to the $G(J)$ function indicates that the quantities within the square brackets are to be averaged over relative-velocity distribution function and also integrated over the impact parameter b. [Compare Eqs. (12) and (13).]

A. Simple Cases

The general results given in Eqs. (21)–(23) are rather complicated. However, one gains considerable insights regarding the collision-induced depolarization by considering some simple transitions. As shown in Ref. 3, the $j_1=\frac{1}{2} \leftrightarrow j_2=\frac{1}{2}$, $j_1=0 \leftrightarrow j_2=1$, $j_1=1 \leftrightarrow j_2=1$, and $j_1=\frac{1}{2} \leftrightarrow j_2=\frac{3}{2}$ transitions can only have one pulse angle. As a result, the triple sum over (l,k,n) reduces to a single term. In addition, the projectors of these transitions also have the property

$$(\mathbf{A}_1\cdot\mathbf{P})z_n = z_n(\mathbf{A}_1\cdot\mathbf{P}) = (\mathbf{A}_1\cdot\mathbf{P}). \quad (24)$$

Therefore, one immediately simplifies Eqs. (21)–(23) to

$$\langle\mathbf{P}\rangle_0 = \sin^2(\tfrac{1}{2}\theta_2)\sin(\theta_1)\langle a|\mathbf{P}|\alpha\rangle\langle\alpha|(\hat{A}_2\cdot\hat{P})|b\rangle \times\langle b|(\hat{A}_1\cdot\hat{P})|\beta\rangle\langle\beta|(\hat{A}_2\cdot\hat{P})|a\rangle, \quad (25)$$

$$\langle\mathbf{A}\rangle = \sum_{Jm}[G(J)]_{\rm av}\begin{pmatrix} j_1 & j_2 & J \\ b & \mu & m \end{pmatrix}\begin{pmatrix} j_1 & j_2 & J \\ b' & \mu' & m \end{pmatrix} \times\sin^2(\tfrac{1}{2}\theta_2)\sin(\theta_1)\langle a|(\hat{A}_2\cdot\hat{P})|\mu\rangle\langle\mu'|(\hat{A}_1\cdot\hat{P})|b\rangle \times\langle b'|(\hat{A}_2\cdot\hat{P})|\nu\rangle\langle\nu|\mathbf{P}|a\rangle, \quad (26)$$

and

$$\langle\mathbf{B}\rangle = \sum_{Jm}[G^+(J)]_{\rm av}\begin{pmatrix} j_1 & j_2 & J \\ a & \nu & m \end{pmatrix}\begin{pmatrix} j_1 & j_2 & J \\ a' & \nu' & m \end{pmatrix} \times\sin^2(\tfrac{1}{2}\theta_2)\sin(\theta_1)\langle a'|(\hat{A}_2\cdot\hat{P})|\mu\rangle\langle\mu|(\hat{A}_1\cdot\hat{P})|b\rangle \times\langle b|(\hat{A}_2\cdot\hat{P})|\nu\rangle\langle\nu'|\mathbf{P}|a\rangle, \quad (27)$$

where the operator $(\hat{A}_i\cdot\hat{P})$ is defined as

$$(\hat{A}_i\cdot\hat{P}) = 2(\mathbf{A}_i\cdot\mathbf{P})/\theta_i.$$

Choosing the quantization axis along the propagating direction of the first pulse, one can readily show by the Wigner-Eckart theorem[11] that

$$\langle a|\mathbf{A}_i\cdot\mathbf{P}|\mu\rangle = \textstyle\sum_q(-1)^{j_1-a+q}A_{iq}\mathcal{P}_{12}\begin{pmatrix} j_2 & j_1 & 1 \\ \mu & -a & -q \end{pmatrix}, \quad (28)$$

where

$$\mathcal{P}_{12} = \langle j_1\|P\|j_2\rangle$$

and

$$A_{i\pm1} = (\mp1/\sqrt{2})A_i e^{\pm i\phi_i},$$

with

$$\phi_1=0,\quad \phi_2=\psi,\quad \text{and}\quad A_0=0.$$

Substituting Eq. (28) into Eqs. (25)–(27), and carrying out the summation over all the magnetic sublevels, we obtain the results for the following cases:

(a) $j_1=\frac{1}{2}\leftrightarrow j_2=\frac{1}{2}$:
We have

$$\langle\mathbf{P}_0\rangle = (1/\sqrt{6})\mathcal{P}_{12}\sin\theta_1\sin^2(\tfrac{1}{2}\theta_2)(\hat{x}\cos2\psi+\hat{y}\sin2\psi) \quad (29a)$$

and

$$\langle\mathbf{A}\rangle = \tfrac{1}{2}[G(0)+\tfrac{1}{3}G(1)]_{\rm av}\langle\mathbf{P}_0\rangle = \langle\mathbf{B}\rangle^*. \quad (29b)$$

(b) $j_1=0\leftrightarrow j_2=1$:
We have

$$\langle\mathbf{P}_0\rangle = (2\mathcal{P}_{12}/\sqrt{6})\sin\theta_1\sin^2(\tfrac{1}{2}\theta_2) \times(\hat{x}\cos^2\psi+\hat{y}\sin\psi\cos\psi) \quad (30a)$$

and

$$\langle\mathbf{A}\rangle = [\tfrac{1}{3}G(1)]_{\rm av}\langle\mathbf{P}_0\rangle = \langle B\rangle^*. \quad (30b)$$

(c) $j_1=1\leftrightarrow j_2=1$:
We have

$$\langle\mathbf{P}_0\rangle = (4/\sqrt{3})\mathcal{P}_{12}\sin\theta_1\sin^2(\tfrac{1}{2}\theta_2) \times(\hat{x}\cos^2\psi+\hat{y}\sin\psi\cos\psi) \quad (31a)$$

and

$$\langle\mathbf{A}\rangle = \tfrac{1}{3}[-G(0)+\tfrac{1}{2}G(1)+\tfrac{1}{2}G(2)]_{\rm av}\langle\mathbf{P}_0\rangle = \langle B\rangle^*. \quad (31b)$$

(d) $j_1=\frac{3}{2}\leftrightarrow j_2=\frac{1}{2}$:
We have

$$\langle\mathbf{P}_0\rangle = (1/6\sqrt{2})\mathcal{P}_{12}\sin\theta_1\sin^2(\tfrac{1}{2}\theta_2) \times[\hat{x}(\cos2\psi+\tfrac{3}{5})+\hat{y}\sin2\psi] \quad (32a)$$

and

$$\langle\mathbf{A}\rangle = \langle B\rangle^* = [-\tfrac{1}{12}G(1)+G(2)]\langle\mathbf{P}_0\rangle. \quad (32b)$$

It must be pointed out that the expressions given in Eqs. (29)–(32) for $\langle\mathbf{P}_0\rangle$ are equivalent to the $\langle\mathbf{Q}\rangle$ given in Ref. (3) for the corresponding transitions. The difference in the functional form is because the propagation direction is chosen as the z axis in the present calculations, whereas in Ref. (3), electric field vector of the second pulse was chosen as the z axis. The equivalence can be readily shown by a coordinate transformation.

We see clearly from the results expressed in Eqs. (29a)–(32b) that the MEDMA [cf. Eq. (10)] can all be written as

$$\langle \mathbf{P} \rangle_{\text{echo}} = \langle \mathbf{P}_0 \rangle (1-\gamma\tau) \rightarrow \langle \mathbf{P}_0 \rangle e^{-\gamma\tau}, \qquad (33)$$

where γ is defined by

$$\gamma \langle \mathbf{P}_0 \rangle \equiv \eta (\langle \mathbf{A} \rangle + \langle \mathbf{B} \rangle) = \eta (\langle \mathbf{A} \rangle + \langle \mathbf{A} \rangle^*). \qquad (34)$$

For the transitions considered above, $\langle \mathbf{B} \rangle$ is equal to the complex conjugate of $\langle \mathbf{A} \rangle$, and therefore the quantity γ is real, corresponding to the collision-induced relaxation rate of the MEDMA. The arrow sign at the right-hand side of Eq. (33) indicates an ansatz,[12] which is equivalent to the *first* Chapman approximation commonly used in the kinetic theory of gases. As the higher-order Chapman correction usually contributes only a few percent to the transport coefficient, the ansatz is expected to be a good approximation, provided that (1) successive binary collisions are not correlated and (2) the average duration of collisions τ_c is short, compared with the average time between collisions (the mean free time). For the gas pressure commonly used in a photon-echo experiment, the conditions are easily satisfied.

We now see clearly from Eqs. (29)–(33) that the echo intensity $\langle I \rangle_{\text{echo}}$ resulting from those transitions decays as

$$\langle I \rangle_{\text{echo}} \propto |\langle \mathbf{P}_0 \rangle|^2 e^{-2\gamma\tau}$$

and that the echo polarization angle is independent of gas pressure. In other words, atomic collisions cannot depolarize the photon echo in the cases of $j_1=\frac{1}{2} \leftrightarrow j_2=\frac{1}{2}$, $j_1=1 \leftrightarrow j_2=0$, $j_1=1 \leftrightarrow j_2=1$, and $j_1=\frac{3}{2} \leftrightarrow j_2=\frac{1}{2}$ transitions. Furthermore, the collision-induced decay of the echo intensity can be accounted for by a simple time constant $(2\gamma)^{-1}$.

Those results are easy to understand for the case of $j_1=\frac{1}{2} \leftrightarrow j_2=\frac{1}{2}$ and $j_1=1 \leftrightarrow j_2=0$ transitions. In these transitions, the electric dipole matrix elements connecting the magnetic sublevels of the upper state $\langle \mathbf{A} \rangle$ and the lower state $\langle \mathbf{B} \rangle$ are all identical. Therefore, if velocities of the dipole excited by the first pulse are not significantly altered by collisions, the interaction of the dipole moment with the second laser pulse will not be affected by collisions. However, if the velocities of the dipoles are changed by collisions, the dipole precessions are then permanently dephased and thus suffer irreversible losses. This type of velocity-changing collision plays a role similar to that of the quenching collisions by which atoms from the states involved in the echo formation are removed, and cannot cause the echo depolarization. To be sure, the velocity-varying collisions contribute significantly to the decay constant γ. In a similar picture, for such simple transitions, one can see that collisions that occurred after the second pulse will have no effect on the echo polarization.

The same description, however, is not quite as clear for the $j_1=1 \leftrightarrow j_2=1$ and $j_1=\frac{3}{2} \leftrightarrow j_2=\frac{1}{2}$ transitions, in which the dipole matrix elements are not all equal. The situations become even more complicated for the case in which one of the states involved in the echo formation has a j_1 (or j_2) ≥ 2. To understand the results of these simple as well as the general transitions, we now return to the expressions given in Eqs. (21)–(23) and consider the general case.

[12] The exponentiation ansatz used to obtain the result at the right-hand side of Eq. (33) is commonly used in the derivation of kinetic equations. For example, in the basic derivations of Eqs. (10) and (11) of the paper by Gersteln and Foley mentioned in Ref. 9, such an ansatz is also implicitly assumed.

B. General Cases

To simplify the calculation, the quantization axis will be chosen along the electric field vector of the second pulse in consideration of the general case. The advantage of choosing such a coordinate system is that the operator $(\mathbf{A}_2 \cdot \mathbf{P})$ is diagonal; thus the projectors defined in Eq. (18) have the property

$$\langle l | Z_{2n} | k \rangle \equiv \langle j_1 l | Z_n(2) | j_1 k \rangle = \delta_{ln} \delta_{kn} \qquad (35)$$

and

$$\sum_m |m\rangle \langle m | Z_n(1) | k \rangle = \mathfrak{D}_{kn}^{(j_1)*}(\mathbf{\Omega}) | n \rangle. \qquad (36)$$

Similar formulas hold for the lower state $|B\rangle$ with angular momentum j_2.

In Eq. (36), $\mathbf{\Omega}$ is the angle between the electric field vector of the first pulse with respect to the quantization axis; if two pulses propagate along the same direction, then $\mathbf{\Omega} = \psi$, where ψ is the angle between the electric field vectors of the first and the second laser pulses.

With the help of Eqs. (17) and (36), we now have

$$\langle \alpha | (\mathbf{A}_1 \cdot \mathbf{P}) Z_n(1) | k \rangle = \tfrac{1}{2} (-1)^{j_2 - n} \mathfrak{D}_{\alpha n}^{(j_2)}(\mathbf{\Omega}) \mathfrak{D}_{kn}^{(j_1)*}(\mathbf{\Omega}) \theta_{1n}. \qquad (37)$$

The use of the formula (the Clebsch-Gordan series),

$$\mathfrak{D}_{m_1' m_1}^{(j_1)}(\omega) \mathfrak{D}_{m_2' m_2}^{(j_2)}(\omega) = \sum_{j m' m} (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m' \end{pmatrix} \times \mathfrak{D}_{m' m}^{(j)*}(\omega) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}$$

simplifies Eq. (37) to

$$\langle \alpha | (\mathbf{A}_1 \cdot \mathbf{P}) Z_n(1) | k \rangle = \tfrac{1}{2} \sum_{j\gamma} (-1)^{j_2 + k - 2n} [4\pi (2j+1)]^{1/2} \times \theta_{1n} \begin{pmatrix} j_2 & j_1 & j \\ \alpha & -k & \gamma \end{pmatrix} Y_{j-\gamma}(\mathbf{\Omega}) \begin{pmatrix} j_2 & j_1 & j \\ n & -n & 0 \end{pmatrix}. \qquad (38)$$

The substitution of Eq. (38) into Eq. (21) gives

$$\langle \mathbf{P}_0\rangle = \sum_{j=|j_1-j_2|}^{j=j_1+j_2} \langle \mathbf{P}_0\rangle_j, \quad (39)$$

where

$$\langle \mathbf{P}_0\rangle_j = \mathcal{P}_{21}[4\pi(2j+1)]^{1/2} \sum_{q\alpha k} \hat{\epsilon}_{-q} \sin\theta_{2k/2} \sin\theta_{2\alpha/2} \times \begin{pmatrix} j_1 & j_2 & 1 \\ \alpha & -k & q \end{pmatrix} \begin{pmatrix} j_2 & j_1 & j \\ \alpha & -k & q \end{pmatrix} \times Y_{j-q}(\mathbf{\Omega}) \left[\sum_n \begin{pmatrix} j_2 & j_1 & j \\ n & -n & 0 \end{pmatrix} \sin\theta_{1n} \right]. \quad (40)$$

Here $\hat{\epsilon}_{-q}$ are the unit vectors in the spherical tensor basis, namely,

$$\hat{\epsilon}_0 = \hat{z},$$

$$\hat{\epsilon}_{\pm 1} = \mp 1/\sqrt{2}(\hat{x} \pm \hat{y}).$$

From Eqs. (39) and (40) it is now simple to obtain the results for the transitions considered above. These results are already given in Ref. (3) and will not be repeated here.

From the right-hand side of Eq. (40) we can observe that the quantity within the square brackets vanishes unless j is odd. Therefore, Eq. (39) becomes

$$\langle \mathbf{P}_0\rangle = \sum_{j\ \text{odd}} \langle \mathbf{P}_0\rangle_j. \quad (41)$$

Before discussing further the meaning of Eq. (41), we will next consider the collision-induced terms $\langle \mathbf{A}\rangle$ and $\langle \mathbf{B}\rangle$. The substitution of Eq. (38) into Eqs. (22) and (23) yields Eqs. (42) and (43), respectively:

$$\langle \mathbf{A}\rangle = \sum_{j\ \text{odd}} \gamma(j)\langle \mathbf{P}_0\rangle_j, \quad (42)$$

$$\langle \mathbf{B}\rangle = \gamma^*(1)\langle \mathbf{P}_0\rangle = \sum_{j\ \text{odd}} \gamma^*(1)\langle \mathbf{P}_0\rangle_j, \quad (43)$$

where

$$\gamma(j) = 2\pi\eta \int bdbd^3v_2 |\mathbf{v}_2| F(\mathbf{v}_2) \textstyle\sum_J G(J) \begin{Bmatrix} j_1 & j_2 & J \\ j_1 & j_2 & j \end{Bmatrix} \quad (44)$$

and $\gamma^*(1)$ is the complex conjugate of $\gamma(1)$. Combining Eqs. (41)–(43), we can write the MEDMA as

$$\langle \mathbf{P}\rangle_{\text{echo}} = \sum_{j\ \text{odd}} \langle \mathbf{P}_0\rangle_j [1-\tau(\gamma(j)+\gamma^*(1))] \rightarrow \sum_{j\ \text{odd}} \langle \mathbf{P}_0\rangle_j e^{-\Gamma_j\tau} = \sum_{j\ \text{odd}} \langle \mathbf{P}\rangle_j, \quad (45)$$

where

$$\Gamma_j = \gamma(j) + \gamma^*(1) = \text{Re}(\Gamma_j) + i\,\text{Im}(\Gamma_j). \quad (46)$$

Here Re and Im mean the real and the imaginary parts, respectively, and the arrow sign indicates an ansatz.

As we see from Eq. (46), Γ_j is generally a complex quantity, except for the $j=1$ case, where Γ_j is real. The complex character of Γ_j corresponds to the collision-induced frequency shift in the MEDMA, and therefore the position where the peak echo intensity occurs will not be exactly at the time τ after the end of the second pulse (τ being the time between pulses).

Because j can only take on odd-integer values, ranging from $|j_1-j_2|$ to j_1+j_2, the cases of $j_1=\frac{1}{2} \leftrightarrow j_2=\frac{1}{2}$, $j_1=1 \leftrightarrow j_2=0$, $j_1=1 \leftrightarrow j_2=1$, and $j_1=\frac{3}{2} \leftrightarrow j_2=\frac{1}{2}$ transitions can now be understood, as only the $j=1$ term is possible for these transitions.

In analogy to the multipole moment picture commonly used in discussing Hanle-effect experiments in gases, the result expressed in Eq. (41) will be interpreted as a collection of multipole moments. One recalls that in Hanle-effect or in optical-pumping experiments, the initial population of atoms excited to different magnetic sublevels is generally viewed as a collection of multipole moments. This description is useful not only in its direct physical meaning, but also in its simplicity of treating the collision-induced relaxation effects. It has been shown that, while collision transfer rates between pairs of magnetic levels are rather anisotropic, the relaxation of each individual moment can be described by a single time constant.[8] The time constants associated with different multipole moments are in general different, and as a result, the fluorescent light emitted by atoms shows partial depolarization. The measurement of the polarization of the fluorescent light gives information about the alignment and the orientation of the excited atoms.

The depolarization can similarly be expected from the photon-echo experiment. The MEDMA given in Eq. (45) is equal to the algebraic sum of individual terms $\langle \mathbf{P}\rangle_j$. If we regard $\langle \mathbf{P}\rangle_j$ as the jth moment of the mean echo dipole moment, we can clearly see from Eq. (45) that $\langle \mathbf{P}\rangle_j$ decays with a single time constant given by $\text{Re}\Gamma_j$. Since $\text{Re}\Gamma_j$ is generally different for different j, the collision-induced decay of $\langle \mathbf{P}\rangle_{\text{echo}}$ cannot be accounted for by a single time constant (except for the simple transitions considered earlier). As a result, the polarization vector of the photon echo will vary with pressure. In addition, the ψ dependence of the echo intensity is also modified by gas pressure.

To see the depolarization effect, one must have a system in which one of the states involved in the echo formation has a value of angular momentum equal to or greater than 2. In such a system, not only the $j=1$ moment is present, but the $j=3$ or higher moment is also present as well. The simplest case to be considered is the $j_1=2 \leftrightarrow j_2=1$ transition.

C. $j_1=2 \leftrightarrow j_2=1$ Transition

For simplicity, we will consider the case when two laser pulses are propagating along the same direction. We immediately obtain from Eqs. (40) and (46)

$$\langle \mathbf{P}\rangle_{\text{echo}} = \langle \mathbf{P}_0\rangle_1 e^{-\Gamma_1\tau} + \langle \mathbf{P}_0\rangle_3 e^{-\Gamma_3\tau}, \quad (47)$$

where

$$\langle \mathbf{P}_0\rangle_1 = (6/5)(\sqrt{\tfrac{1}{10}})\mathcal{P}_{21}[\sin\theta_{11} + (1/\sqrt{3})\sin\theta_{12}] \times\{\hat{z}[\sin^2(\tfrac{1}{2}\theta_{21}) + \tfrac{2}{3}\sin^2(\tfrac{1}{2}\theta_{22})]\cos\psi + \hat{x}(2/\sqrt{3})\sin(\tfrac{1}{2}\theta_{21})\sin(\tfrac{1}{2}\theta_{22})\sin\psi\} \quad (48)$$

and

$$\langle \mathbf{P}_0\rangle_3 = [\mathcal{P}_{21}/35(\sqrt{10})][\sin\theta_{11} - \tfrac{1}{2}\sqrt{3}\sin\theta_{12}] \times\{\hat{z}[\sin^2(\tfrac{1}{2}\theta_{21}) - \sin^2(\tfrac{1}{2}\theta_{22})](2\cos^3\psi - 3\cos\psi\sin^2\psi) - \hat{x}(1/2\sqrt{3})\sin(\tfrac{1}{2}\theta_{21})\sin(\tfrac{1}{2}\theta_{22}) \times(4\cos^2\psi\sin\psi - \sin^3\psi)\}. \quad (49)$$

Here θ_{i1} and θ_{i2} are pulse angles induced by the ith pulse for the $j_1=1 \leftrightarrow j_2=2$ transition. They are given by

$$\theta_{i1} = \frac{2\mathcal{P}}{(\sqrt{10})}\int \epsilon_i(t)dt,$$

$$\theta_{i2} = 2\left(\frac{2}{15}\right)^{1/2}\mathcal{P}\int \epsilon_i(t)dt.$$

As is clearly demonstrated by Eqs. (48) and (49), even for the $j_1=2 \leftrightarrow j_2=1$ transition, the MEDMA is already a complicated function of θ_{11}, θ_{12}, θ_{21}, θ_{22}, and ψ. Since the echo intensity is proportional to $|\langle \mathbf{P}\rangle_{\text{echo}}|^2$, we have

$$I_{\text{echo}} \propto |\langle \mathbf{P}_0\rangle_1|^2 e^{-2\Gamma_1'\tau} + |\langle \mathbf{P}_0\rangle_3|^2 e^{-2\Gamma_3'\tau} + 2|\langle \mathbf{P}_0\rangle_1\cdot\langle \mathbf{P}_0\rangle_3| e^{-(\Gamma_1'+\Gamma_3')\tau}, \quad (50)$$

where $\Gamma_i' = \gamma + \text{Re}(\Gamma_i)$, with γ the rate constant due to radiative decay, included phenomenologically.

In contrast to the simple transition cases, the echo-intensity maximum for a $j_1=2 \leftrightarrow j_2=1$ transition requires three rate constants to account for relaxation. As Γ_1' generally differs from Γ_3', the echo-intensity maximum cannot be described by a single exponential term. Moreover, defining an echo polarization angle Φ with respect to the electric field vector of the second pulse as

$$\Phi = \tan^{-1}\{\text{Re}[\hat{x}\cdot\langle \mathbf{P}\rangle_{\text{echo}}]/\text{Re}[\hat{z}\cdot\langle \mathbf{P}\rangle_{\text{echo}}]\},$$

we find from Eqs. (47)–(49) that Φ satisfies the equation

$$\tan\Phi = [g(\psi,\theta,\tau)/f(\psi,\theta,\tau)]\tan\psi, \quad (51)$$

where

$$g(\psi,\theta,\tau) = (1/\sqrt{3})\{12[\sin\theta_{11} + (1/\sqrt{3})\sin\theta_{12}]e^{-\Gamma_1\tau} + (1/7)(\sin\theta_{11} - \tfrac{1}{2}\sqrt{3}\sin\theta_{12}) \times(4\cos^2\psi - \sin^2\psi)e^{-\Gamma_3\tau}\}\sin\tfrac{1}{2}\theta_{21}\sin\tfrac{1}{2}\theta_{22}, \quad (52)$$

$$f(\psi,\theta,\tau) = 2\{3[\sin\theta_{11} + (1/\sqrt{3})\sin\theta_{12}] \times[\sin^2(\tfrac{1}{2}\theta_{21}) + \tfrac{2}{3}\sin^2(\tfrac{1}{2}\theta_{22})] \times e^{-\Gamma_1\tau} + (1/7)[\sin\theta_{11} - \tfrac{1}{2}\sqrt{3}\sin\theta_{12}] \times[\sin^2(\tfrac{1}{2}\theta_{21}) - \sin^2(\tfrac{1}{2}\theta_{22})] \times(2\cos^2\psi - 3\sin^2\psi)e^{-\Gamma_3\tau}\}. \quad (53)$$

The result given above reduces to that of Ref. 3 only when $\Gamma_1' = \Gamma_3'$. Depolarization arises when $\Gamma_1' \neq \Gamma_3'$. In such a situation, Φ becomes a function of gas pressure of perturbing atoms.

The situation becomes even more complicated for echoes resulting from a pair of higher angular momentum states. For any integer $j_1 \leftrightarrow j_2$ transition with $j_1 \geq j_2$, the echo maximum versus τ function consists of $\tfrac{1}{2}j_1(j_1+1)$ exponential terms, each characterized by a relaxation time constant. The corresponding formula for any half-integer $j_1 \leftrightarrow j_2$ transition is $\tfrac{1}{2}(j_1+\tfrac{1}{2})(j_1+\tfrac{3}{2})$, with $j_1 \leq j_2$. In addition, for fixed ψ, θ, and τ, the echo polarization angle Φ associated with large angular momentum states becomes a rather complicated function of gas pressure.

IV. SUMMARY

Photon-echo calculation in gaseous systems has been extended by the inclusion of atomic collisions. It has been shown that the echo amplitude can be regarded as a collection of odd multipole moments. The decay of each moment is characterized by a time constant. For an echo arising from a $j_1 \leftrightarrow j_2$ transition, with $j_1 \geq j_2$, there are $j_1 + j_2$ moments, and $\tfrac{1}{2}j_1(j_1+1)$ exponential functions are needed to describe the echo intensity, j_1 being an integer. The corresponding formula for the half-integer case is $\tfrac{1}{2}(j_1+\tfrac{1}{2})(j_1+\tfrac{3}{2})$, with $j_1 \leq j_2$. As a result, except for simple cases such as $j_1=\tfrac{1}{2} \leftrightarrow j_2=\tfrac{1}{2}$, $j_1=1 \leftrightarrow j_2=0$, $j_1=1 \leftrightarrow j_1=1$, and $j_1=\tfrac{3}{2} \leftrightarrow j_2=\tfrac{1}{2}$ transition, the echo is necessarily depolarized by atomic collisions. The careful study of pressure dependence of photon-echo polarization angle Φ not only can provide information about atomic collisions, but may also supplement spectroscopy in differentiating between an echo arising from states of high angular momenta and an echo arising from the states of low angular momenta.

ACKNOWLEDGMENT

I wish to thank Dr. J. P. Gordon for commenting on the manuscript.