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Resonant third-harmonic generation in I_2 with circularly polarized light

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Magnetic-field-induced resonant third-harmonic generation in I_2 with circularly polarized light is studied. With a magnetic field perpendicular to the propagating direction of the light, the axial symmetry is broken and the angular momentum is no longer conserved in such a system, and the third harmonic may be generated under such conditions. Quantum beats in photon-echo-like third-harmonic generation with nonsynchronous laser pulses are also studied. The intensity of the harmonic generated may be interpreted in terms of the interference between a molecule and itself as well as the interference between different molecules. The gyromagnetic ratio of the resonant states is measured.

I. INTRODUCTION

Third-harmonic generation (THG) in gas is widely believed to be an approach to provide useful coherent source of radiation in the vacuum-ultraviolet region of the spectra.[1-3] Recently, techniques developed in classical spectroscopy, such as the level crossing[4,5] and the photon echo,[6-8] were applied to the resonant-harmonic generation[9,10] in I_2. Polarization rotation of THG (Ref. 11) and THG with nonsynchronous pulses[12] were also studied. The detailed dynamics of the coherent process of wave mixing and the various mechanism of saturation as well as the properties of the resonant states may be studied by this approach. In this work, progress in this approach based on the angular momentum nonconservation in a symmetry-broken geometry is presented.

Because of the conservation of angular momentum in a field-free circumstance, the third harmonic cannot be generated in a gas with circularly polarized light. However, the conservation of angular momentum is associated with the axial symmetry of the system. As a result, the third harmonic may be generated with circularly polarized light if a magnetic field is applied in a direction perpendicular to the propagating direction of the laser beam. The intensity of the harmonic generated is a measurement of the molecular energy-level splitting caused by the magnetic field.

In quantum mechanics, resonant-harmonic generation in gas with circularly polarized light under transverse magnetic field may be interpreted in terms of interference between the dipole moments created in a molecule by the laser beam. The magnetic field may modulate the intensity of the harmonic generated through modifying the relative phase difference between the dipole moments caused by the Zeeman splitting of the resonant states. As a result, one might expect to be able to observe the quantum beats in the third harmonic generated in a gas medium if a pulse is used to create the coherent dipole moments and another pulse is used to probe the resultant total dipole moment at a later time. However, this approach meets the difficulty caused by the short coherent lifetime (<1 ns) of the macroscopic dipole moment in the optical spectral region. For this reason, techniques based on the photon-echo process, which has a long "effective coherent lifetime" is applied to the harmonic generation to study the quantum beats in wave mixing.

Photon-echo process in I_2 may be studied with the technique of harmonic generation with nonsynchronous circularly polarized pulses. This method has the advantage of eliminating most of the background that may be produced by each individual pulse. In this approach the first circularly polarized laser pulse creates coherent density-matrix elements between the excited and the ground state. The second pulse, which is delayed by τ from the first pulse and is also circularly polarized, reverses the precession direction of the density-matrix elements. Rephasing of the density-matrix elements of a macroscopic quantity of molecules at a later time is responsible for the generation of the photon echo. The third harmonic may be generated in the sample if a laser pulse which is delayed by τ from the second pulse and is oppositely circularly polarized is focused into the same region that has been irradiated with the first two pulses.

The rephasing of the matrix elements which is essential for the harmonic generation in the photon-echo process may be modulated with an external field applied in a direction perpendicular to the propagating direction of the laser beam. The magnetic field may split the energy level of the molecule and the rephasing of the density-matrix elements may not be complete. With a well-defined delay time τ between the pulses, quantum beats may be detected in the harmonic generation associated with the photon-echo process.

The method of quantum beats in wave mixing with nonsynchronous pulses has the advantage of being able to separate the signal from the intense primary beam, achieve full collinear overlap of the pulses, and satisfy the phase-matching condition. Also, this technique may be used to measure events in the nanosecond time scale without the need of a fast detector and needs no optical shutter as compared to the conventional photon-echo techniques. Quantum beats in photon-echo process was reported by Baer and Abella[13] and Alekseev.[14]

II. THEORY

For simplicity, a simplified model that assumes only resonances in a $|g\rangle$-$|e\rangle$ transition is presented in this section to discuss the third-harmonic generation with a circularly polarized laser beam in a system that has no axial symmetry. Quantum beats in harmonic generation with nonsynchronous pulses is discussed in a system that is assumed to have no hyperfine structure. Besides its effect on the coherent lifetime, the interference between different molecules[9] is also neglected in this section. Effects caused by the deviation from the simplified model of the harmonic generation in I_2 will be discussed in Sec. III.

A. Third-harmonic generation with circularly polarized light

Third-harmonic generation in I_2 is enhanced with simultaneous resonances in one- and two-quantum resonances.[15] A theory of doubly resonant third-harmonic generation in molecules with nearly degenerate states was discussed in another paper.[11] The process of the harmonic generation in I_2 is shown in Fig. 1. The ensemble averaged macroscopic (total) nonlinear dipole moment responsible for the wave mixing in a unit volume in the sample may be written as

$$\vec{P}^{\,\mathrm{nl}}=\sum{}'\left[\sum_{g,n}\rho_{ng}^{\mathrm{nl}}\vec{d}_{gn}\right], \tag{1}$$

where the prime denotes summation over all molecules in a unit volume. Here $\vec{d}_{gn}$ is the matrix element of $\vec{d}$, the dipole moment operator. $|g\rangle$ and $|n\rangle$ are sublevels of the ground and excited states. ρ_{ng}^{nl} is the density-matrix element created in the sample by the laser beam. If saturation can be neglected, the intensity of the harmonic generated is proportional to the square of the macroscopic nonlinear dipole moment,

$$I\propto|P^{\mathrm{nl}}|^2$$

or

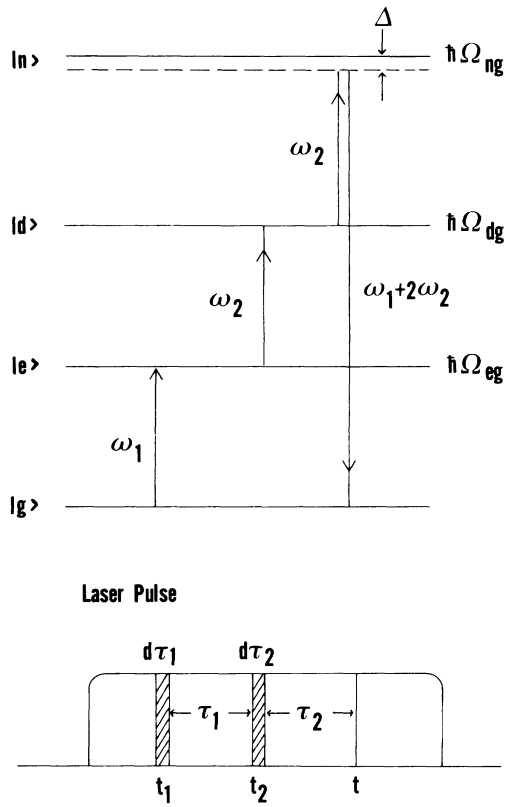

FIG. 1. Schematic diagram of the doubly resonant third-harmonic generation process. Calculation of the nonlinear dipole moment $\vec{P}^{\,\mathrm{nl}}(t)$ is performed by dividing the time period before t into many small time intervals.

$$I\propto\sum_{g,n;g',n'}(\vec{U}\cdot\vec{d})_{gn}\rho_{ng}^{\mathrm{nl}}\rho_{g'n'}^{\mathrm{nl}}(\vec{U}^{*}\cdot\vec{d})_{n'g'}\,. \tag{2}$$

The proportional constant depends on the density of the vapor as well as the profile of the laser beam. $\vec{U}$ is the polarization vector of the mixed wave. With the electric field of the laser given by $\vec{E}(\vec{r},t)=\vec{E}\exp[i(\omega t-kz)]$, the density matrix is given by[11]

$$\rho_{ng}^{\mathrm{nl}}\rho_{g'n'}^{\mathrm{nl}}=\sum_{\substack{e,d\\e',d'}}\frac{c_s c_{s'}^{*}}{\theta_1-\theta_2}\left[\frac{2}{\sqrt{\pi}}\left[e^{-\theta_1^2}\int_0^{\theta_1}e^{t^2}dt-e^{-\theta_2^2}\int_0^{\theta_2}e^{t^2}dt\right]-i(e^{-\theta_1^2}-e^{-\theta_2^2})\right]+\mathrm{c.c.} \tag{3}$$

Here

$$\theta_1=\frac{\Omega_{ee'}}{\sqrt{2}kv_b},\quad \theta_2=\frac{\Omega_{dd'}}{2\sqrt{2}kv_b},\quad \Omega_{ee'}=\Omega_{eg}-\Omega_{e'g'}\,,$$

$\Omega_{d'd}=\Omega_{d'g'}-\Omega_{dg}$, and $v_b=(2k_BT/m)^{1/2}$. k_B is the Boltzmann constant, T is the temperature, and m is the molecular weight. Ω_{dg},Ω_{eg} are defined in Fig. 1. c_s is proportional to $d_{eg}d_{de}d_{nd}$.

Although the intensity of the harmonic generated as given by Eqs. (2) and (3) may be calculated with a computer, an analytical solution based on a simplified model may reveal more closely the physics of the harmonic generation with circularly polarized light.

For simplicity, let us consider the harmonic generation in a sample of free atoms or molecules that is enhanced by only one resonance. The process is shown in Fig. 2(b). With the laser beam circularly polarized, one may choose the reference system S, as shown in Fig. 2(a), to describe the process of the excitation. In reference system S, the z axis is parallel to the propagation direction of the laser beam. The electric field of the laser may be expressed as $E[(\hat{x}-i\hat{y})/\sqrt{2}]e^{-i(kz-\omega t)}+\mathrm{c.c.}$ Here E is assumed to be a slow function of time. $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors along the x, y, and z axis. The selection rule in system S is $\Delta m=+1$. If there is no external field, m is a good quan-

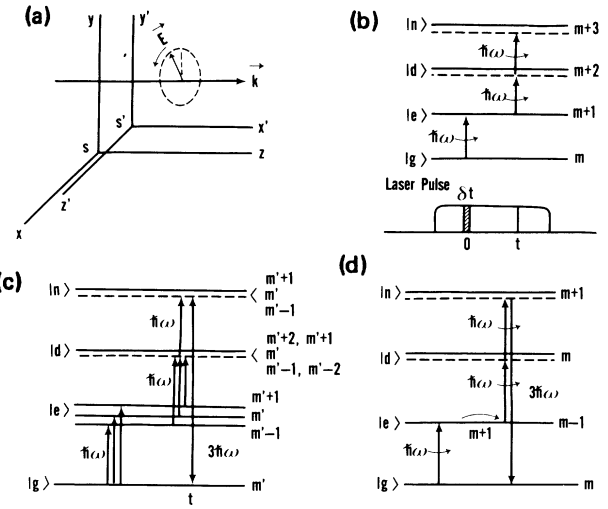

FIG. 2. (a) Process of the resonant-harmonic generation in a system by a plane-wave laser pulse may be described in system s or system s'. (b) Because of the conservation of angular momentum, no third harmonic can be generated if there is no external field ($H=0$) in the x-y plane. (c) Under a magnetic field, the energy level splits. In the coordinate system s' sublevels $|m'\rangle_e$, $|m'+1\rangle_e$ $|m'-1\rangle_e$ are coherently excited. The relative phase difference of the density matrices $(\rho_{m',m'})_{eg}$, $(\rho_{m'+1,m'})_{eg}$, $(\rho_{m'-1,m'})_{eg}$ are functions of (t_2-t_1). At $t_2=t_1+h\pi/g_J\mu_n H$, the phase differences between the density matrices are the same as that between the density matrices created by an oppositely circularly polarized light pulse at time t_2. (d) In coordinate system s, $|m\rangle$ is not a good quantum number and resonant third harmonic may be generated by a circularly polarized light if there is no axial symmetry.

tum number and $J_z=m\hbar$ is independent of time. As shown in Fig. 2(b), third-harmonic generation is forbidden in this case.

With a magnetic field H applied in the direction perpendicular to the propagation direction of the light, one may choose the coordinate system S', as shown in Fig. 2(a), to describe the process of the excitation. In coordinate system S', the electric field of the laser beam is described as $E[(\hat{z}'-i\hat{y}')/\sqrt{2}]e^{i(kx'-\omega t)}+\text{c.c.}$ Since

$$id_{y'}=\tfrac{1}{2}(d_{x'}+id_{y'})-\tfrac{1}{2}(d_{x'}-id_{y'})=-\frac{1}{\sqrt{2}}(d_+ +d_-)\ ,$$

sublevels $|e,m\rangle$, $|e,m+1\rangle$, $|e,m-1\rangle$ are coherently excited. Here it is assumed that the Zeeman splitting is less than the reciprocal coherent lifetime. Because of the Zeeman splitting, the relative phase of the density-matrix elements $(\rho_{m,m})_{eg}$, $(\rho_{m+1,m})_{eg}$, $(\rho_{m-1,m})_{eg}$, is a function of time. With respect to $(\rho_{m,m})_{eg}$, $(\rho_{m+1,m})_{eg}$, and $(\rho_{m-1,m})_{eg}$ has an additional phase shift of $\Delta\theta\approx\pm g_J H t\mu_n/\hbar$ at time t after the excitation. Here g_J is the gyromagnetic ratio of the state $|e\rangle$ and μ_n is the nuclear magneton. At $t=\hbar\pi/g_J\mu_n H$, the relative phase shift $\Delta\theta=\pi$ and the phase relation between the density-matrix elements is identical to that created by an oppositely circularly polarized laser pulse that was turned on at time t. As shown in Fig. 2(d), in coordinate system S, $(\rho^{(t)}_{m-1,m})_{eg}\neq 0$ and the third harmonic may be generated.

Note that in the coordinate system S, $|J,m\rangle_e$ is not an eigenstate of the molecule and m_j is not a good quantum number.

The H-field dependence of the harmonic generated may be easily derived in the low and high H-field limit. Define $\theta=g_J H\mu_n T^*/\hbar$. Here $T^*=1/\sqrt{2}kv_b$ is the coherent lifetime of the density matrix. In the low-field limit ($\theta\ll 1$), one has

$$(\rho_{m-1,m})^s_{eg}\propto\frac{1-\cos\theta}{2}\ .$$

Here $(\rho_{m-1,m})^s_{eg}$ is the density-matrix element in the coordinate system S. The intensity of the third harmonic generated is proportional to $(1-\cos\theta)^2$.

At high magnetic field the maximum value of $|P^{\rm nl}|$ $(Pc^{\rm nl})$ with a circularly polarized light is proportional to

$$E^3(d_-)^{gn}_{m,m+1}(d_+)^{nd}_{m+1,m}(d_+)^{de}_{m,m-1}(d_+)^{eg}_{m+1,m}\ .$$

The value of $P^{\rm nl}(P^{\rm nl}_l)$ with a linearly polarized light is proportional to

$$E^3(d_0)^{gn}_{m,m}(d_0)^{nd}_{mm}(d_0)^{de}_{m,m}(d_0)^{eg}_{mm}\ .$$

Here $d_0=d_z$ and $(d_i)^{kl}_{m,m'}$ are the matrix elements of d_i between states $|k,m\rangle$ and $|l,m'\rangle$. Since $P^{\rm nl}_c$ is of the same order of magnitude of $P^{\rm nl}_l$, the third harmonic generated with circularly polarized light may have an intensity of

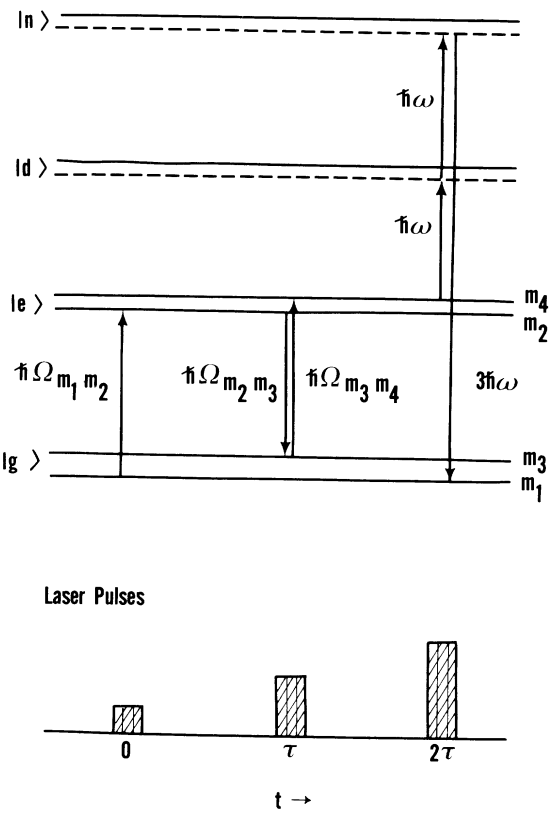

FIG. 3. Process of resonant third-harmonic generation in free atom or molecule associated with the photon-echo process. Zeeman splitting is exaggerated in this diagram.

the order of the harmonic generated with linearly polarized light under the same condition.

B. Quantum beats in harmonic generation with nonsynchronous pulses

From the above discussion it seems clear that quantum beats may be observed if the harmonic generated by two separated and circularly polarized laser pulses is measured as a function of the magnetic field. However, this approach in a gas with a laser of visible wavelength encountered with the difficulty caused by the short duration of the coherent lifetime T^*. This difficulty may be overcome with the technique of resonant-harmonic generation with photon-echo process. In a photon-echo process the "effective coherent lifetime" may be increased to 30 ns.

Figure 3 shows the process of resonant third-harmonic generation in I_2 associated with the photon-echo process. Since the power of the first two pulses is quite weak (<30 kW; $\tau\approx 8$ ns), coherent delayed density matrix ρ_{dg} created by the first two pulses may be neglected although THG in I_2 is enhanced by simultaneous resonances in one- and two-quantum transitions.

The density-matrix elements of a single molecule evaluated in a reference frame rotating at the frequency ω of the incident field is given by[6,16]

$$\tilde{\rho}_{eg}(t)=e^{-iH(t-t_1)}e^{-i\vec{A}_2\cdot\vec{d}}e^{-iHt_1}e^{-i\vec{A}_1\cdot\vec{d}}\rho(0)\times e^{i\vec{A}_1\cdot\vec{d}}e^{iHt_1}e^{i\vec{A}_2\cdot\vec{d}}e^{iH(t-t_1)}. \tag{4}$$

Here H is the effective Hamiltonian in the rotating frame and $\vec{A}_i=\int_0^{\Delta\tau}dt\,\vec{\epsilon}_i(t)/\hbar$, where $\Delta\tau$ is the pulse duration. The electric field of the laser pulse is assumed to be $\vec{E}_i(t)=\vec{\epsilon}_i(t)e^{i(\vec{k}\cdot\vec{r}-\omega t)}$. The initial density matrix $\rho(0)$ is equal to $1/(2J_g+1)\,|g\rangle\langle g|$. J_g is the angular momentum quantum number of the ground state. The density matrix ρ_{eg} characterizes a system having sets of ground states ($|g\rangle$) and excited states ($|e\rangle$). Following the analysis of Gordon *et al.*,[16] when the pulse operator is written as $e^{-i\vec{A}\cdot\vec{d}}=\cos(\vec{A}\cdot\vec{d})-i\sin(\vec{A}\cdot\vec{d})$ one may see from the parity that the $\sin(\vec{A}\cdot\vec{d})$ operator is nonzero only for matrix elements between $|g\rangle$ and $|e\rangle$ while the $\cos(\vec{A}\cdot\vec{d})$ leaves the system in the ground or the excited state. Assuming the system has a large inhomogeneous linewidth, we need only retain these terms that have the time dependence of approximately $e^{-i\Omega_{eg}(t-2\tau)}$. Those terms contribute to the coherent nonlinear dipole moment that is responsible for the photon echo. In the rotating frame, one has

$$\tilde{\rho}_{eg}(t)=\frac{1}{2(2J_g+1)}\sum_{g'e'}\exp\left[-i[\Omega_{eg}(t-\tau)-\Omega_{e'g'}\tau]\right]\langle e|\sin(\vec{A}_2\cdot\vec{d})|g'\rangle\langle g'|\sin(2\vec{A}_1\cdot\vec{d})|e'\rangle\times\langle e'|\sin(\vec{A}_2\cdot\vec{d})|g\rangle+\text{c.c.}. \tag{5}$$

Here $\Omega_{eg}=(E_e-E_g)/\hbar$.

The off-diagonal—density-matrix elements responsible for the generation of the third harmonic were discussed in another paper.[10] If the process of harmonic generation is also resonant in the two-quantum transitions, one has

$$\tilde{\rho}_{eg}(t)\propto\frac{i}{\hbar}\frac{t}{\Delta}\sum_{g',e',e,d}\exp\{-i[\Delta\Omega_{eg}(t-\tau)-\Delta\Omega_{e'g'}\tau]\}\langle n|\vec{\epsilon}_3\cdot\vec{d}|d\rangle\langle d|\vec{\epsilon}_3\cdot\vec{d}|e\rangle\langle e|\sin(\vec{A}_2\cdot\vec{d})|g'\rangle\times\langle g'|\sin(2\vec{A}_1\cdot\vec{d})|e'\rangle\langle e'|\sin(\vec{A}_2\cdot\vec{d})|g\rangle+\text{c.c.} \tag{6}$$

Here Δ is the energy detuning of the $|g\rangle$-$|n\rangle$ transition.

In the experiment of THG associated with photon-echo process $t\approx 2\tau$. Because of the oscillatory terms at the splitting frequencies of the nearly degenerate states, the intensity of the third harmonic generated may oscillate as a function of the pulse separation time or the strength of the magnetic field. The $|e\rangle$ ("B") state in I_2 has a very small g_J factor.[17–19] If we neglect the Zeeman splitting in $|e\rangle$ state, we have

$$\tilde{\rho}_{eg}(2\tau)\propto\sum_{g',e'}\exp-i(\Delta\Omega_{g'g}\tau)\langle e|\sin(\vec{A}_2\cdot\vec{d})|g'\rangle\langle g'|\sin(2\vec{A}_1\cdot\vec{d})|e'\rangle\langle e'|\sin(\vec{A}_2\cdot\vec{d})|g\rangle+\text{c.c.} \tag{7}$$

Formula (7) has the form of

$$\tilde{\rho}_{eg}(2\tau)\propto ae^{-ig_g\mu_nH\tau/\hbar}+b+ce^{+ig_g\mu_nH\tau/\hbar}.$$

Here a,b,c are constants. If $g_g\mu_nH\tau/\hbar=2n\pi$, the rephasing of the density matrix associated with a single molecule, $\tilde{\rho}_{eg}(2\tau)$, is complete and $\tilde{\rho}_{ng}(2\tau)$, which is proportional to $\tilde{\rho}_{eg}(2\tau)$, is also a maximum under this condition. Maximum intensity of THG is expected in this case. If $g_J\mu_nH\tau/\hbar\neq 2n\pi$, the rephasing is not complete and the intensity of the THG is expected to be less than the maximum. As a result, modulation of the THG intensity is expected when it is measured as a function of τ or H.

III. EXPERIMENT

A. Third-harmonic generation in I_2 with circularly polarized light

The light source in this experiment is a Molectron DL-II tunable dye laser pumped by a Molectron MY-32

pulsed Nd:YAG (yttrium aluminum garnet) laser. The laser pulses have a duration at half maximum of approximately 8 ns. The total pulse duration is approximately 14 ns. The repetition rate is 10 pulses per second. A Molectron MY-SP smooth pulse assembly is put inside the Nd:YAG laser cavity to reduce the modulation and give temporally smooth pulses. The laser power is approximately 15 mJ per pulse at 5660 Å. In order to avoid saturation, filters are used to reduce the power of the laser pulse. The beam is collimated with a $f=100$ cm lens to the center of a 5-cm-long quartz cell containing I_2 at room temperature. A Glan prism is put between the lens and the cell to ensure that the beam is nearly 100% linearly polarized before it passes a Babinet compensator which is put between the Glan prism and the cell. The Babinet compensator can be adjusted for a quarter wave retardation. The I_2 cell is placed in the center of a 9-in. electromagnet. The third harmonic generated in the cell is separated from the primary beam by a 60° uv prism, filtered by a narrow-band uv interference filter, and detected by a EMI Gencom Inc. G-26G315 rubidium telluride ultraviolet tube with a magnetic shield. The tube is placed approximately 2 m from the cell. The output of the tube is fed into a Princeton Applied Research (PAR) 160 Boxcar integrator and is recorded on a chart recorder.

Figure 4 shows the experimental result of the intensity of the harmonic generated with circularly polarized light measured as a function of a magnetic field applied in a direction perpendicular to the propagating direction of the beam. The wavelength of the beam is 5668 Å. The power of the laser pulse is approximately 220 μJ per pulse. Because of the depolarization occurring at the cell window and/or the limit of the performance of the optical polarization components, a small background in the third-harmonic generation cannot be eliminated even at $H=0$.

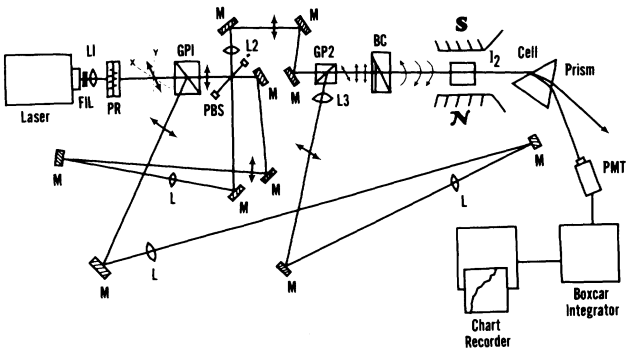

FIG. 5. Schematic diagram of the experimental apparatus of quantum beats in THG associated with photon-echo process. The laser pulse is split into two orthogonally linearly polarized beams by a Glan prism (GP1). The relative intensity of the two beams may be adjusted with a PR. One of the linearly polarized beams is further split into two by a PBS. After being delayed by mirrors, the three beams are realigned to superimpose on each other by means of the PBS and another Glan prism (GP2). Those beams are converted by a BC to circularly polarized light and are focused into a cell containing I_2 vapor. The generated third harmonic is separated from the primary beam by a prism and is detected by a photomultiplier tube (PMT). The signal is averaged by a boxcar integrator and is recorded by a chart recorder as a function of a magnetic field. The magnetic field is applied in a direction perpendicular to the propagation direction of the light.

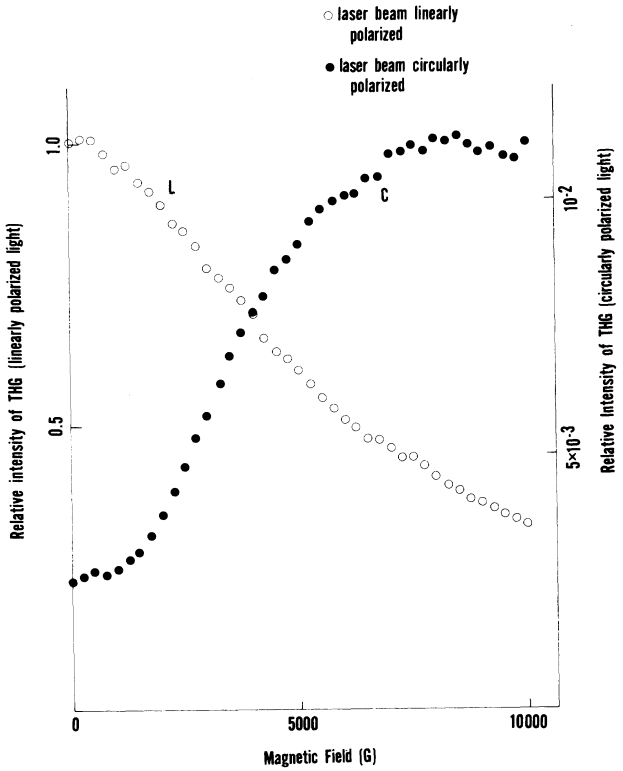

FIG. 4. Third-harmonic generation in I_2. *C*, with a circularly polarized light. *L*, with a linearly polarized light. Note the difference between the scales of the two curves. At $H\sim7500$ G, third harmonic generated by a circularly polarized light is approximately 3% of that produced by a linearly polarized light under similar conditions.

The intensity of the harmonic generated increases rapidly as the magnetic field is increased to above 2000 G, and approaches a constant at $H\approx7000$ G. With this experimental result and the theory given before, one may arrive at the conclusion that at $H\approx7000$ G, $\theta\approx g_d\mu_n HT^*/h\approx\pi$, or $g_d\approx90$. This conclusion, however, is not correct since the effect of the interference between different molecules[9,11] is neglected in that calculation.

A measurement of the intensity of the third harmonic generated with the laser beam linearly polarized as a function of the magnetic field, which is parallel to the polarized direction of the light, is also shown in Fig. 4. The level crossing curve of the third-harmonic generation is believed to be caused by the interference between molecules originating from different sublevels in the ground state. Now it becomes clear that the saturation of THG generated with circularly polarized light at $H\approx7000$ G is the result of two competing processes. Decreasing caused by the loss of phase coherence between molecules originating from different sublevels of the ground state will compensate the increasing in THG caused by the increase of θ associated with each individual molecules as the H field increases. As the H field is further increased, the intensity

of THG is expected to decrease. Note that, even at its maximum, the intensity of the harmonic generated with circularly polarized light is only 3% of that produced by a linearly polarized light with the same power at the same field. Correction for the transmission efficiency difference of the two polarization direction, S and P, of the light by the Prism should increase the value of THG with circularly polarized light by a factor of 1.25.[11]

As is discussed before, the Zeeman splitting of the $|e\rangle$ state may be neglected. As a result, the g factor of the $|d\rangle$ state may be estimated. With

$$\frac{P_c^{\rm nl}}{P_l^{\rm nl}} \approx \frac{1-\cos\theta}{2} \approx \left[\frac{I_c}{I_l}\right]^{1/2} \approx \frac{1}{6} ,$$

one has $\theta \approx 48°$ and $|g_d| \approx 24$. This result agrees reasonably well with the value derived from the experiment of the polarization rotation of the harmonics.[11]

With this technique θ is derived from the ratio of the intensity of harmonic generated with circularly polarized light I_c, and that with linearly polarized light I_l, this result should not be sensitive to the saturation effect caused by the excitation of a non-negligible amount of atoms to the excited states.

B. Quantum beats in third-harmonic generation associated with photon-echo process

The experimental setup for this experiment is shown in Fig. 5. The laser pulse from the dye laser is linearly polarized. A filter (FIL) is put in front of the laser to avoid the laser pulse from damaging the optics. A $f=1$ m lens is used to collimate the laser beam. A Glan prism (GP1) is then used to separate the laser beam into two orthogonally linearly polarized beams. A polarization rotator (PR) is put between the lens and the Glan prism so that the relative intensity of the two beams may be adjusted. One of the linearly polarized beams is further split into two by a pellicle beam splitter (PBS) which transmits approximately 70% and reflects approximately 20% of the light. After an appropriate time delay of the transmitted beam, the two pulses polarized in the same direction are "recombined" (in space, not in time) collinearly by means of the same beam splitter. After passing through a lens ($L2, f=2$ m), three mirrors, another Glan prism (GP2), and a Babinet compensator (BC), the two beams are focused to the center of the I_2 cell put inside the electromagnet. The magnetic field generated in the electromagnet is perpendicular to the propagating direction of the beams. The third pulse, which is polarized perpendicular to the first two pulses, is reflected through several mirrors and passes through several lenses so that its delay path is twice that of the second pulse. This beam is then "recombined" with the first two pulses by means of the second Glan prism (GP2) and is focused to the cell with a lens ($L3, f=1$ m). The Babinet compensator is adjusted for quarter wave retardation so that the three pulses are all circularly polarized. THG in I_2 is then separated from

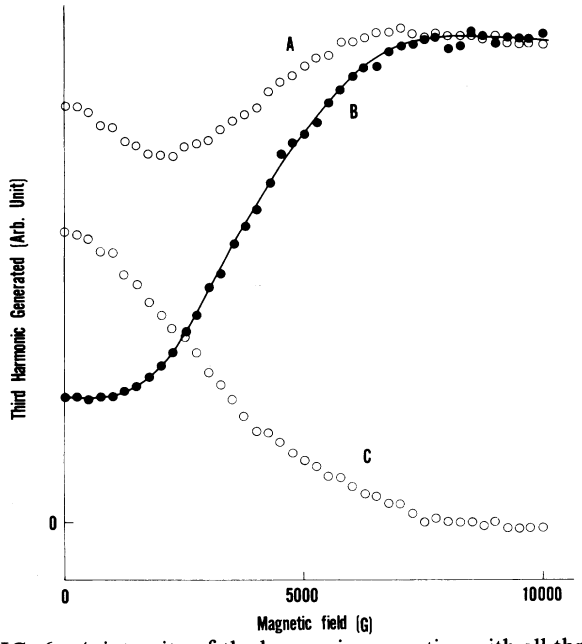

FIG. 6. A, intensity of the harmonic generation with all three pulses present. B, background signal produced by the pulses individually. C, difference between A and B is the intensity of THG associated with the photon-echo process. Wavelength is 5668 Å. The time delay between the pulses are $\tau_{12}=\tau_{23}=17$ ns.

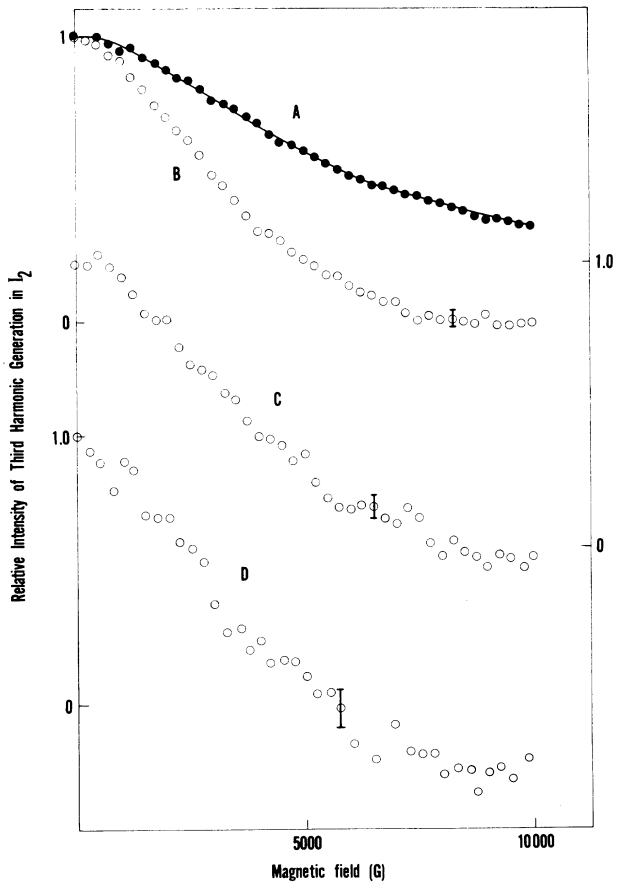

FIG. 7. Normalized intensity of THG. A, with a linearly polarized laser pulse. B, THG associated with photon-echo process with $\tau_{12}=\tau_{23}=17$ ns. C, same as B except that $\tau_{12}=\tau_{23}=20.4$ ns. The scale of the intensity is shown on the right-hand side of the diagram. D, same as B except that $\tau_{12}=\tau_{23}=23.6$ ns.

the laser beam by a prism, filtered by an interference filter, detected by a uv-sensitive tube, averaged with a boxcar integrator, and displayed on a chart recorder as discussed before.

Figure 6 shows the intensity of the harmonic generation associated with the photon-echo process measured as a function of the magnetic field. The delay time between the pulses is $\tau_{12}=\tau_{23}=17$ ns. Curve A is the sum of 15 measurements of the total signal generated with all three pulses present. The intensity of the background is the sum of the third harmonic generated by each beam individually as also shown in Fig. 6. Curve B is a smoothed curve of 10 measurements of the background signal normalized by a factor of $\frac{3}{2}$. The signal of the echo process in curve C is the difference between the total signal A and the smoothed background B. The experimental result with $\tau_{12}=\tau_{23}=17$, 20.4, and 23.6 ns are shown in Fig. 7. A level crossing curve of the THG with a linearly polarized laser beam is also shown in Fig. 7. Dephasing of the dipole moments associated with a single molecule is mainly responsible for the faster decreasing of the signal associated with the photon-echo process as compared to the level crossing curve. At high field, there seems to be no contribution to the harmonic generation by the photon-echo process. This is contrary to the harmonic generation with a single circularly polarized pulse which increases with the magnetic field. With the data shown in Fig. 7, there seems to be no quantum beat detected with $\tau_{12}=\tau_{23}=17$ ns. Data with $\tau_{12}=\tau_{23}=20.4$ and 23.6 ns may have some quantum beatlike structure. However, since the signal-to-noise ratio deteriorates as the signal associated with the photon-echo process decreases with the increased time of delay, this experiment is inconclusive. The g factors dependence on the hyperfine structure of I_2 may be responsible for the failure in detecting the quantum beats.

The hyperfine structure of I_2 has been well studied and it is known that the overall hyperfine separation of the B-X ($|e\rangle$-$|g\rangle$) transition is larger than the Doppler width but still much smaller than the linewidth of the laser beam. The Zeeman Hamiltonian may be written as

$$\mathscr{H}_z=g_J\mu_n HJ_z-(g_I+g_1)\mu_n HI_z \ . \tag{8}$$

Here I_z is the z component of the total nuclear spin I of the I_2 molecule, g_J is the rotational g factor, g_I is the g factor of the ^{127}I nucleus. $g_I=1.12$ (Ref. 20) and g_1 is negligible.[21] Since the spin of atomic iodine is $\frac{5}{2}$, I_z may have a value from -5 to 5 (or -4 to 4 if J is odd). Since Ig_I has a value comparable to g_J, the rephasing of the dipole moments associated with molecules in the different hyperfine states is not complete at any fields besides zero. As a result, the intensity of the quantum beats at high field decreases. The relatively long laser pulse duration (halfwidth ≈ 8 ns, total width ≈ 14 ns) may also be partly reponsible for the failure to detect the quantum beats, especially when the time of delay between the pulses is short.

In Figs. 6 and 7, one may also notice that the intensity of the THG associated with the photon-echo process is "negative" at high magnetic fields. This is due to the neglected saturation effect caused by the loss of molecules from the ground state.[12] Since molecules removed from the ground state by the first two pulses can no longer participate in the resonant-harmonic generation of the third pulse, the intensity of THG generated with all three pulses is less than the summation of THG generated with each individual pulse if the THG associated with the photon-echo process can be neglected.

In an ideal situation, where the laser pulse duration is negligibly small as compared to the time of delay between the pulses, the molecules will not be influenced by the intense laser field during the time that the relative phase difference is accumulated. Under this condition, the technique of quantum beats should not be sensitive to the saturation which broadens the linewidth. In the present experiment the line broadening may not be negligible and efforts will be made in the future to shorten the laser pulse duration.

In Fig. 8, the ratio of the intensity of the "signal" (third harmonic associated with the photon-echo process) to the background (third harmonic produced by each individual pulse) is plotted as a function of T, the time delay between the first and the third pulse. The data indicate that this ratio decreases exponentially with the time of delay. If one writes $I=I_0e^{(-PT/\alpha)}$ and with $P\approx 0.23$ Torr, one has $\alpha\approx 1.7$ ns Torr, which is not very different from the corresponding value obtained in the photon-echo work on atoms.[22] The intensity of the signal is proportional to $(E_1E_2^2E_3^2)^2$ while the background depends on $(E_1^6+E_2^6+E_3^6)$ if saturation can be neglected. Here E_i is the electric field associated with the ith pulse. In the work of measurement of the relative intensity of the third harmonic associated with the photon-echo process as a function of the time of delay, E_1 is fixed and $E_3>E_2>E_1$. The ratio of the signal to the background is then proportional to E_2^4/E_3^2 which is "linear" with respect to the laser

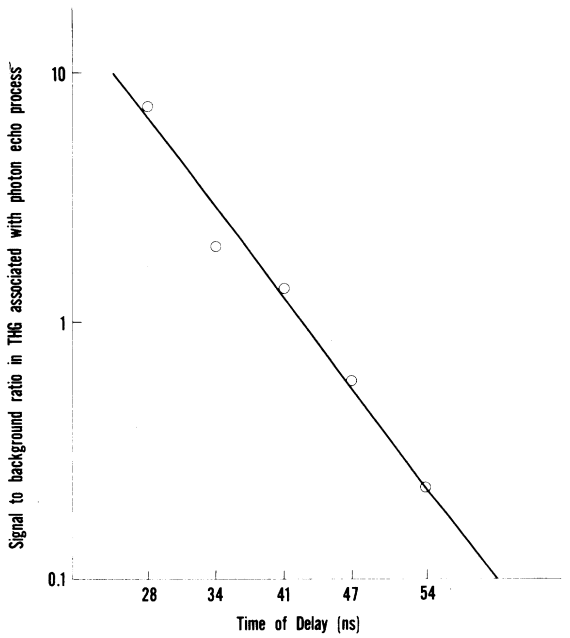

FIG. 8. Ratio of the intensity of THG associated with the photon-echo process plotted as a function of the time of delay between the first and the third pulse.

power. As a result, systematic errors caused by the decreasing of the power density of E_2 and E_3 with increasing delay time ($\approx 20\%$) is small in the measurement of the factor α.

IV. CONCLUSION

In this work angular momentum nonconservation in a system that has no axial symmetry is studied in a coherent nonlinear process of wave mixing in gas. Resonant third-harmonic generation in I_2 with a circularly polarized laser pulse ($\lambda = 5668$ Å) increases fast when a transverse magnetic field is increased from 2000 to 6000 G. The harmonic generated maximizes at approximately 8000 G and decreases slowly at higher H. Since the intensity of the harmonic generated is only 3% of that produced with a linearly polarized light under similar conditions at 8000 G, this effect cannot be explained with the interference between a molecule and itself alone. Interference between different molecules is believed to be responsible for the low intensity of the harmonic generated at high field.

The techniques of resonant third-harmonic generation associated with the photon-echo process may increase the effective coherent lifetime in a coherent process to approximately 30 ns. The increased effective coherent lifetime makes it possible to study the properties of the resonant states with the quantum beats method with a laser of pulse duration approximately 10 ns.

The method of harmonic generation with circularly polarized light discussed in this work is a general technique. This technique may be applied to other nonlinear optical mixing processes, such as the coherent anti-Stokes Raman spectroscopy. Because of the simplicity of the experimental arrangement, the easy eliminating of the intense fundamental laser beam and the capability of making nanosecond measurements of the quantities without the need of a fast detector, this technique may have a wide range of applicability to the study of atomic and molecular states as well as the detailed dynamics of the coherent process.

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