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Resonant wave mixing in I_2 with nonsynchronous pulses

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A technique of third-harmonic generation (THG) with nonsynchronous pulses is applied to study the dynamics of resonant wave mixing. A circularly polarized laser pulse is focused into a cell containing I_2 vapor to create the coherent dipole moments. An oppositely circularly polarized pulse is then focused into the same region to generate the third harmonic. Since no THG is produced by any individual pulse, correlated THG can be easily measured without using any fast detection scheme. A theory is presented to explain the measured coherent lifetime of approximately 1 ns. The technique of wave mixing with two linearly polarized pulse is applied to study saturation in resonant THG and to measure the homogeneous relaxation rate of the molecular states. This technique is also applied to study the photon echo generating process.

I. INTRODUCTION

Resonant third-harmonic generation (THG) in atomic[1-10] and molecular vapor[11] has attracted considerable attention as a means of extending coherent radiation sources to the vacuum ultraviolet region of the spectrum. Since a single-quantum resonance is associated with strong linear absorption, the two-quantum resonant scheme is applied in most of the work on resonant THG. Recently, it was shown by Tai and Dalby[12] that with simultaneous resonances in one- and two-quantum transitions, the efficiency of THG in I_2 can be much higher than that due to resonance only in the two-quantum transition under similar conditions. By measuring the intensity of the resonant THG in I_2 as a function of a magnetic field, the modulation of the interference of the oscillating dipoles of molecules with a different magnetic quantum number was also studied.[13] The symmetry and the gyromagnetic ratio of the excited resonant states can be determined by this technique. This experiment of Hanle-effect-like level crossing in THG indicates that, in the case of resonant enhancement, the excited molecule has a coherent lifetime of the order of the reciprocal of the Doppler linewidth. In order to interpret the experiment on coherent level crossing correctly, it is important to have this coherent lifetime measured directly. Reported work on wave mixing with two circularly polarized pulses[14,15] showed that the decay of the coherence may be faster than the theoretical predictions that assume only velocity dephasing in some cases.

Experiments on transient effects in resonant THG include photon-echo-like and free-induction-like effects in correlated THG by temporally separated pulses. Transient effects on wave mixing can be applied to study the coherent lifetime, the longitudinal relaxation time, the oscillator strength, and the collision cross section of excited molecules. This technique also has the advantage of being able to achieve full overlap of the pulses, satisfy the phase-matching condition and measure events in the subnanosecond time scale without the need of using a fast detector. This technique may also provide a basis of applying the resonant enhancement of the one-quantum transition to the multiresonant wave mixing by overcoming the linear absorption.

In Sec. II of this paper a theoretical analysis of the resonant THG in a molecular (including atomic) gas that is prepared in a mixed state is presented. The total nonlinear dipole moment of the sample which is responsible for the harmonic generation (including wave mixing) in a cell containing molecules or atoms with a Maxwell velocity distribution will be discussed in Sec. III. The experimental arrangement and the data analysis will be presented in Sec. IV.

II. FUNDAMENTAL EQUATIONS

The theory of resonant THG in gases has been widely discussed.[3,8,16-19] However, in most of the previous calculations, the nonlinear dipole moment is calculated in a steady state that requires a laser of long pulse duration. In order to interpret the experiment results of the transient effects of THG, I will present a general discussion of THG by a probe pulse from a sample prepared in a mixed state by one or more pulses prior to the probe beam. For convenience, all the pulses are assumed to be short compared to the radiative relaxation rate of the particles. Since the pulses are of a duration less than 5 ns while the lifetime of the excited states of molecules are of the order of 1 μs, this assumption is justified. The process of the delayed wave mixing is shown in Fig. 1. Before the time $t=0$, the molecule has been irradiated by one or more pulses of polarization σ_- (σ_+). Because of the conservation of angular momentum, no THG is produced by each

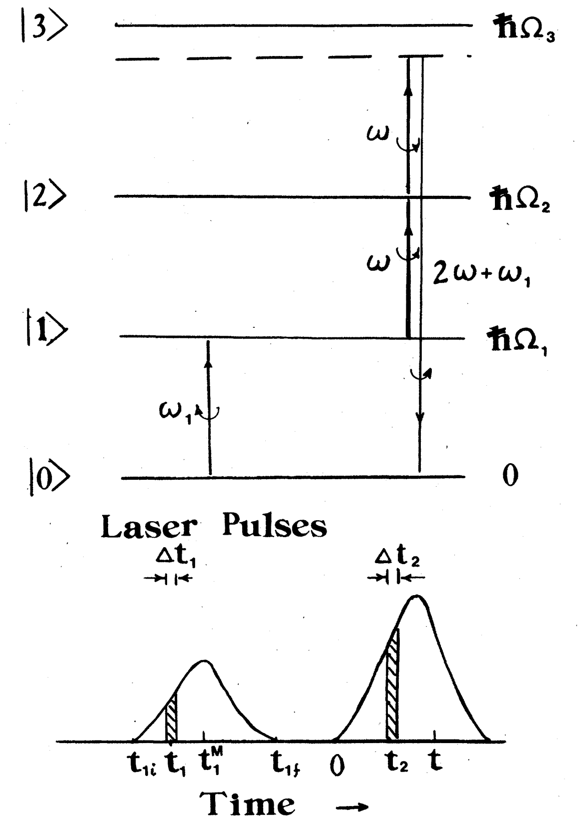

FIG. 1. Schematic diagram of the resonant molecular states and the laser-pulse sequences in the third-harmonic generation correlated to two circularly polarized pulses. Calculation of the macroscopic nonlinear dipole moment of the system at time t is performed by dividing the time that the laser pulses are on into many small time intervals.

individual pulse.[20] The state of the molecule in this sample, at time $t=0$, may be expressed in the general form of the density matrix ρ of a four-level molecule given by

$$\rho=\begin{bmatrix} \rho_{00} & \rho_{01} & 0 & 0 \\ \rho_{10} & \rho_{11} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} . \tag{1}$$

Here we have assumed that only the transition $(0-1)$, which is a $\Delta m=-1$ $(+1)$ transition, is in resonance with the pulses before $t=0$, where m is the magnetic quantum number of the ground state. The time evolution of the molecule is determined by the Schrödinger equation

$$\frac{d\psi(t)}{dt}=-i\hbar^{-1}(H_0+V)\psi(t) . \tag{2}$$

Here H_0 is the Hamiltonian for the unperturbed molecule and V represents the molecule-excitation field interaction.

At $t=0$ a pulse of duration τ and polarization σ_+ (σ_-) is turned on. For the molecule at position $\vec{r}$, the electric field it sees is given by

$$\vec{E}_\pm=\varepsilon[\hat{x}\cos(\omega t-\vec{k}\cdot\vec{r})\pm\hat{y}\sin(\omega t-\vec{k}\cdot\vec{r})] . \tag{3}$$

Here ε is the amplitude, ω is the angular velocity, and $\vec{k}$ is the wave vector of the electric field. If the dipole moment is defined as $\vec{d}'=e(\vec{x}+\vec{y}+\vec{z})$, then in the dipole approximation, the perturbation V becomes

$$V=e\left(\frac{x\pm iy}{2}\right)\varepsilon\exp[-i(\omega t-\vec{k}\cdot\vec{r})]+\text{c.c.}, \tag{4}$$

where e is the charge of the electron. Now we define the transition dipole moment

$$d_{ij}=\left\langle i\left|\frac{e(x\pm iy)}{2}\right|j\right\rangle,$$

where the basis vectors are chosen to be the time-independent eigenstate of H_0, given by

$$H_0=\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \hbar\Omega_1 & 0 & 0 \\ 0 & 0 & \hbar\Omega_2 & 0 \\ 0 & 0 & 0 & \hbar\Omega_3 \end{bmatrix} , \tag{5}$$

where $\hbar\Omega_n$ $(n=1,2,3)$ is the unperturbed energy of the nth molecular state. We now have

$$V=\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -d_{12}^*\varepsilon\exp[i(\omega t-\vec{k}\cdot\vec{r})] & 0 \\ 0 & -d_{21}\varepsilon\exp[-i(\omega t-\vec{k}\cdot\vec{r})] & 0 & -d_{23}^*\varepsilon\exp[i(\omega t-\vec{k}\cdot\vec{r})] \\ 0 & 0 & -d_{32}\varepsilon\exp[-i(\omega t-\vec{k}\cdot\vec{r})] & 0 \end{bmatrix} . \tag{6}$$

Now by transforming to a "triply rotating" frame[19] we can remove the explicit time-dependency from the Hamiltonian. This transformation is accomplished by defining an interaction-picture wave function $\tilde{\psi}(t)=\exp(iAt)\psi(t)$ with

$$A=\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & \Omega_1 & 0 & 0 \\ 0 & 0 & \Omega_1+\omega=\Omega_2 & 0 \\ 0 & 0 & 0 & \Omega_1+2\omega \end{bmatrix} . \tag{7}$$

Here we have assumed that the pulse turned on at $t=0$ is in resonance with the transition $(1-2)$ which is a $\Delta m=+1(-1)$ transition. In general this pulse is not in resonance with the $(2-3)$ transition. The wave function ψ then satisfies $d\tilde{\psi}/dt=-i\hbar^{-1}\tilde{H}\tilde{\psi}$, where $\tilde{H}=\exp(iAt)(H_0+V-A\hbar)\exp(-iAt)$ is given by

$$\tilde{H}=\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & b^* & 0 \\ 0 & b & 0 & c^* \\ 0 & 0 & c & \Delta \end{bmatrix} . \tag{8}$$

Here

$$\begin{aligned} b &= -d_{21}\,\varepsilon\exp(i\vec{k}\cdot\vec{r}) , \\ c &= -d_{32}\,\varepsilon\exp(i\vec{k}\cdot\vec{r}) , \\ \Delta &= \hbar(\Omega_3-\Omega_1-2\omega) . \end{aligned} \tag{9}$$

The density matrix of the system at $t>0$ in the interaction picture can be found from the relation $i\hbar(\partial\tilde{\rho}/\partial t)=[\tilde{H},\tilde{\rho}]$. The off-diagonal density-matrix elements responsible for the generation of a wave oscillating at a frequency of $\Omega_1+2\omega$ are $\tilde{\rho}_{30}$ and $\tilde{\rho}_{03}=\tilde{\rho}_{30}^*$. The equations of motion become

$$i\hbar\,\frac{\partial\tilde{\rho}_{30}}{\partial t}=c\tilde{\rho}_{20}+\Delta\tilde{\rho}_{30} , \tag{10}$$

$$i\hbar\,\frac{\partial\tilde{\rho}_{20}}{\partial t}=b\tilde{\rho}_{10}+c^*\tilde{\rho}_{30} . \tag{11}$$

One should be careful in solving Eqs. (10) and (11) when $\tau>T_2^*$, where T_2^* is the coherent lifetime of the macroscopic nonlinear dipole moment. If we assume that the probe beam is weak and sufficiently short such that $\tau\ll T_2^*$, then the density-matrix element $\tilde{\rho}_{10}$ is essentially the same as that at the initial time $(t=0)$ and we can eliminate $\tilde{\rho}_{20}$ from Eqs. (10) and (11) to arrive at

$$\hbar\,\frac{\partial^2\tilde{\rho}_{30}}{\partial t^2}+i\hbar\Delta\,\frac{\partial\tilde{\rho}_{30}}{\partial t}+cc^*\tilde{\rho}_{30}=-cb\tilde{\rho}_{10} . \tag{12}$$

The solution of Eq. (12) depends on the physical situation. In our experiment, excitation to the level $|3\rangle$ is a virtual transition and $\Delta\gg(4cc^*)^{1/2}$. The solution for $\tilde{\rho}_{30}$ is

$$\tilde{\rho}_{30}=-\frac{b\tilde{\rho}_{10}}{c^*}\left(1-e^{i(cc^*/\hbar\Delta)(t)}\right) . \tag{13}$$

Here we have used the initial condition of $\tilde{\rho}_{30}(0)=[d\tilde{\rho}_{30}(t)/dt]_{t=0}=0$ and we have neglected the small term that is oscillating at frequency $(\Delta/\hbar+cc^*/\hbar\Delta)$ which has an amplitude of $2bc\tilde{\rho}_{10}/\Delta^2$.

For $t\ll\hbar\Delta/cc^*$, we have

$$\tilde{\rho}_{30}=-\frac{ibc\tilde{\rho}_{10}}{\hbar\Delta}\,t . \tag{14}$$

The oscillating dipole moments $\vec{p}$ can be found from the relation $\vec{p}=\mathrm{Tr}(\rho\vec{d})$. After we transform the $\tilde{\rho}$ back to ρ, the nonlinear polarization that oscillates at frequency $\Omega+2\omega$ is given by $\vec{p}^{(\Omega+2\omega)}(t)=\tilde{\rho}_{30}d_{03}+\mathrm{c.c.}$ When Eq. (14) is substituted into the above relation for $\vec{p}^{(\Omega+2\omega)}$, it is clear that the nonlinear polarization for each molecule increases linearly with time for t less than the coherent lifetime T_2^*. If the pulse duration τ is much less than the coherent lifetime, all the dipole moments of the atoms are oscillating coherently and the total nonlinear polarization increases with time and cannot be expressed simply as $\vec{P}^{(\Omega+2\omega)}(t)=\chi^{(\Omega+2\omega)}\vec{E}^{\Omega}(t)\vec{E}^{(\omega)}(t)\vec{E}^{(\omega)}(t)$, especially if there is no overlap of the pulses $\vec{E}^{\Omega}$, $\vec{E}^{\omega}$ in time.

It will be shown in Sec. III that the coherent lifetime, of the order of 1 ns in the visible spectrum, is much shorter than the homogeneous relaxation rate Γ_{ij} of the dipole moment of each individual molecule. As a result, $\tilde{\rho}_{30}$ is approximately $-(ibc\tilde{\rho}_{10}/\hbar\Delta)T_2^*$ if τ is much longer than T_2^*. This conclusion should also be valid for all resonant THG and wave mixing.

III. APPLICATION

A. Wave mixing with two pulses

1. Circularly polarized light

The THG with two circularly polarized and temporally separated laser pulses can be applied experimentally to the measurement of the coherent lifetime T_2^* directly.

Consider a sample being irradiated by two circularly polarized pulses of polarization σ_-, σ_+ which are separated in time by the time duration T. As shown in Fig. 1, the only resonant transition caused by the first pulse is the transition $|0\rangle-|1\rangle$, the only nonzero off-diagonal density-matrix elements are $\rho_{10}(t)=\rho_{01}^*(t)$. The Hamiltonian is $H=H_0-\vec{d}\cdot\vec{E}_1$. The equation of motion is

$$\dot{\rho}_{ij}=-\frac{i}{\hbar}\,[H,\rho]_{ij}-\Gamma_{ij}\rho_{ij} . \tag{15}$$

Here Γ_{ij} is the phenomenological relaxation rate of ρ_{ij}, which includes decay due to spontaneous emission, collisional dephasing, etc. $\vec{E}_1$ is given previously with ε, ω replaced by ε_1, ω_1. We have[21]

$$\tilde{\rho}_{10}(t) = \frac{-i\alpha}{2|\alpha|} \sin|\theta_1|\, e^{-\Gamma_{10}(t - t_1^m)} , \tag{16}$$

where

$$\theta_1 = \frac{2d_{10}}{\hbar} \int \varepsilon_1(\vec{x}, t') e^{-ik_1 \cdot \Delta\vec{r}_1(t')} e^{-\Gamma_{10}\Delta t}\, dt' ,$$
$$\alpha = -d_{10}\varepsilon_1 \exp i(\vec{k}_1 \cdot \vec{r}_1). \tag{17}$$

Here $\Delta\vec{r}(t') = \vec{r} - \vec{r}_1^m$, $\vec{r}_1^m$ is the location of the molecule when the pulse has its maximum intensity. It is also assumed that the electric field of the jth beam is given by

$$\vec{E}_j = \sqrt{2}\,\varepsilon_j[\hat{x}\cos(\vec{k}_1 \cdot \vec{r} - \omega_1 t) \mp \hat{y}\sin(\vec{k}_1 \cdot \vec{r} - \omega_1 t)] ,\quad t_j - \frac{\tau_j}{2} < t < t_j + \frac{\tau_j}{2} . \tag{18}$$

Here $j = 1$. For a pulse short enough so that the molecule can be considered stationary, $|\theta_1|$ is simply the tipping angle produced by the first pulse. Now one can solve Eqs. (10) and (11) in the general case that the pulse duration is comparable or longer than the coherent time T_2^* by dividing the time period that the probe (second) pulse is on into many small intervals of $\hbar/\Delta < \delta t \ll T_2^*$. During the time δt, $\tilde{\rho}_{20}$ may be regarded as a constant and the solution of Eq. (15) is

$$\tilde{\rho}_{30} = -\frac{c\tilde{\rho}_{20}}{\Delta} \exp\left(\frac{i\Delta}{\hbar}\, t\right) + \frac{c\tilde{\rho}_{20}}{\Delta} . \tag{19}$$

Since $\rho_{30} = \tilde{\rho}_{30}\exp[-i(\omega_1 + 2\omega)t]$, the part of $\tilde{\rho}_{30}$ that is responsible for the generation of the wave oscillating at frequency $\omega_1 + 2\omega$ is given by $c\tilde{\rho}_{20}/\Delta$. This result indicates that $\tilde{\rho}_{30}$ is simply proportional to $\tilde{\rho}_{20}$. Now since $\tilde{\rho}_{30}$ is small, $\delta\tilde{\rho}_{20}$ can be solved from Eq. (15) by neglecting the term $c^*\tilde{\rho}_{30}$. The result is

$$\delta\tilde{\rho}_{20} = -\frac{i}{\hbar}\, b\tilde{\rho}_{10}\delta t . \tag{20}$$

As a result,

$$\tilde{\rho}_{30} = \frac{c}{\Delta}\,\tilde{\rho}_{20}$$
$$= \frac{c}{\Delta} \int \frac{-ib\tilde{\rho}_{10}}{\hbar}\, dt . \tag{21}$$

Similarly we can divide the time period that the first pulse is on into many small time intervals and write

$$\tilde{\rho}_{10} = \int_{t_{1i}}^{t_{1f}} \frac{\partial\tilde{\rho}_{10}}{\partial t_1}\, dt_1 . \tag{22}$$

Here we have assumed that the first pulse has lasted from t_{1i} to t_{1f}. If the first pulse is also weak, we can write

$$\tilde{\rho}_{10}(t') = \int_{t_{1i}}^{t_{1f}} -\frac{i\alpha}{\hbar}\, e^{-\Gamma_{10}(t'-t)}\, dt_1 . \tag{23}$$

The total radiating dipole moment $\vec{p}_{13}^{NL}$ at $\vec{r}$ is proportional to the sum of the nonlinear dipolement $\vec{p}^{NL} = \tilde{\rho}_{30}d_{03} + \text{c.c.}$ of all molecules at $\vec{r}$. This sum is equivalent to the integral of $\vec{p}^{NL}$ over the thermal velocity distribution $n(v) = n(0)\, e^{-v^2/v_D^2}$. Here $n(0)$ is a constant and $v_D = 2k_BT/m$, k_B is the Boltzmann constant, T is the absolute temperature, and m is the molecular weight. If saturation can be neglected, the total polarization is proportional to:

$$\exp i[(\vec{k}_1 + 2\vec{k}) \cdot \vec{r} - (\omega_1 + 2\omega)t]\, e^{-\Gamma_{10}(t - t_1)}$$
$$\times \int\int\int d\vec{v}\, dt_1\, dt_2 \exp\{-i\vec{v} \cdot [\vec{k}_1(t - t_1) + \vec{k}(t - t_2)]\}\, \varepsilon_2(t)\varepsilon_1(t_1)\varepsilon_2(t_2)^* e^{-v^2/v_D^2} . \tag{24}$$

The term $\exp i[(\vec{k}_1 + 2\vec{k}) \cdot \vec{r} - (\omega_1 + 2\omega)t]$ describes the macroscopic coherence of the sample which is the average phase at each point as a function of $\vec{r}$. The radiation at frequency $\omega_1 + 2\omega$ emitted by a molecule will remain in phase with the radiators it passes if it is a traveling wave with the form $\exp i[\vec{k}_3 \cdot \vec{r} - (\omega_1 + 2\omega)t]$. From this we have the familiar phase-matching condition $\vec{k}_1 + 2\vec{k} = \vec{k}_3$.

In this work $\vec{k}_1 = \vec{k}$. The magnitude of the total polarization at $\vec{r}$ is given by

$$\vec{P}^{NL}(\vec{r}, t) \propto \int_0^t \int_{t_{1i}}^{t_{1f}} \int_{-\infty}^{\infty} dv_z\, dt_1 dt_2\, \varepsilon_1(t_1)\varepsilon_2^2(t_2) e^{-v_Z^2/v_D^2} e^{iv_z[k_1(t-t_1)+k(t-t_2)]}\, e^{-\Gamma_{10}(t-t_1)} . \tag{25}$$

Here v_z is the velocity of the molecule in the direction of $\vec{k}$. The integration of Eq. (28) depends on ε_2 and ε_1. If the pulse duration τ is so short that $2v_D k_2 \tau \ll 1$, then we have $k(t-t_2) \approx 0$, $k_1(t_{1f}) \approx k_1 t_{1i} \approx k_1 t_1^m$. After carrying out the integration over the velocity distribution, we have

$$\vec{P}^{NL}(\vec{r},t) \propto \sqrt{\pi}\, v_D e^{-(v_D^2/4k_1^2)\Delta t^2} e^{-\Gamma_{10}\Delta t} \times \int_0^t \varepsilon_2^2\, dt_2 \int_{t_{1i}}^{t_{1f}} \varepsilon_1(t_1)\,dt_1 \;. \tag{26}$$

Here $\Delta t = t - t_1^m$ and t_1^m is the time that ε_1 has its maximum value. The total THG is proportional to $\int [\vec{P}^{NL}(\vec{r},t)]^2\, dt$, or varies with

$$e^{-v_D^2(t-t_1^m)^2 k_1^2/2} e^{-2\Gamma_{10}(t-t_1^m)} \left(\int_0^t \varepsilon_2^2\, dt_2\right)^2 \times \left(\int_{t_{1i}}^{t_{1f}} \varepsilon_1(t_1)\,dt_1\right)^2 \;. \tag{27}$$

As a result, "decay" of the correlated THG is composed of two factors, the inhomogeneous coherent decay given by $e^{-v_D^2(t-t_1)^2 k_1^2/2}$, and the incoherent homogeneous decay given by $e^{-2\Gamma_{10}(t-t_1)}$. In general, Γ_{10} depends on the pressure and can be measured by the technique of photon-echo experiment or photon-echo-like three-pulse correlated THG to be discussed later. At low vapor pressure Γ_{10} is essentially the decay due to spontaneous emission and is of the order of ($1\,\mu\mathrm{s}^{-1}$). The term corresponding to the coherent decay, $e^{-v_D^2(t-t_1)^2 k_1^2/2}$ is nonexponential. It decreases slowly when $\Delta t = t_1 < \sqrt{2}/v_D k_1 \equiv T_2^*$ and decreases quickly when $\Delta t > T_2^*$. The coherent lifetime may be written as

$$T_2^* = \frac{1}{\pi}\left(\frac{\ln 2}{2}\right)^{1/2} \frac{1}{\Delta \nu_D} \;. \tag{28}$$

Here $\Delta\nu_D$ is the Doppler linewidth. The Doppler width of the first resonant state of I_2 in this experiment is approximately $(5\ \mathrm{ns})^{-1}$ and the coherent lifetime is about 0.96 ns, which is much shorter than the homogeneous lifetime. Since the coherent time is inversely proportional to the Doppler width, resonant enhancement in the one-quantum transition may be more favorable than that in the two-quantum transition in the THG.

Because of the important role played by the coherent lifetime on THG, in general, it may not be justified in writing the standard expressions for the nonlinear susceptibility[18] as

$$\chi_R^{(3)} = \mathrm{const} \int dv\, \exp(-v^2/v_D^2) \times \frac{1}{[\omega - \Omega_{21}(1 - v/c) \pm i\Gamma_{ij}]} \tag{29}$$

for the THG in a gas medium by a short pulse. In the above formula, the nonlinear susceptibility $X_R^{(3)}$ is calculated from the summation of the dipole moment of the different molecules. However, in this formula, the nonlinear susceptibility for a single molecule, as given by const/ $[\omega - \Omega_{21}(1 - v/c) \pm i\Gamma_{ij}]$, is the result of integration over a time period longer than $1/\Gamma_{ij}$. It is not clear that this formula can be applied to explain the THG produced by a short pulse. Nor can it be applied to explain the transient effects.

2. Linearly polarized light

Saturation of the THG in gases may be caused by the loss of molecules participating in the production of THG. Molecules excited to the upper states have a coherent lifetime of T_2^*. After staying in the excited state for a time $t > T_2^*$, the excited molecules can no longer participate in the process of resonant coherent emission (including THG). The loss of molecules from the ground state in the process of resonant THG can be measured by the technique of correlated THG with linearly polarized light. After the first linearly polarized pulse, the density matrix may have the general form

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} & \rho_{02} & \rho_{03} \\ \rho_{10} & \rho_{11} & \rho_{12} & \rho_{13} \\ \rho_{20} & \rho_{21} & \rho_{22} & \rho_{23} \\ \rho_{30} & \rho_{31} & \rho_{32} & \rho_{33} \end{pmatrix} \;. \tag{30}$$

When the second linearly polarized pulse is on the induced nonlinear dipole moments oscillating at frequency 3ω (or $\omega_1 + 2\omega$, $2\omega + \omega$ if $\omega_1 \neq \omega$) will be proportional to $\tilde{\rho}_{03}\, d_{30} + \mathrm{c.c.}$ and

$$\tilde{\rho}_{03} = (\tilde{\rho}_{00}\, \alpha_{01}\, a_{12}\, b_{23}) + \cdots \tag{31}$$

(where the ellipsis represents terms proportional to $\tilde{\rho}_{10}$, $\tilde{\rho}_{21}$, etc.)

If the second pulse is separated from the first pulse by $\Delta t \gg T_2^*$, contributions from terms depending on the off-diagonal density-matrix elements are negligible and the THG produced by pulse 2 is simply proportional to ρ_{00}^2. By measuring the intensity of the THG due to the second pulse as a function of the intensity and polarization of the first laser pulse, or as a function of the time delay between the two pulses, we can measure the relaxation rate of the system and study the mechanism of saturation due to the loss of molecules from the ground state.

B. Wave mixing with three pulses

The two-pulse photon echo has been studied extensively.[22-26] The echo-generating coherent state can also be monitored by the technique of correlated THG. Since THG can be easily separated from the primary beam, no optical shutter nor magnetic field is needed to prevent the saturation of a detector by the intense laser beam. Phase matching and full overlap of the pulses can also be achieved. The technique of correlated THG may also be extended to study echo effect in states not accessible to one-quantum transition by creating and monitoring the coherence in the excited states by multiquantum transitions. Work on photon-echo-like three-pulse correlated THG in I_2 will be reported in another paper.[27]

IV. EXPERIMENT

A. Three-pulse correlated THG

THG in I_2 is enhanced by simultaneous resonances in one- and two-quantum transitions.[12] Since the laser power in this work is less than 50 kW, coherence in the two-quantum state created by the first one or two pulses may be neglected. Since the coherent lifetime of the two-quantum state is shorter than that of the single-quantum state and the three-pulse correlated THG is essentially a fifth-order effect, there should be little, if any, deviation in experiment caused by neglecting the possibility of the $\omega_1+\omega_1+\omega_2$ process.

The experimental setup for the work of pulse-correlated THG is very simple. The setup for three-pulse correlated THG is shown in Fig. 2. A NRG DL-0.03 grating tuned dye laser pumped by a NRG-0.9-5-270 nitrogen laser provides ~100 μJ/pulse pulses of bandwidth approximately 0.3 Å at wavelength 5754 Å. The laser beam is collimated by a 70-cm focal-length lens and is split into two linearly polarized pulses polarized perpendicular to each other by a Glan prism. One of the pulses is further split into two pulses by a silver-coated beam splitter. After a proper arrangement of mirrors to achieve the required time delay between the three pulses, they are realigned by using another Glan prism and a mirror. After passing through a quarter-wave plate and an iris of diameter 2 mm, they were focused by a $f=20$ cm lens to the center of a 5-cm-long quartz cell containing pure I_2 vapor at the room temperature corresponding to an I_2 pressure of 0.2 Torr. THG is separated from the primary beam by a prism and is focused by a quartz lens of a focal length 30 cm to an EMI G-26G 315 rubidium telluride ultraviolet tube protected by a narrow-band uv interference filter. The output of the tube is fed into a PAR 160 boxcar integrator and is recorded by a chart recorder. The power of the pulses are measured with a Molectron J-3 joulemeter.

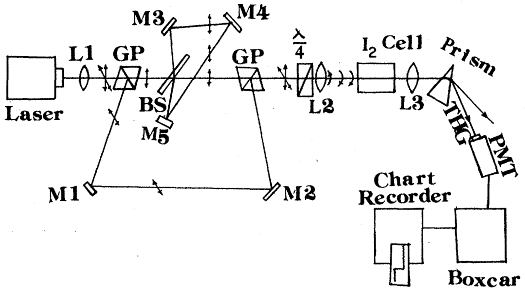

FIG. 2. Schematic diagram of the experimental apparatus of three-pulse correlated third-harmonic generation. Unpolarized laser pulse from the dye laser is collimated with a lens ($L1$) and is split into two linearly polarized beams by a Glan prism (GP). One of the beams is further split into two beams by a beam splitter (BP). After being delayed by the mirrors ($M1$-$M5$) the three beams are realigned to superimpose on each other by another Glan prism. Those beams are converted by a quarter-wave plate ($\lambda/4$) to circularly polarize 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.

With the power of the pulses as: 6 μJ/pulse (first pulse), 15 μJ/pulse (second pulse), and 40 μJ/pulse (third pulse) and the time delay between the peak of the pulses as $T_{21}=7.0$ ns, $T_{32}=7.2$ ns, the correlated THG is much more intense than the two-pulse correlated THG between pulses 2 and 3. The relative intensity of the three pulse correlated THG as compared to the THG by the probe (third) beam if the probe beam is linearly polarized is

$$\frac{I\text{ (correlated THG)}}{I_p\text{(THG by linearly polarized probe beam)}} \cong 3\% \;.$$

Since no decay of the three-pulse correlated THG is observed with a 20-ns time delay between the pulses (t_{31}), one arrives at the conclusion that $1/\Gamma_{10} \gg 20$ ns, as is expected from the lifetime of the excited state.

B. Wave mixing with two circularly polarized pulse

By removing the silver-coated beam splitter, one has the experimental setup for the two-pulse correlated THG. By changing the time delay between the two pulses, a curve of the decay of the correlated THG is recorded. As shown in Fig. 3, the intensity of the correlated THG decreases rapidly when the time delay between the two pulses is longer than 5 ns. The laser pulse has the form shown in Fig. 4. Since the two pulses have a maximum duration of approximately 5 ns which is longer than the coherent lifetime of approximately 1 ns, correlated THG should be calculated by the following equation:

$$\underline{P}^{NL} \propto \int_{t_{2i}}^{t_{2f}} \int_{t_{1i}}^{t_{1f}} \varepsilon_1(t_1)\varepsilon^2(t_2)e^{-v_D^2\{[(t-t_1)k_1+(t-t_2)k]^2/4\}} \times dt_1\, dt_2 \,. \qquad (32)$$

It is clear that the correlated THG will be small unless the separation between the two pulses, or $t_{2i} - t_{1f}$, is less or comparable to T_2^*. T_2^* derived from the data is approximately 1 ns, and agrees well with the theory. Comparison of this result to that of the three-pulse correlated THG, one has $T_2^* \ll 1/\Gamma_{01}$. This relation justifies the neglect of the effect of the homogeneous decay to our calculation of T_2^* and $\vec{P}^{NL}$. From this work it is clear that although the oscillating dipoles created in the sample have a lifetime of $1/\Gamma_{10}$, they can no longer participate in the process of coherent THG if they have been excited for a time t longer than T_2^*. Spontaneous decay and collisional deexcitation should be the only processes for these excited molecules to relax to the ground state. As will be shown in the experiment of THG correlated to two linearly polarized light pulse, incoherent excited molecules may be responsible for the saturation of the THG.

With the technique of THG correlated to two circularly polarized pulses described above, very high sensitivity is achieved in measuring the correlation. In the present work, a signal of correlated THG equal to 1/1000 of the THG by the two pulses if they are linearly polarized can be easily detected. The main limitation of this technique is the background level which may be caused by the imperfect polarization of the pulses. Since the time delay is measured from the optical path of the pulses and no THG is produced by each individual pulse, no fast detector or timing is needed.

C. Wave mixing with two linearly polarized pulse.

The process of relaxation of the system of the I_2 cell to its equilibrium state can be studied by the technique of THG correlated to two linearly polarized light. By removing the quarter-wave plate from the experimental setup for the two-circularly-polarized-pulse correlated THG experiment, one has the experimental setup for this experiment. Figure 5 shows the intensity of the THG due to the probe beam measured as a function of the power of the first pulse. One may define the correlated THG as

Correlated THG = (THG with both beams on)
– (THG of the first pulse only)
– (THG of the second pulse only).

Since the THG produced by the first pulse is not affected by the second pulse, the correlated THG is the decrease in the THG of the second pulse caused by the first pulse. Since the intensity of the THG is proportional to ρ_{00}^2, one has

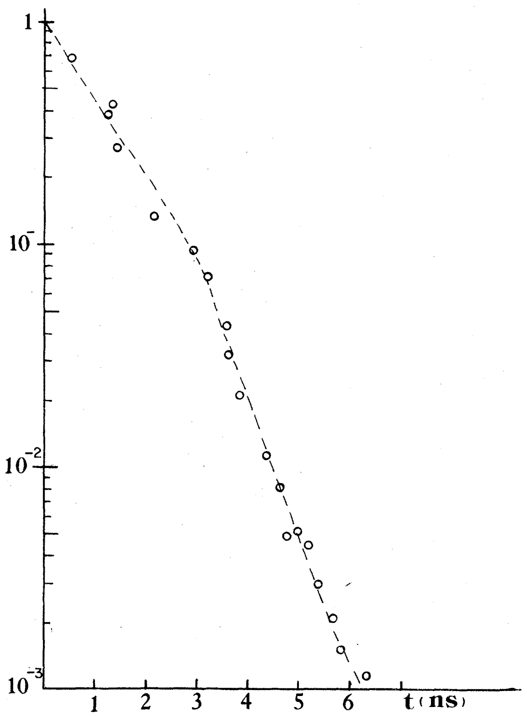

FIG. 3. Normalized third-harmonic generation with two circularly polarized light pulses measured as a function of the delay between the two pulses. The time delay between the two pulses is measured from the differences in their optical path and is accurate to 0.01 ns.

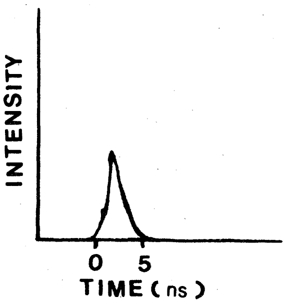

FIG. 4. Intensity of the laser pulse measured by a Hadron 105C S-1 photodiode. The rise time of the photodiode is 0.3 ns. The pulse is recorded from the trace on a Tektronix 519 oscilloscope.

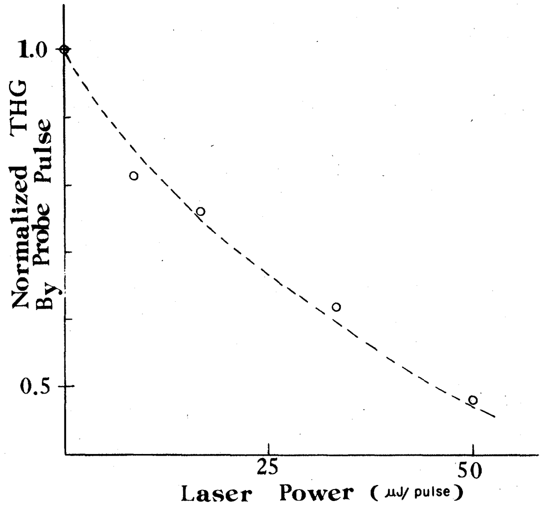

FIG. 5. Normalized third-harmonic generation of the probe beam measured as a function of the intensity of the first pulse. The time delay between the two pulses is 7.4 ns.

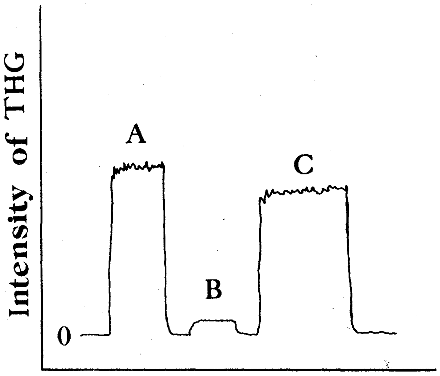

FIG. 6. Recorded data of the THG with two linearly polarized light pulses in arbitrary units. (A) THG by the probe pulse alone. (B) THG by the first pulse alone. (C) THG when both the pulse 1 and the probe pulse are present. Note that because of the saturation effect on the THG of the probe pulse caused by the pulse 1, THG in case (C) may be less than that in (A).

$$\rho_{00} \propto \left(\frac{\text{THG of pulse 2+correlated THG}}{\text{THG of pulse 2}}\right)^{1/2} . \tag{33}$$

As shown in Figs. 5 and 6, the result of this experiment indicates that there is considerable saturation even with the power of the first beam as low as 50 μJ/pulse. Experiment also indicates that no relaxation of the system to its equilibrium is detectable with the separation of the two-pulse $t_{21} = 10$ ns. As a result, one has $1/\Gamma_{00} \gg 10$ ns. This result also agrees with the expected lifetime of the molecule and the relaxation rate of the system.

CONCLUSION

The technique of pulse correlated THG in gas has high sensitivity in studying the excited states of molecules or atoms as well as the study of the coherent process of harmonic generation and wave mixing. It can be applied to study events in the subnanosecond time scale without the need of using any fast detector or timing. Because of the simplicity of this technique, it should have wide application.

Coherent lifetime of the excited molecules measured by this technique, approximately 1 ns in the visible spectrum, is much shorter than the homogeneous lifetime in a dilute gas. As a result, the coherent lifetime may be an important limiting factor on the efficiency of the resonant wave mixing in gases. By using a short 2π pulse to excite the molecules to the one-quantum state and using another intense laser pulse resonant to the $|1\rangle - |2\rangle$ transition simultaneously to generate wave mixing may overcome the linear absorption of the sample.

In the work of THG in I_2, since the THG is not limited by the nonlinear photoionization which is a five-photon process, loss of phase coherence of the excited molecules after being excited for a period of $\Delta t > T_2^*$ may be the main mechanism of the partial saturation of the THG. The direct measurement of the coherent lifetime may also justify the technique of Hanle-effect-like level crossing experiments in the coherent process of wave mixing.

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