PHOTON ECHO IN THE MOLECULAR GASES BCl₃ AND SF₆

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The photon echo effect has been observed in BCl_3 and SF_6, and the collision dephasing time T_2 has been measured for these gases. The polarization dependence of the photon echo in SF_6 has been investigated for several CO_2 laser emission lines and certain conclusions have been drawn with regard to the transitions responsible for the formation of the echo at these frequencies.

NONLINEAR effects which appear during the coherent interaction between pulsed radiation and media showing resonance absorption have attracted deserved interest because they can serve as a convenient means of investigating the more important parameters of such media. The coherence of the interaction which, in this case, means that

$$\tau_p \ll T_2, \tag{1}$$

i.e., the interaction time or the pulse length is much less than the transverse relaxation time, lead to self-induced transparency, the photon echo, and the nutation effect. These phenomena were first investigated by Hahn[1] by the NMR method, and subsequently a number of workers obtained optical analogs of these phenomena.[2] The work of Patel[3] deserves particular attention. Patel was the first to observe self-induced transparency and the photon echo in the infrared part of the CO_2 laser emission in SF_6 gas.[3] In our previous paper [4] we used the self-induced transparency of BCl_3 to estimate such parameters of this gas as the dipole moment matrix element, the time T_2, and the number of particles participating in the effect. This gas is of particular interest because it has already been widely used.[5]

The present paper is concerned with the photon echo in BCl_3 and SF_6 gases. These studies have enabled us to obtain a reliable value for T_2 in BCl_3 and to use the polarization dependence to draw certain conclusions with regard to the type of the absorption transition in SF_6, using several lines in the CO_2 laser emission.

1. Consider a plane-parallel beam of linearly polarized radiation incident on the medium. We shall suppose that the radiation can be represented by $E(z, t) = e\mathcal{E}(z, t) \cos(\omega t - kz)$, where e is the direction of polarization and $\mathcal{E}(z, t)$ is the envelope, and that this satisfies the condition

$$\theta = \mu_0 \int \mathcal{E}(z, t)\, dt = \frac{\pi}{2}, $$

where μ_0 is the dipole moment matrix element and τ_p is the pulse length. It is well known that a pulse of this kind will produce the maximum polarization of the medium in the propagation region. The set of particles in a unit volume of the medium, which are taken by the $\pi/2$ pulse to the upper excited state, forms an ensemble of dipoles for which the following statements are valid.

a. The ensemble contains only those particles within the unit volume of the medium for which the radiation frequency of the laser pulse has the resonance value, i.e., the frequencies of these particles lie in the range $\omega_0 \pm \delta$ as a result of the Doppler effect, where ω_0 is the center of the Doppler absorption line and the detuning δ is, in our case ($\tau_i \gg T_2^*$), determined by the pulse width $1/\tau_p$ when $\mu_0 \mathcal{E} \ll 1/\tau_p$, and by the Doppler line width $1/T_2^*$ when $\mu_0 \mathcal{E} \gg 1/\tau_p$. In the case of the $\pi/2$ pulse, we have $\mu_0 \mathcal{E} \approx 1/\tau_p$ and, consequently, $1/\tau_p < \delta < 1/T_2^*$.

b. During a time interval which is small in comparison with the transverse relaxation time T_2 the dephasing of the dipole oscillations due to their frequency distribution within the interval $\omega_0 \pm \delta$ leads to a loss of cohereence by the ensemble and, consequently, to the cessation of the dipole radiation by the system practically immediately after the passage of the exciting pulse.

An important point in this context is the fact that the decay of the coherent state of the dipole ensemble, which is due to the above mechanism of inhomogeneous broadening, is not connected with the relaxation processes in the system and, therefore, at least in principle this decay is reversible. A purely conceptual time reversal within the system at some time τ_s will definitely return the ensemble to the initial coherent state at time $2\tau_s$ (τ_s is the separation time for the exciting pulses). The equivalent of the "time reversal" is the application at time τ_s to the ensemble of a perturbation which transforms the particle polarization P_ω to $-P_\omega$. This perturbation can be produced by introducing into the medium at time τ_s a second exciting pulse with $\theta = \pi$. The radiation pulse appearing at time $2\tau_s$ due to the re-establishment of the coherent state of the ensemble is often referred to as the "photon echo."

The theoretical description of the photon echo effect originates essentially from the work of Hahn on the spin echo,[1] and was given by Kurnit in the case of ruby.[2] A more complicated case of the photon echo in gases was discussed in [6].

In this case, the sensemble of molecules is represented by a two-level degenerate system and is described by the density matrix formalism, where the density matrix ρ_t satisfies the following equation of motion:

$$id\rho / dt = [\hat{H}_0 + 2\hat{V}(t)\cos \omega t, \rho], \tag{2}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian and the perturbation $\hat{V}(t) = -e\mathcal{E}(t)\hat{\mu}$ is due to the effect of the pulse

with the envelope $\mathscr{E}(t)$, which is polarized along the direction of $\mathbf{e}$, and $\hat{\mu}$ is the dipole moment operator.

When the solution of Eq. (2) is derived, the pulse field is assumed to be the only external field for the molecules, i.e., the secondary effect of the field connected with the polarization of the medium on the polarization is neglected, which is fully justified if the intensity of the photon echo is much lower than the intensity of the radiation pulses. Moreover, by assuming that $T_2 \gg 2\tau_S$, we eliminate the influence of irreversible dephasing and neglect the detuning δ at the time of application of the pulses, which is equivalent to the condition that $V_{12} \gg \delta$. The last assumption is undoubtedly a substantial idealization under the conditions of our experiment ($V_{12} \approx \delta$). Nevertheless, this does not affect the results of the polarization dependence although it will probably effect the dependence of the photon-echo intensity on the intensity of the exciting pulses.

The polarization of the medium in which we are interested is defined by $\langle \mathbf{P} \rangle = \mathrm{Sp}\,[\mu\rho(t)]$, where $\rho(t)$ is the solution of Eq. (2). The polarization which is independent of δ at time $t = 2\tau_S$ is given by

$$\langle \mathbf{P} \rangle_{\text{echo}} = \frac{i \exp\{-i\delta(t - 2\tau_p)\}}{2(2J+1)} \mathrm{Sp}[\mu \sin(A_2\mu)\sin(2A_1\mu)\sin(A_2\mu)] \quad (3)$$

and is responsible for the appearance of the photon echo at this time. In these expressions $A_1 = \mathbf{e}_1 \int_1 \mathscr{E}(t)\,dt$, $A_2 = \mathbf{e}_2 \int_2 \mathscr{E}(t)\,dt$, and the integrals are evaluated with respect to time within the first and second pulses. The intensity and polarization of the photon-echo pulse is wholly determined by the trace on the right-hand side of Eq. (3):

$$W = \mathrm{Sp}[\mu \sin(A_2\mu)\sin(2A_1\mu)\sin(A_2\mu)], \quad (4)$$

and this quantity is, in fact, analyzed by Gordon.[6] Figures 1a and 1b show the calculated intensity (b) and direction of polarization (a) of the photon echo as functions of the angle between the polarization of the exciting pulses for the vibrational-rotational transitions with the rotational quantum number changes $\Delta J = \pm 1$ (P and R branches), $\Delta J = 0$ (Q branch), and different values of J.

Figure 1a shows that the photon-echo polarization behaves in a different way, depending on the type and number of the absorbing transition. For the P(1) and Q(1) transitions the photon-echo polarization follows the polarization of the second pulse, and the intensity of the echo varies as $\cos^2\psi$. However, for $J > 1$ the echo polarization is a much more complicated function of the angle ψ. For the Q branch, the photon-echo polarization lies within the angle ψ between the polarizations of the pulses, while for the P and R branches it lies outside this angle. For high values of the angular momentum J (Q branch), we can go over to the quasiclassical description, assuming that the dipole-moment distribution over the various degenerate states is continuous. This enables us to express Eq. (4) in terms of analytic functions. When $\theta_2 = 2\theta_1$ and $\psi = 0$

$$W \sim e\mu_0 \left(\frac{3J_{3/2}(\theta_1)}{\theta_1^{3/2}} - \frac{J_{3/2}(3\theta_1)}{(3\theta_1)^{3/2}} \right), \quad (5)$$

where $J_{3/2}$ is the Bessel function, and the parameter θ is determined in the language of the effective dipole
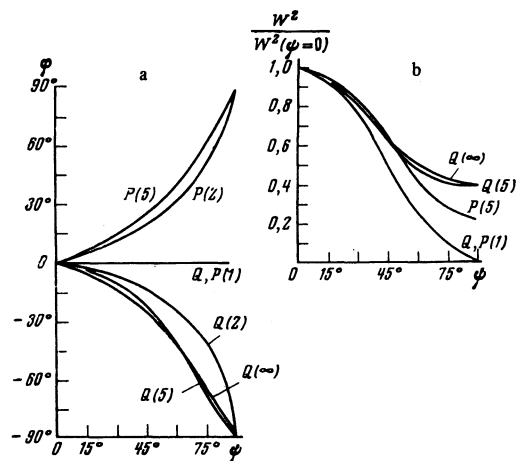

FIG. 1. Calculated polarization dependence of the photon echo: a—angle φ between the polarizations of the echo and of the second exciting pulse as a function of the angle ψ between the polarizations of the exciting pulses; b—dependence of the photon-echo intensity on ψ.

moment μ_0. It is quite clear from this result that the photon-echo intensity is an oscillating function of θ, which falls rapidly with increasing θ. The damped nature of the photon-echo intensity as a function of increasing incident-pulse intensity exists only for a degenerate system and is explained by the large set of values of the dipole moment matrix elements corresponding to different degenerate states. These states behave in the same way only for $\theta < \pi$, but when $\theta \gg \pi$ the macroscopic polarization of the medium vanishes as a result of interference between the individual degenerate states.

We have so far neglected the collision mechanism in our discussion of the photon-echo effect, i.e., we have neglected the irreversible dephasing of the ensemble of molecules, which is fully justified if $T_2 \gg 2\tau_S$. The dependence of the echo amplitude on τ_S when this mechanism is taken into account for $T_2 \geq 2\tau_S$ can readily be established by recalling that the rate of decay of a fully correlated behavior of the ensemble is proportional to $1/T_2$. The photon echo pulse amplitude, in this case, looked upon as a function of the separation time for the exciting pulses, is clearly of the form

$$\mathscr{E}_{\text{echo}} \sim \exp(-2\tau_p / T_2), \quad (6)$$

and the intensity is given by

$$I_{\text{echo}} \sim \exp(-4\tau_p / T_2). \quad (7)$$

It follows that an experimental study of the photon-echo effect in gases can be used to determine the time of collisional dephasing, T_2, from the form of the polarization dependence, and the dependence of the photon-echo intensity on the intensity of the input pulses can be used to draw certain conclusions with regard to the type and number of the transitions responsible for the formation of the photon echo.

2. The apparatus which we employed is shown schematically in Fig. 2. It consists of two doubly Q-switched CO_2 lasers L and L' with discharge tubes having lengths of 1 m and internal diameters of 2.5 cm. The laser resonators are formed by plane-parallel germanium plates 1 and 1', rotating mirrors 2 and 2', a common rotating
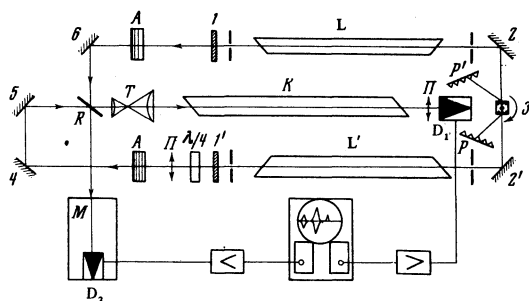
FIG. 2. Schematic diagram of the experimental setup.

mirror 3, and diffraction gratings P and P'. The use of the common rotating mirror 3 is necessary for the synchronization of the times of emission of the two lasers, whereas the two rotating mirrors 2 and 2' can be used to vary the time interval between the radiation pulses within sufficiently broad ranges. The diffraction gratings are used to tune the laser frequencies to the required radiation line, and this is controlled by the monochromator M with a resolution of 0.2 cm^{-1}. Radiation pulses 200 nsec long and having an intensity of 100 W/cm^2 are reduced by the attenuators A, whilst the rotating mirrors 4–6 and the splitter R are used to direct the pulses onto the sample cell K containing the gas under investigation, the length of which is 3 m. The telescope T is used to magnify the beam diameter and, consequently, the number of particles participating in the effect. It is also used to compensate the diffraction divergence and absorption losses. Radiation is detected by Cd-Hg-Te receivers with time constants of 5 nsec (D_1 and D_2). The angle between the polarization directions of the exciting pulses is varied by mounting a $\lambda/4$ plate and the polarizer Π in the beam of one of the lasers.

An experimental study was carried out of the photon echo pulse intensity as a function of the time interval between the exciting pulses and their intensities, and the polarization and intensity of the photon-echo pulse as functions of the angle between the polarization directions of the incominb pulses.

As indicated above, measurements of the intensity of the photon-echo pulse as a function of the separation time between the exciting pulses can be used to determine the irreversible dephasing time T_2.

These measurements were performed in BCl₃. Figure 3 shows photographs of a series of photon-echo pulses recorded for different separation times of the exciting pulses. They illustrate the exponential decay of the photon echo with increasing τ_S, which was mentioned above.

Measurements of the photon-echo intensity as a function of $2\tau_S$ are shown on a semilogarithmic scale in Fig. 4. The time T_2 for BCl₃, calculated from the slope of the straight line, was found to be $T_2 = 27$ nsec/torr. The value of T_2 measured for SF₆ in the same way was found to be $T_2 = 24$ nsec/torr. The accuracy with which T_2 was obtained was 20%, and this was determined by the accuracy with which the gas pressure in the sample cell could be measured with the LT-2 ionization gauge calibrated against a McLeod manometer. It is important to note that the amplitude of the photon echo is not stable even when the amplitude of the exciting pulse is
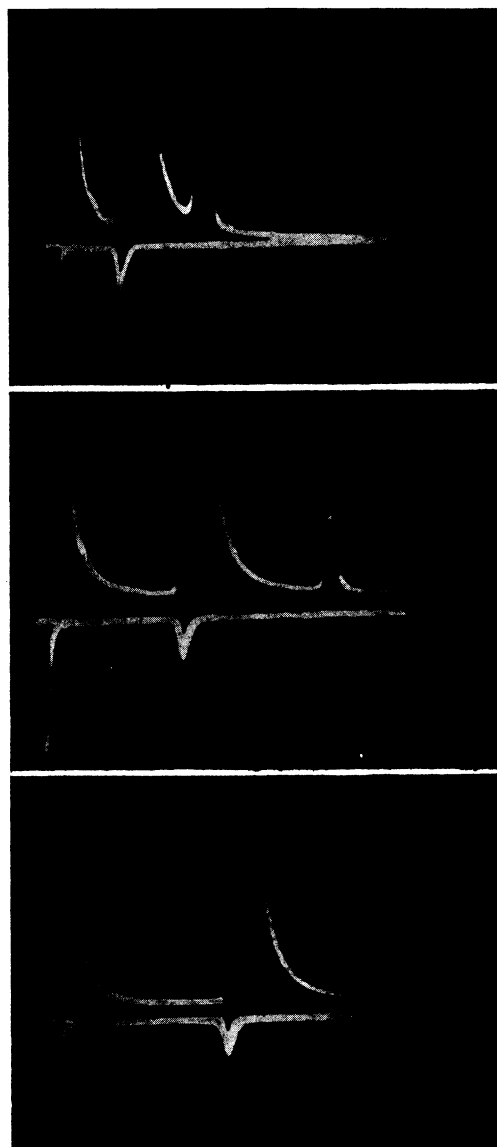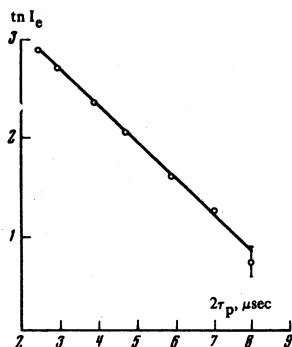

FIG. 3. Photographs of a series of output pulses with τ_S increasing. The third pulse is the photon echo. Its intensity falls exponentially with increasing τ_S and amounts to a few percent of the intensity of the exciting pulses. The lower trace shows the control-channel pulses (D_2). The time scale is 1 μsec.

ideally stable. This fact may be the result of the frequency instability of the lasers within the amplification bandwidth, while the use of a single laser to produce both exciting pulses is experimentally exceedingly difficult because it requires the introduction of microsecond delays. We have therefore measured the maximum values of the photon-echo intensity, when the frequency of the laser and the transition frequency responsible for the echo are equal. This is readily carried out because of the relatively high repetition frequency (25 Hz).

Since the photon-echo amplitude is proportional to the dipole moment matrix element, further investigation of the photon-echo polarization was performed in SF₆ gas, whose dipole moment for the P(16)-P(20) CO₂ lines was higher by an order of magnitude as compared with BCl₃.

Figures 5a and b show the experimental polarization

FIG. 4. Intensity of the photon echo in BCl_3 as a function of the separation time of the exciting pulses. Gas pressure—5×10^{-3} torr.

FIG. 5. Measurements of the polarization dependence of the photon echo in SF_6 at different CO_2 emission lines: □—P(16), ○—P(20), ●—P(18): a—angle φ between echo and second-pulse polarizations as a function of the angle ψ between the polarizations of the exciting pulses; b—echo intensity versus ψ.

dependence of the photon echo in SF_6 gas for the P(16), P(18), and P(20) CO_2 laser lines. For the photon echo at 947.73 cm^{-1} [P916)] the experimental curves are in good agreement with theoretical predictions for Q-branch transitions with sufficiently high J. The weak dependence of the calculated curves in Fig. 1 on J has prevented us from estimating the value of J. However, the experimentally observed attenuation of the photon-echo intensities with increasing intensity of the incident pulses lead us to the conclusion that the transition responsible for the formation of the echo at 947.73 cm^{-1} [P(16)] is highly degenerate, and the value of J is high. The photon echo was also observed on the second maximum of the relation given by Eq. (4) for $\theta_1 = 3\pi/2$, but we did not detect the passage through zero of the echo intensity for $\theta_1 = \pi$. In these experiments the point $\theta = \pi$ was found with the aid of the self-induced transparency effect by using the inflection on the absorption curve and the strong distortion of the pulse with $\theta \approx \pi$.[4]

The dependence of the photon-echo intensity on the intensity of the input pulses at 944.15 cm^{-1} [P(20)] and 945.94 cm^{-1} [P(18)] has a similar character. However, the polarization dependence of the echo at these frequencies behaves quite differently. The polarization of the photon echo is practically identical with the polarization of the second pulse, and it is only for the crossed polarizations of the exciting pulses that we find that the polarization of the echo becomes parallel to the first pulse, although its intensity is low and amounts to only 2–3% of the maximum intensity. This last effect does not appear to have been observed by Patel,[3] and the fact that the polarization of the echo follows the polarization of the second pulse was used to draw the conclusion (which, in our view, is incorrect) that the formation of the echo at 944.15 cm^{-1} [P(20)] was due to the well-resolved non-degenerate Q(1) or P(1) transition. This conclusion seems to us to be incorrect, mainly because it is in conflict with the damped nature of the dependence of echo intensity on the intensity of the exciting pulses, which also was noted by Patel. It would appear that the polarization dependence cannot be explained by the assumption put forward by Rhodes[2] that the echo polarization should follow the polarization of the second pulse as a result of the variation in the parameter θ of the exciting pulses along the length of the specimen, because the polarization of the photon echo at the frequency 947.73 cm^{-1} [P(16)] behaves in a normal fashion. Moreover, an artificial and substantial increase in the thickness of the
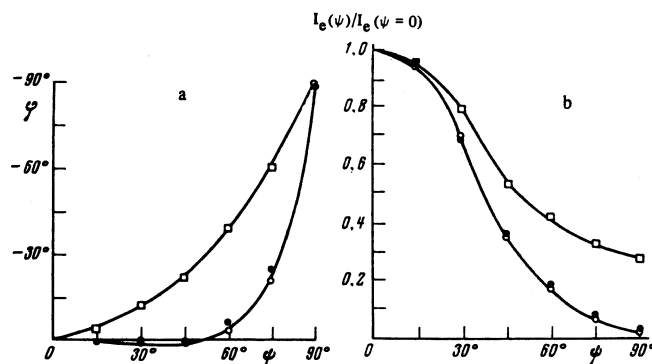
specimen did not result in a change in the behavior of the polarization dependence of the photon echo at this frequency.

The measured polarization dependence is, in our view, the result of the very complicated structure of the absorbing transition. This is supported by the results of Lamb spectroscopy of SF_6,[7] which indicate the presence of a number of valleys within the Doppler width of the absorption line. It is therefore important to remember the possibility that several transitions may be participating in forming the echo. These transitions have close frequencies and this may, in fact, be the reason for the amplitude instability of the echo pulse.[8]

We would therefore conclude that the experimental studies of the photon echo in BCl_3 and SF_6 have enabled us to determine the transverse relaxation time T_2 in these gases. Moreover, the nature of the polarization dependence of the photon echo pulse leads us to the suggestion that at 947.73 cm^{-1} [P(16)] in SF_6 the echo is due to an absorbing transition on the Q branch with a high value of J. The transitions responsible for the echo at 944.15 cm^{-1} [P(20)] and 945.94 cm^{-1} [P(18)] are also highly degenerate but the final identification of these transitions will have to await a more detailed theoretical analysis of the photon echo in gases.

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