INVESTIGATION OF SELF-INDUCED TRANSPARENCY IN GASEOUS BORON TRICHLORIDE

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An investigation was made of the propagation of CO_2-laser radiation pulses in gaseous boron trichloride. The self-induced transparency effect was investigated. The influence of degeneracy was determined and estimates were obtained of the collision phase-detuning time T_2, of the maximum transition matrix element μ_0, and of the number of particles participating in the absorption in BCl_3.

THE problems of propagation of coherent radiation pulses in resonantly absorbing media are attracting deserved attention. The self-induced transparency and the photon echo effects are convenient means for investigating the characteristics of absorbing media. In the optical range these effects were first investigated by Kurnit et al.[1] and by McCall and Hahn,[2] who based their studies on the well-known investigation of the spin echo in nuclear magnetic resonance.[3] The self-induced transparency and the photon echo in gaseous SF_6 were first investigated in the infrared range by Patel and Slusher[4] were somewhat incomplete because no allowance was made for the degeneracy, which is known to occur in molecular gases.

The purpose of our investigation was to determine the principal parameters of gaseous BCl_3 by studying the self-induced transparency with a suitable allowance for the degeneracy.

Gaseous boron trichloride is widely used in CO_2 lasers for passive Q-switching,[5] for frequency tuning of the laser radiation,[6] and for many other purposes. BCl_3 is superior to the well-known gaseous SF_6 because of the much wider range of resonances with the CO_2-laser radiation.

1. If a medium can be regarded as a two-level system which resonates under the influence of a given radiation and if the pulsed radiation field can be represented by a plane linearly polarized wave $E(z, t) = \mathscr{E}(z, t)\cos(\omega t - kz)$, where $\mathscr{E}(z, t)$ is a slowly varying field amplitude, i.e., $|\partial\mathscr{E}/\partial t| \ll \omega|\mathscr{E}|$, $|\partial\mathscr{E}/\partial z| \ll |\mathscr{E}|/\lambda$, it is found that the simultaneous solution of the Maxwell and Schrödinger equations subject to reasonably unrestrictive—in the experimental sense—conditions $\tau_p \ll T_1, T_2$ (τ_p is the pulse duration, T_1 is the longitudinal relaxation time, and T_2 is the time constant of irreversible collision-induced phase detuning) yields the following equation which applies under exact resonance conditions:

$$\frac{d\theta}{dz} = -\frac{\alpha}{2}\sin\theta, \quad \theta(z) = \frac{\mu}{\hbar}\int_{-\infty}^{\infty}\mathscr{E}(z, t)\,dt, \tag{1}$$

where the parameter $\theta(z)$ is proportional to the area under the pulse envelope and to the dipole transition matrix element μ, and the constant $\alpha = 8\pi^2 n\mu^2\omega/\hbar c\Delta\omega_L$ is the linear absorption coefficient. Here, n is the difference between the level populations and $\Delta\omega_L$ is the width of the absorption line. For low values of θ, Eq. (1) corresponds to the usual linear absorption in accordance with the Bouguer–Beer law.

The solution of Eq. (1) is of the form

$$\theta(z) = 2\,\mathrm{arctg}\left[\left(\mathrm{tg}\frac{\theta_0}{2}\right)\exp\left(-\frac{1}{2}\alpha z\right)\right], \tag{2}$$

where $\theta_0 = \theta(z = 0)$. Consequently, an input pulse characterized by θ_0 slightly larger than the critical value $\theta_0 = \pi$ will become broadened. The value of θ increases to 2π in a distance $z \gg \alpha^{-1}$ and the pulse assumes the stable shape

$$\mathscr{E}(z, t) = \frac{2\hbar}{\mu\tau_p}\,\mathrm{sech}\left[\frac{1}{\tau}\left(t - \frac{z}{V}\right)\right].$$

Next, the pulse travels at a constant velocity $V < c$ without energy losses and without distortion of shape because that part of the energy which is lost during the first half of the pulse $t < z/V$ because of the absorption and the consequent excitation of the system is compensated exactly by the energy evolved in the system during the second half of the pulse $t > z/V$. This sequence of events delays the pulse by a time $\tau_d = \frac{1}{2}\alpha L\tau_p$. This is the essence of the self-induced transparency effect in its pure form.

The delay of a π pulse, i.e., a pulse with $\theta_0 = \pi$, is much longer. This delay can be estimated easily by assuming that θ varies slowly in the vicinity of π and that the pulse energy decreases exponentially: we then find that $\tau_d \approx \frac{1}{2}\tau_p\exp(\alpha L/2)$.

The right-hand side of Eq. (1), which applies to a nondegenerate system, contains an oscillatory function. Consequently, the pulses characterized by $\theta_0 = 3\pi, 5\pi, \ldots$ behave like the π pulse. However, an allowance for the degeneracy,[7] which is always present in the case of vibration-rotation transitions in molecules, alters drastically the situation. In this case Eq. (1) becomes

$$\frac{d\theta}{dz} = -\frac{\alpha}{2}\sum_i r_i\sin r_i\theta, \tag{3}$$

where the summation is carried out over all the degenerate states $i = 1, 2, \ldots, 2J + 1$; $r_i = \mu_i/\mu_0$; μ_0 is the maximum dipole matrix element; μ_i is the matrix element of the i-th degenerate state; and the parameters θ and α are defined in terms of the maximum matrix element μ_0:

$$\theta(z) = \frac{\mu_0}{\hbar}\int_{-\infty}^{\infty}\mathscr{E}(z, t)\,dt, \quad \alpha = \frac{8\pi^2 n\mu_0^2\omega}{\hbar c\Delta\omega_L}.$$

In the case of a symmetric top molecule the Q branch is characterized by $r_i = (J - i + 1)/J$, whereas the P and R branches of the vibration-rotation transitions are characterized by $r_i = \sqrt{J^2 - (J - i + 1)^2}/J$.

An analysis of Eq. (3) shows that if $\theta_0 < 2\pi$ and the optical thickness of the medium is equal to several absorption lengths, a degenerate system behaves as if it were nondegenerate except for the value of the first unstable solution of Eq. (3). In the case of a nondegenerate system this solution is exactly equal to π, whereas for a degenerate system the value of the first unstable solution depends on the nature and the serial number of the transition. For example, we find that $\theta_0 = 1.06\pi$ for the Q(2) transition in the Q branch and $\theta_0 = 1.37\pi$ for the Q(10) transition. At high values of J the summation in Eq. (3) can be replaced by integration on the assumption that the distribution of μ is continuous. In this case, we find that $\theta_0 = 1.2\pi$ for the P and R branches and $\theta_0 = 1.43\pi$ for the Q branch.

Considerable differences in the behavior of a degenerate system appear for pulses with $\theta_0 \gg \pi$. Then, the right-hand side of Eq. (3) tends to zero when θ is increased and, consequently, the macroscopic polarization of the medium tends to zero. The system as a whole ceases to re-emit radiation.

Thus, an investigation of the propagation of coherent radiation pulses in degenerate systems near the π region, where degenerate and nondegenerate systems behave similarly, should make it possible to determine experimentally the values of the maximum dipole matrix element and of the time constant T_2.

2. The experimental arrangement used in our study is shown in Fig. 1. The apparatus consisted of a laser operating under double Q-switching conditions.[8] The resonator was formed by a plane-parallel germanium plate 1, a rotating mirror 2, and a diffraction grating. The double Q-switching technique made it possible to generate laser pulses of 10 kW/cm^2 intensity and of 50–600 nsec duration. These pulses consisted of the weak CO_2-laser radiation lines P8, P10, and P12, which corresponded to the maximum values of the absorption coefficient of BCl_3.

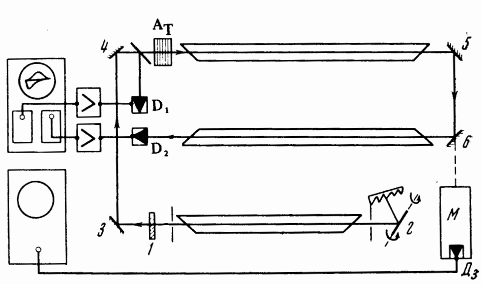

FIG. 1. Layout of the apparatus.

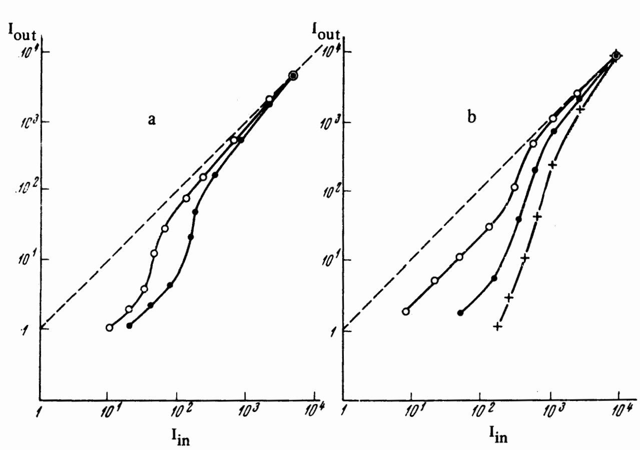

FIG. 2. Dependences of the output intensity I_{out} on the input intensity I_{in} (in relative units): a) for different pulse durations: O) τ_p = 360 nsec, ●) τ_p = 80 nsec; b) for different gas pressures: O) P = 40 mtorr, ●) P = 75 mtorr, +) P = 120 mtorr.

Tiltable mirrors 3–6 were used to direct the radiation pulses to gas-filled cuvettes of 40 mm diameter. The total length of the cuvettes was 6 m. The pulses were picked up by two Ge-Zn-Sn detectors (77°K) with a pass band 30 MHz wide. These detectors (D_1 and D_2) were placed at the entry and exit of the cuvette system. The laser emission frequency was measured by means of a monochromator M whose resolution was 0.2 cm^{-1}. The radiation intensity was varied by means of a calibrated attenuator A made of Teflon film.

We investigated experimentally the dependence of the intensity, shape, and delay of the output pulse on the input pulse intensity. This dependence was determined for various pulse durations in the range of gas pressures in the cuvette from 1 to 100 mtorr. A definite inflection was found in dependences of this type (Fig. 2). The position of this inflection I_i depended on the pulse duration (Fig. 2a) but was independent of the gas pressure (Fig. 2b). At laser radiation intensities $I < I_i$ a pulse was absorbed linearly in accordance with the Bouguer–Beer law and its shape was not distorted. In the range $I > I_i$ the absorbing medium was practically transparent and $I_{out} \to I_{in}$. However, in the latter case there were some energy losses in the leading edge of the pulse because of the need to excite the system. The trailing edge of the pulse was not affected (Fig. 3). The observation of only one inflection in the curves of Fig. 2 was evidence of the influence of degeneracy on the self-induced transparency of a molecular gas.

Figure 4 shows, by way of illustration, the photographs of a series of output pulses obtained for different values of the input intensity.

The pulse shape changed considerably at intensities in the region where $I = I_i$. The pulse became broader and more symmetric and its delay time increased to its maximum value (Fig. 4c). This behavior was typical of the case characterized by $\tau_p < t_2$. When the value of T_2 was reduced by increasing the pressure, it was found that the $I_{out}(I_{in})$ curves no longer had a definite inflection (Fig. 2b). Moreover, the shape of the output pulse changed in a different way. As before, the output pulse was delayed because of the absorption of its leading edge in the cuvette gas but the trailing edge became shorter because the reverse process of re-emission lasted only for a time T_2 (Fig. 5). This enabled us to estimate the time constant T_2 which was found to be 30 nsec/torr. However, an exact value of T_2 could be obtained only in photon echo experiments.

The large change in the absorption coefficient, the distortion of the pulse, and the maximum delay observed in the region where $I = I_i$ suggested that the inflections in the curves plotted in Fig. 2 corresponded to $\theta_0 \approx \pi$. Having measured the absolute value of the input intensity at the inflection point, we could determine quite accurately the maximum transition matrix element of the

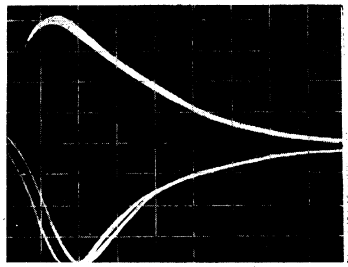

FIG. 3. Superposition of two output pulse oscillograms obtained for $\theta_0 \gg \pi$ using an empty cuvette and a cuvette filled with gas to a pressure of 100 mtorr. Traces of the input pulses in the upper half of the figure coincide. Time scale 20 nsec.

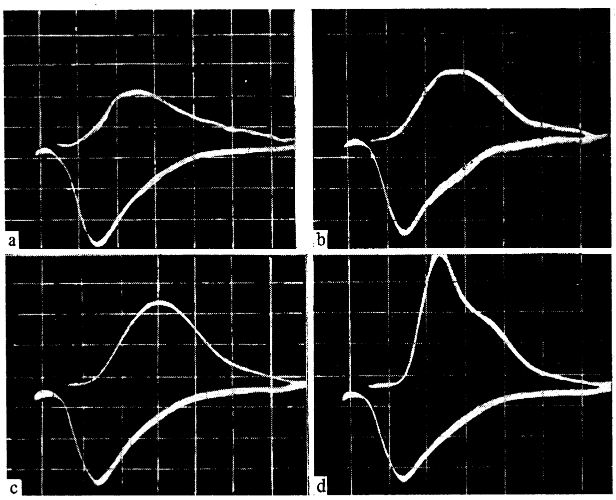

FIG. 4. Oscillograms of a series of output pulses obtained for increasing intensities of the input pulse. The pulse shown in Fig. 4c is the π pulse. The input pulses are shown in the lower halves of the oscillograms. Time scale 50 nsec.

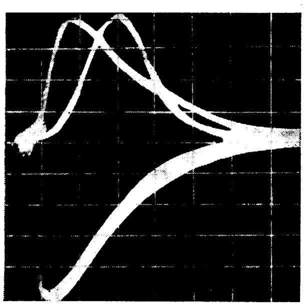

FIG. 5. Superposition of two pulse oscillograms obtained for $\theta_0 \approx \pi$ and $\theta_0 \gg \pi$ (gas pressure in the cuvette 100 mtorr). The input pulses are shown in the lower half of the figure. Time scale 100 nsec.

gas under investigation from the relationship

$$\frac{\mu_0}{\hbar}\frac{8\pi}{c}\sqrt{I_i}\,\tau_p \approx \pi.$$

Since the system was degenerate and the transitions responsible for the absorption in BCl_3 were not identified, the value of the quantity on the right-hand side of the above relationship—which was the first unstable solution of Eq. (3)—could lie between π and 1.43π. This introduced some indeterminacy in the estimate of μ_0 although we could assume that the vibration-rotation transitions participating in the absorption were characterized by jarge values of J. We estimated μ_0 by assuming that θ_0 was 1.4π and this gave $\mu_0 \approx 5 \times 10^{-20}$ cgs esu for the absorption of the P12 CO_2-laser radiation line.

This value of μ_0 was then used to estimate the total number of particles participating in the absorption. This was done by measuring the linear absorption coefficients of BCl_3 for various lines of a CO_2 laser. The absorption coefficient for the P12 line was $\alpha = 0.15\ \text{cm}^{-1} \cdot \text{torr}^{-1}$. The expression for the linear absorption coefficient was of the form

$$\alpha = \frac{8\pi^2 n}{\hbar c(2J+1)\Delta\omega_L}\sum_i \mu_i^2\omega,$$

where

$$\frac{1}{2J+1}\sum_i \mu_i^2 \approx \frac{1}{3}\mu_0^2.$$

for the Q branch of the vibration-rotation transitions; n is the concentration of the particles participating in the absorption; and $\Delta\omega_L$ is the width of the absorption line which can be regarded as the Doppler width right up to pressures of the order of a few torr. Hence, it was found that $n/N = 10^{-2}$. This ratio could be estimated roughly by assuming that the distribution of the particles over the rotational sublevels of the ground vibrational state was of the Boltzmann type. This procedure yielded $n/N = 5 \times 10^{-4}$ at $T = 300\,^\circ K$ on the assumption that the rotational constant was $B = 0.10$.[9] The difference between the theoretical and the experimental estimates indicated that there were several vibration-rotation lines within the Doppler width.

3. Thus, an experimental investigation of the propagation of CO_2-laser radiation pulses in gaseous boron trichloride made it possible to determine the influence of degeneracy on the self-induced transparency effect and to find the range of durations and intensities of the pulses which behaved similarly to the π pulses in a nondegenerate two-level system. This made it possible to estimate the time constant T_2, the maximum transition matrix element μ_0, and the number of particles participating in the absorption.

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