Application of the double-resonance method to the study of vibrational energy transfer between CH_3F and CH_4 molecules

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The double resonance method has been used to determine the rate of transfer of vibrational energy between CH_3F and CH_4 molecules. It was shown that the rate of the process at high argon pressures was determined exclusively by the intermolecular energy transfer whereas, at low pressures, it depended on the rate at which equilibrium was established on the lower vibrational levels of the excited CH_3F molecules. The rate constants for the processes were determined.

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There has been considerable recent interest in the selective effect of infrared laser radiation on chemical reactions. For example, selective vibrational excitation of a particular isotopic species of molecules can be used to ensure that this particular species will preferentially enter a chemical reaction.[1] However, such processes are impeded by the high rate of transfer of vibrational energy in collisions between molecules of different isotopes.[2] The model problem for this type of process is the selective behavior of a chemical reaction in a mixture of molecules with similar chemical properties. The rates of transfer of vibrational energy on collision between these molecules may be much lower than in collisions of isotopic molecules.

We have measured the rate of transfer of vibrational energy during collisions between CH_4 and CH_3F molecules. This was done with the aid of a modification of the method of double resonance. The principle is as follows. Radiation from a continuously operating helium-neon laser is passed through a mixture of gases containing CH_3F and CH_4. The laser radiation is in resonance with one of the vibrational-rotational transitions in the CH_4 molecule. A pulse of radiation from a CO_2 laser excites a proportion of the CH_3F molecules. In the course of the vibrational–vibrational relaxation, some of the methane molecules are found to be excited and the development of this process in time can be followed by examining the intensity of the He–Ne laser beam transmitted through the mixture because the absorption coefficient decreases when a proportion of the methane molecules becomes excited. This system has certain advantages as compared with the more usual arrangement involving two CO_2 lasers.[3] Firstly, the He–Ne laser radiation can readily be separated from the CO_2 laser pulse and, secondly, the high absorption coefficient of methane enables us to use low pressures and examine fast processes.

EXPERIMENTAL METHOD

The experimental arrangement is illustrated in Fig. 1. The gas mixture was leaked into the glass container 1 with NaCl windows. The container length was 80 cm and internal diameter 3 cm. The beam from the Q-switched CO_2 laser 9, using the rotational line $P(20)$ of the 00^01-02^00 transition, was allowed to pass through the germanium plate 2 mounted at the Brewster angle and then continued along the axis of the container. The CO_2 laser pulse energy amounted to 2 mJ and the pulse length was 1–2 μsec. A small proportion of the CO_2 laser radiation was reflected by the germanium plate onto the sensor 3, the output of which was fed into the first channel of a double-beam oscillograph. The beam from the He–Ne laser 10, operating at a wavelength of $\lambda = 3.39\ \mu$, entered the plate 2 after passing through the quartz beam splitter 4. The plane of polarization of the He–Ne laser beam was perpendicular to the plane of polarization of the CO_2 laser beam, so that more than 60% of the He–Ne radiation reflected from the plate 2 passed through the container along its axis, in the same way as the CO_2 laser beam. After the container, the CO_2 beam was absorbed by the quartz plate 5, whereas the He–Ne laser beam was intercepted by the sensor 6 after passing through this plate. Radiation reflected from the beam splitter 4 was intercepted by the sensor 7. Signals from sensors 6 and 7 were amplified and then fed to different inputs of the differential amplifier in the second channel of the oscillograph. The use of the differential amplifier ensured that the recording system was largely insensitive to the amplitude noise of the He–Ne laser.

The three sensors were in the form of liquid-nitrogen-cooled Ge–Au photoresistors. Sensors 6 and 7 were connected in a circuit described by Vasilenko and Skvortsov,[4] and sensor 3 was connected to a 200 Ω resistor. The double-beam S1-17 oscillograph was used

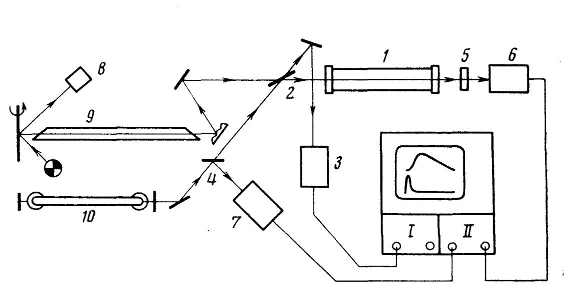

FIG. 1. Block diagram of apparatus.

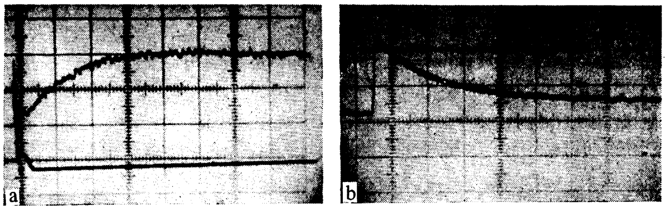

FIG. 2. Typical oscillograms of the double-resonance signals: a) 20 sec/division, $P(CH_4) = 0.134$ Torr, $P(CH_3F) = 0.071$ Torr, $P(Ar) = 20$ Torr; b) 200 sec/division, $P(CH_4) = 0.12$ Torr, $P(CH_3F) = 0.74$ Torr, $P(Ar) = 34$ Torr.

to record the signal. The overall time constant of the first channel of the recording system was less than 200 nsec and that of the second was about 1 μsec. The oscillograph time base was triggered by the CO_2 laser pulse or, somewhat in advance, by the output of the photocell 8.

Figure 2 shows photographs of some typical oscillograms. It is clear that, immediately after the CO_2 laser pulse, there is a rapid rise in the intensity of the He–Ne laser beam transmitted by the mixture (Fig. 2a). This is followed by a slow exponential decay (Fig. 2b). The stage corresponding to the rising signal is due to processes involving the transfer of vibrational energy from the excited CH_3F molecules to the methane molecules. The slow fall is the vibrational–translational relaxation of the CH_4–CH_3F mixture, in which fast processes involving the transfer of vibrational energy ensure that the quasiequilibrium ratio is established between the concentrations of excited molecules of both components. The relative increase in the intensity of the He–Ne laser beam after the pulse in Fig. 2 amounts to about 1%. This is in good agreement with the energy estimate according to which about 3% of the CH_3F molecules should be initially excited.

During the $V-T$ relaxation process, there is some increase in the temperature of the gas in the region containing the excited molecules, and this leads to a reduction in density, i.e., a reduction in the absorption of the He–Ne laser beam. This explains the fact that the signal tends not to its initial magnitude, but to a somewhat higher level during the decay phase (Fig. 2b). However, despite the fact that the observed transmission is partly due to heating, the decay stage can be described by the formula

$$I = A \exp(-t/\tau_{V-T}) + \text{const}, \qquad (1)$$

i.e., the vibrational-translational relaxation time can be obtained from this formula by plotting it on a semilogarithmic scale. The point is that, at sufficiently high pressures when the thermal relaxation time of the gas is long, $\tau_{th} \gg \tau_{v-t}$, the temperature of the gas after the pulse, and together with it the contribution of heating to transmission, increase in proportion to the factor $1 - \exp(-t/\tau_{v-t})$, i.e., they are also described by (1). The condition $\tau_{th} \gg \tau_{v-t}$ is well satisfied for gas-mixture pressures $\geqslant$ 5–10 Torr.

The relative magnitude of the thermal contribution to the transmission becomes small in mixtures that are highly diluted with argon. For example, it is less than 7% for the mixture $P(CH_4) + P(CH_3F) + P(Ar) = 0.23 + 0.36 + 56$ Torr. When the total pressure of the mixture is < 1 Torr, the decay stage of the signal becomes nonexponential. At such pressures, the main reason for the fall in the concentration of excited molecules along the axis of the container is not vibrational–translational relaxation, but diffusion out of the region in which they were originally produced.

All the measurements were carried out at room temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

1. *Vibrational–translational relaxation on argon.* Figure 3 shows the reciprocal of the time constant, $1/\tau$, in mixtures of CH_3F, CH_4, and Ar as a function of the pressure of the mixture for different partial pressures of CH_4 and CH_3F. For both mixtures, the quantity $1/\tau$ is a linear function of argon pressure, and the slope of the corresponding straight line gives the relaxation constant for collisions with argon atoms. For the first mixture, this turns out to be 56 ± 10 sec^{-1} $Torr^{-1}$ and, for the second, 51 ± 5 sec^{-1} $Torr^{-1}$. The published relaxation constants of CH_4 and CH_3F on argon were obtained by examining infrared luminescence. They are: 39 sec^{-1} $Torr^{-1}$ for CH_3F[5] and 67 sec^{-1} $Torr^{-1}$ for CH_4.[6] Intermediate values of the relaxation constants are expected for mixtures and this is, in fact, confirmed by observations.

2. *Transfer of vibrational energy.* Since the signal rise and decay times differ by 1–2 orders of magnitude (Fig. 2), the rise time can be determined independently of the decay time. All that needs to be done is to plot, on a semilogarithmic scale, the difference between the maximum value of the signal and its magnitude at short times after the pulse. As a rule, the result is a straight line, i.e., the rising part of the curve can be described by a single exponential.

Figure 4 shows the reciprocal of the rise time obtained in this way as a function of CH_3F pressure for different argon pressures. It is clear from the figure that, when the argon pressure is 6 Torr, the dependence on the CH_3F pressure is linear (curve 1). At argon

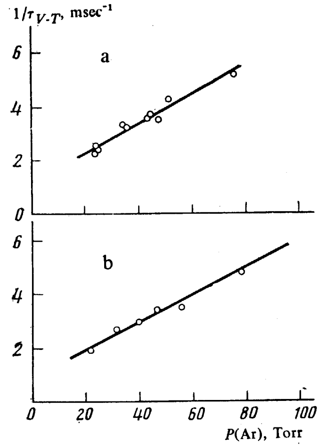

FIG. 3. $V-T$ relaxation time of CH_4, CH_3F as a function of argon pressure for a) $P(CH_4) = 0.12$ Torr, $P(CH_3F) = 0.74$ Torr; b) $P(CH_4) = 0.23$ Torr, $P(CH_3F) = 0.36$ Torr.

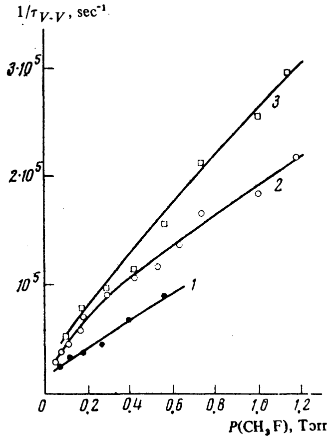

FIG. 4. Dependence of the time for energy transfer to CH_4 molecules as a function of CH_3F pressure for $P(CH_4) = 0.174$ Torr, ● – $P(Ar) = 6$ Torr, ○ – $P(Ar) = 20$ Torr, □ – $P(Ar) = 70$ Torr.

pressures of 20 Torr (curve 2), the dependence is nonlinear, but eventually reaches a straight line parallel to curve 1. For argon pressures of 70 Torr (curve 3), the reciprocal time is the same as at 20 Torr and, at higher CH_3F pressures, the experimental points lie above curve 2.

To understand the observed kinetic relationships, we must consider the level scheme for the lower vibrational states of the CH_4 and CH_3F molecules, shown in Fig. 5. Absorption of CO_2 laser quanta takes a proportion of the CH_3F molecules to the vibrational state ν_3 (valence C–F vibrations). If we suppose that the vibrationally excited CH_4 molecules are produced directly during collisions with primary excited CH_3F molecules, i.e., in accordance with the reaction

$$CH_3F(\nu_3)+CH_4(0) \underset{K_{-0}}{\overset{K_0}{\rightleftarrows}} CH_3F(0)+CH_4(\nu_4), \tag{2}$$

where K represents the relaxation constants, it is readily shown that the equation for the concentration of the $CH_4(\nu_4)$ molecules is

$$[CH_4(\nu_4)] = \text{const}\cdot\{1-\exp\{-t(K_0[CH_4]+K_{-0}[CH_3F])\}\} \tag{3}$$

(vibrational–translational relaxation processes can be neglected at short times). It follows from this formula that the reciprocal of the rise time should be a linear function of CH_3F pressure:

$$1/\tau = K_0[CH_4]+K_{-0}[CH_3F] \tag{4}$$

and is independent of the argon pressure, which is not in agreement with the experimental data in Fig. 4.

The observed relationships can be understood qualitatively if we take into account one further energy-transfer channel that involves intramolecular energy transfer in the CH_3F molecule and the subsequent transfer to the methane molecule:

$$CH_3F(\nu_3) \overset{+M}{\rightleftarrows} CH_3F^* \rightleftarrows CH_4(\nu_4). \tag{5}$$

The overall rate of the process consisting of the last two stages is slower. Since the intramolecular transition in the CH_3F molecule can occur on collision with any particle, including the argon atom, it is clear that, by increasing the argon pressure, one can ensure that the intermolecular transfer stage becomes the limiting stage. Further increase in argon pressure should have no further effect on the rate of transfer. The measured signal rise time obtained under these conditions should be equal to the energy-transfer time between the CH_3F molecule (on whose vibrational levels a certain equilibrium has already been established) and the CH_4 molecules. It is clear from Fig. 4 that this case is realized at an argon pressure of 20 Torr (curve 2) for CH_3F pressures less than 0.3 Torr. In fact, an increase in the argon pressure from 20 to 70 Torr no longer results in an increase in the rate of transfer, although an increase in this pressure from 60 to 20 Torr increases it by a factor of almost two.

The process of intermolecular transfer of vibrational energy in the case of equilibrium on vibrational states of each of the molecules can be formally described by introducing the direct and reverse energy-transfer constants, the values of which describe the variation of the overall number of excited molecules of each type. We can then formally consider that the process continues in a single stage, the equation of which is analogous to (2) whilst the signal rise time is a linear function of the CH_3F pressure in accordance with (4). The slope of the initial segment of curve 2 should, therefore, determine the formal energy-transfer constant between methane and CH_3F. Its numerical value is $(2.7\pm0.4)\times10^5$ sec^{-1} Torr^{-1}.

When the CH_3F pressure is increased, the rate of the second stage of the process (5) increases, and the rate of intermolecular transfer varies only slightly because this rate is determined mainly by the argon pressure. The intermolecular transfer process ceases to govern the rate of the overall process. This results in a slower increase in the rate of transfer with increasing CH_3F pressure, and this is confirmed experimentally at argon pressures of 20 Torr.

To write down the specific kinetic scheme suitable for the analysis of experimental results, we must establish which particular vibrational level of CH_3F is the intermediate state in the process of transfer of excitation to the methane molecule. In general, there can be a large number of intermediate levels. Inspection of

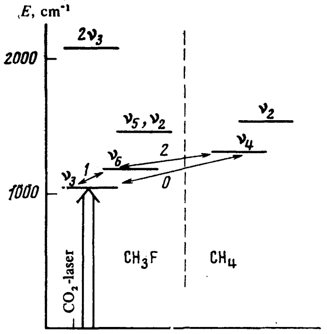

FIG. 5. The lower vibrational levels of the CH_3F and CH_4 molecules.

Fig. 5 will show that the intermediate stage can be ν_6 (doubly degenerate deformational H–C–F vibrations) and ν_2 and ν_5 (deformational H–C–H vibrations). Since ν_3 and ν_5 lie about 300 cm^{-1} above ν_6, one would expect that their contribution to the energy transfer process would be small.

The equations for the above processes must therefore be

$$CH_3F(\nu_3)+M \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} CH_3F(\nu_6)+M, \tag{6}$$

$$CH_3F(\nu_6)+CH_4(0) \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} CH_3F(0)+CH_4(\nu_4). \tag{7}$$

The corresponding set of kinetic equations is

$$\begin{gathered} dn(\nu_3)/dt=-K_1[M]n(\nu_3)+K_{-1}[M]n(\nu_6),\\ dn(\nu_6)/dt=K_1[M]n(\nu_3)-(K_{-1}[M]+K_2[CH_4])n(\nu_6)+K_{-2}[CH_3F]n(\nu_4),\\ dn(\nu_4)/dt=K_2[CH_4]n(\nu_6)-K_2[CH_3F]n(\nu_4). \end{gathered}$$

Here, $n(\nu_3)$, $n(\nu_6)$, and $n(\nu_4)$ are the deviations from the thermal equilibrium values of the concentrations of CH_3F molecules in states ν_3 and ν_6 and of the CH_4 molecules in the state ν_4. The initial conditions for this system are as follows:

$$n(\nu_3)|_{t=0}=n_0, \quad n(\nu_6)|_{t=0}=n(\nu_4)|_{t=0}=0.$$

These equations can be solved by a standard method. It turns out that the time dependence of the concentration of excited methane molecules $CH_4(\nu_4)$ in which we are interested is the superposition of two exponentials. Analysis shows that this can be approximately replaced by an expression of the form $A(1-e^{-t/\tau})$, i.e., an analytic form that was used in the processing of oscillograms for which the rise time is given by

$$\frac{1}{\tau}=\frac{K_1[M]K_2[CH_4]+(K_1+K_{-1})[M]K_{-2}[CH_3F]}{(K_1+K_{-1})[M]+K_2[CH_4]+K_{-2}[CH_3F]}. \tag{8}$$

In this expression, the product $K[M]$ represents the sum of the products of the component concentrations by the corresponding rate constants for intramolecular energy transfer. For example,

$$K_1[M]=K_1^{CH_4}[CH_4]+K_1^{CH_3F}[CH_3F]+K_1^{Ar}[Ar].$$

If, in addition to (6) and (7), we take into account (2), i.e., we allow for the direct transfer of energy from the state ν_3 of CH_3F to the state ν_4 of CH_4, the right-hand side of (4) must be added to the right-hand side of (8).

In actual fact, one would have to solve the set of kinetic equations corresponding to all three processes, namely, (2), (6), and (7). However, the solution of this set of equations is too laborious. On the other hand, by solving the equations corresponding to (6) and (7), and by approximating the solution by a formula containing only only one exponential, we have essentially replaced two successive energy transfers by an equivalent direct energy transfer from the ν_3 level of CH_3F to the ν_4 level of CH_4. This leaves us with two parallel processes with the same initial and final states. The rate of the overall process must be set equal to the sum of the rates of the two parallel processes.

The signal rise time is, therefore, finally given by

$$\frac{1}{\tau}=\frac{K_1[M]K_2[CH_4]+(K_1+K_{-1})[M]K_{-2}[CH_3F]}{(K_1+K_{-1})[M]+K_2[CH_4]+K_{-2}[CH_3F]}+K_0[CH_4]+K_{-0}[CH_3F]. \tag{9}$$

Let us consider the dependence on the right-hand side of (9) on CH_3F pressure. When the argon pressure is sufficiently high so that

$$(K_1+K_{-1})[M]\gg K_2[CH_4], \tag{10}$$

then at low CH_3F pressures the formula given by (9) assumes the form

$$1/\tau=\text{const}_1+(K_{-2}+K_{-0})[CH_3F]. \tag{11}$$

An increase in CH_3F pressure should be accompanied by a deviation from linearity because of the presence of the term $K_{-2}[CH_3F]$ in the numerator, and the transition to the new straight line whose equation is

$$\frac{1}{\tau}=\text{const}_2+\left\{\frac{(K_1^{CH_3F}+K_{-1}^{CH_3F})K_{-2}}{K_1^{CH_3F}+K_{-1}^{CH_3F}+K_{-2}}+K_{-0}\right\}[CH_3F]. \tag{12}$$

In contrast to (11), in which both parameters of the straight line are independent of the argon pressure, the intercept in (12) is a function of argon pressure, as follows:

$$\text{const}_2=\text{const}_3+\frac{K_1^{Ar}+K_{-1}^{Ar}}{\{1+(K_1^{CH_3F}+K_{-1}^{CH_3F})/K_{-2}\}^2}[Ar]. \tag{13}$$

Here, const_3 is a function of only the CH_4 pressure.

For (10) to be valid, it is, in practice, sufficient to ensure that the observed signal rise time is independent of the argon pressure. The initial segment of curve 2 in Fig. 4 was recorded with (10) satisfied. It follows that the slope of the initial segment of curve 2 defines the quantity $K_{-2}+K_{-0}$. The slope of the segment of curve 2 at high pressures, or the slope of curve 1, both of which are equal to $(1.3\pm0.15)\times10^5$ sec^{-1} Torr^{-1}, determines the combination of constants on the right-hand side of (12). If we accept that the quantity $K_1(CH_3F)+K_{-1}(CH_3F)$, measured in[7], is equal to $(1.06\pm0.2)\times10^5$ sec^{-1} Torr^{-1}, we obtain two equations for the unknowns K_{-0} and K_{-2}. The solution of the corresponding equations yields

$$K_{-2}=(2.1\pm0.6)\cdot10^5 \text{ sec}^{-1}\text{ Torr}^{-1};\ K_{-0}=(6\pm3)\cdot10^5 \text{ sec}^{-1}\text{ Torr}^{-1}.$$

We can now estimate $K_1(Ar)+K_{-1}(Ar)$, i.e., the vibrational–vibrational relaxation constant of the CH_3F molecules during collisions with argon atoms. It is clear from (13) that this can be done by comparing the intercept cut by the asymptote of curve 2 with the intercept cut by curve 1. The difference between them is 45 000 ±15 000 sec^{-1}. Using the resulting value of K_{-2} and the above value of $K_1(CH_3F)+K_{-1}(CH_3F)$, we obtain

$$K_1(\mathrm{Ar})+K_{-1}(\mathrm{Ar})=(8\pm4)\cdot10^3\ \mathrm{sec^{-1}\ Torr^{-1}}.$$

The constants K_2, K_0, K_1, and K_{-1} can be determined with the aid of the principle of detailed balancing. Since the vibrational state ν_3 of CH_3F is nondegenerate, ν_6 is doubly degenerate, and ν_4 of CH_4 is triply degenerate, we have at room temperature

$$K_0=0.87K_{-0};\quad K_2=0.82K_{-2};\quad K_1=1.05K_{-1}.$$

The measured values of the vibrational energy-transfer constants K_{-0} and K_{-2} correspond approximately to 160 and 45 gas-kinetic collisions whereas, according to Earl *et al.*,[2] the number of collisions for transfer between the isotopic molecules $^{12}CH_3F$ and $^{13}CH_3F$ is about 6. It is, therefore, much easier, in fact, to excite selectively CH_3F in the CH_3F–CH_4 system than in the $^{12}CH_3F$–$^{13}CH_3F$ system.

In conclusion, the authors express their gratitude to A. A. Savenko who participated in the experiments.

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Self-induced transparency and photon echo in lithium aluminate

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Self-induced transparency and photon echo were investigated in a lithium aluminate crystal activated with trivalent chromium ions. The dynamics of the deformation and self-contraction of the laser beam in this crystal was investigated. A study of the character of the bleaching of the medium has made it possible to determine the electric dipole moment of the resonant transition. An experimental study of the character of the decrease of the photon-echo intensity with increasing time between the pulses has made it possible to find the values of the times of the transverse irreversible relaxation of the system in a constant magnetic field and without a field. The concentration dependence of the photon-echo intensity has a quadratic character, so that superradiance model can be used for a description of this phenomenon.

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1. INTRODUCTION

The phenomena of photon echo (PE)[1,2] and self-induced transparency (SIT)[3] have by now found various scientific and technical applications. The most thoroughly studied were the formation of the PE and SIT effects in gases (see, e.g., [6,7]), although they were first observed in ruby.[2,3] The reason lies in the technical difficulty of performing PE and SIT experiments in solid-state samples, which must be at liquid-helium temperatures to suppress rapid relaxation processes. The performance of such experiments, however is promising because in relatively small solid volumes it is possible to obtain a high concentration of active centers. Such investigations are needed also because so close a packing of the active centers in crystals and different (compared with gases) mechanisms of inhomogeneous broadening of the spectral lines exert appreciable influences on the course of these processes and on their parameters. The symmetry of the real environment of the active center influences the PE and SIT to a considerable degree. All this makes experiments on the observation of PE and SIT in solids an urgent problem.

The present paper is devoted to an investigation of the conditions and singularities of the onset of PE and SIT in a lithium aluminate crystal (ordered phase of $LiAl_5O_8 + Al_2O_3$[8]) activated by trivalent chromium ions.

To observe the PE and STP effects it is necessary that the time of resonant interaction of the field with the medium be shorter than the time T_2 of the transverse irreversible relaxation. In this case the nonequilibrium electric polarization of the resonance medium, which is a nonlinear function of the intensity amplitude and of the phase of the exciting waves, preserves the information on the characteristics of the coherent excitation that has been effected at preceding instants of time.

In the present experiment the duration of the exciting pulses, Δt was 10–18 nsec, and the time τ between