

# Features of stimulated scattering of radiation from a XeCl laser in heptane

V.Ya. Artyukhov, N.G. Ivanov, V.F. Losev, S.V. Nikolaev, Yu.N. Panchenko

**Abstract.** The efficiency of stimulated scattering of laser radiation in heptane is studied. The reasons for the shortening of a reflected pulse and a decrease in the reflection coefficient with increasing the spectral width of pump radiation are analysed. A mechanism of photodissociation of molecules in a nonlinear medium is proposed that explains the reduction in the efficiency of stimulated scattering.

**Keywords:** XeCl laser, stimulated scattering, pump beam, two-photon absorption, photodissociation.

## 1. Introduction

At present, excimer lasers are the most powerful sources of UV radiation. However, the field of their applications is restricted by a low quality of radiation. The use of selective resonators improves the parameters of a laser beam; however, additional losses introduced into the resonator substantially reduce the output energy. It is known that the brightness of laser radiation can be substantially increased, without decreasing the output energy, by using nonlinear processes [1, 2].

The first papers on the use of stimulated scattering in phase conjugation for improving the quality of radiation of excimer lasers were published in 1981 [3, 4]. As nonlinear media, aliphatic hydrocarbons, such as heptane ( $C_7H_{16}$ ), hexane ( $C_6H_{14}$ ), etc. were used in these experiments. By now a number of studies were reported devoted to the analysis of this process. Nevertheless, most experimental papers report a low efficiency of stimulated scattering (the ratio of the energy of scattered radiation to the pump energy), which is caused not only by a low peak-power reflectivity but also by the shortening of a scattered signal duration with respect to that of the pump pulse [5, 6]. Some papers also note a poor quality of phase conjugation [7–9].

The problems encountered in the producing narrow-band radiation from excimer lasers stimulated the studies

aimed at obtaining efficient stimulated scattering of broad-band radiation [10, 11]. It is known that the threshold pump power increases proportionally to the ratio  $\Delta\nu_p/\Delta\nu_{Br}$  (where  $\Delta\nu_p$  and  $\Delta\nu_{Br}$  are the widths of the pump line and spontaneous Brillouin scattering lines, respectively), which can enhance the role of other processes such as, for example, two-photon absorption [12, 13], optical breakdown, etc.

In this paper, we study stimulated scattering of radiation from a XeCl laser in heptane and consider the possible reasons responsible for decreasing its efficiency.

## 2. Experimental setups and calculation methods

In experiments on the irradiation of a nonlinear medium by a XeCl laser, we varied the spectral width of the laser line and the intensity, shape, and duration of the pump pulse. The divergence of laser radiation was always close to the diffraction limit. The optical schemes of experimental setups producing radiation with specified parameters are presented in Fig. 1.

Fig. 1a shows the scheme in which a laser operated in the regime of amplification of radiation from a master oscillator. In this case, the output beam had a diameter of 15 mm, an output energy of 30–70 mJ, and a full width at half-maximum (FWHM) of 14–20 ns [13]. In the scheme in Fig. 1b, one of the lasers was used as a master oscillator, the second one operated in the regime of injection synchronisation, and the third one served as an amplifier. The output laser beam of diameter 20 mm contained about of 60% of energy within the diffraction angle. The laser pulse duration was 80 ns [6]. The width of the laser line could be varied in both these schemes between 0.01 and 25  $cm^{-1}$ . In the scheme in Fig. 1c, a laser had a composite resonator and emitted 140-ns pulses. The first resonator consisted of a quartz plate and a semitransparent mirror with the reflectivity  $R = 20 - 50\%$ . The second resonator appeared upon reflection from a nonlinear medium placed behind the quartz plate [6]. The  $Q$  factor of the first resonator was varied by the quartz plate misalignment.

We studied stimulated scattering of radiation from a XeCl laser in chemically pure heptane and hexane with linear absorption coefficients of 0.05 and 0.03  $cm^{-1}$ , respectively.

The shape of radiation pulses was detected with a FEK 22-SPU photodiode and 6LOR and TDS 3032 Tektronix oscilloscopes. The radiation energy was measured with an IMO-2H power meter and the spectral linewidths were measured with an IT28-30 interferometer and an STE-1 spectrograph. The radiation divergence was determined by

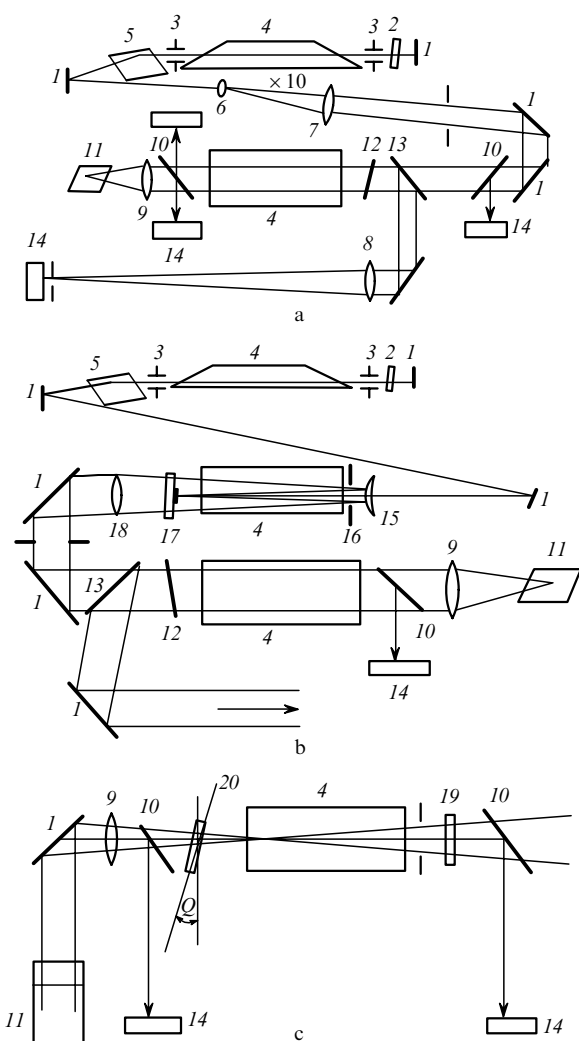
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**Figure 1.** Optical schemes of experimental setups: (1) highly reflecting mirror; (2) solid-state 10-mm Fabry–Perot etalon; (3) diaphragm of diameter 1.4 mm; (4) active medium of a XeCl laser; (5) 2400 lines  $\text{mm}^{-1}$  diffraction grating; (6) positive lens with  $F = 100$  mm; (7) positive lens with  $F = 1000$  mm; (8) positive lens with  $F = 10$  m; (9) positive lens with  $F = 10 - 1000$  mm; (10) quartz plate; (11) cell with a nonlinear medium; (12)  $\lambda/4$  plate; (13) film polariser; (14) measurement unit; (15) convex mirror with  $R = 80\%$ ; (16) diaphragm of diameter 10 mm; (17) semitransparent mirror of diameter 3.8 mm with  $R = 30\%$ ; (18) positive lens with  $F = 2000$  mm; (19) semitransparent mirror with  $R = 8 - 40\%$ ; (20) quartz plate.

the energy transmitted through calibrated diaphragms placed in the focal plane of a long-focus lens.

We also studied theoretically the possibility of photodissociation of the  $C_n - C_m$  and  $C_n - H_m$  bonds in a heptane molecule upon two-photon absorption using a quantum-mechanical approach [14], where  $n$  and  $m$  are the ordinal numbers of carbon and hydrogen atoms in the molecule (see Fig. 5). At the first stage, we performed quantum-chemical calculations and determined the nature of excited electronic states and the degree of localisation of the electronic energy on individual molecular bonds. Then, we found the bonds whose strength was reduced in the corresponding electronic states, indicating the possibility of their dissociation. The strength of a bond was characterised by a parameter, which we called the bond population between atoms C and H. A decrease in the bond population

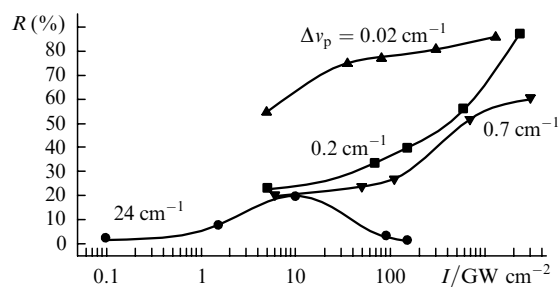
upon an electronic transition indicates a weakening of the C–C or C–H bond. At the next stage, we calculated the spectra of excited states by varying the bond lengths, which allowed us to find the potential curves of the molecule in the corresponding excited state and to determine the photodissociation states of the molecule.

We calculated the electronic structure, energies, and wave functions of heptane by the semiempirical INDO (incomplete neglect of differential overlap) method with a special spectroscopic parametrisation [15]. After the INDO calculation of the wave functions, we calculated the matrix elements of the operator of spin–orbital interaction, the rate constants of intramolecular nonradiative processes, and the populations of chemical bonds (after Malliken [16]). The rate constants of intersystem crossing ( $k_{ISC}$ ) and internal conversion ( $k_{IC}$ ) were calculated according to [15]. We should note that the energy of the  $S_0 \rightarrow S_1$  transition found by parametrisation in quantum-mechanical calculations [15] was substantially lower than that observed experimentally [17]. For this reason, we changed the values of parameters for carbon atoms in order to describe the absorption spectra more adequately.

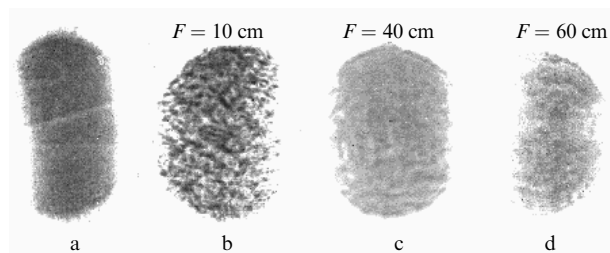
We calculated the spectral properties of the heptane molecule and studied the photodissociation mechanism by using the structural model of heptane where all the C–C and C–H bond lengths were assumed equal to 1.53 and 1.11 Å, respectively.

### 3. Results and discussion

We found in experiments, using the setup shown in Fig. 1a, that the reflection coefficient upon stimulated scattering in heptane can be as high as 90% (Fig. 2). The reflection coefficient decreased with increasing the pump line width. For a maximum  $\Delta\nu_p$ , the reflection coefficient did not exceed 20%. In addition, radiation was almost completely absorbed by heptane at high pump intensities. Note that no optical breakdown was observed in heptane under any experimental conditions. We found that the fraction of stimulated Brillouin scattering (SBS) decreased with increasing the pump intensity, the pump line width being constant, whereas the fraction of stimulated thermal scattering (STS) increased [13]. A change in the scattering mechanisms is also confirmed by a change in the intensity distribution of reflected radiation when lenses (9) with different focal lengths were used (Fig. 3). When STS dominated over SBS, the intensity distribution had a fine-dispersion structure, becoming more homogeneous when these components were levelled off.

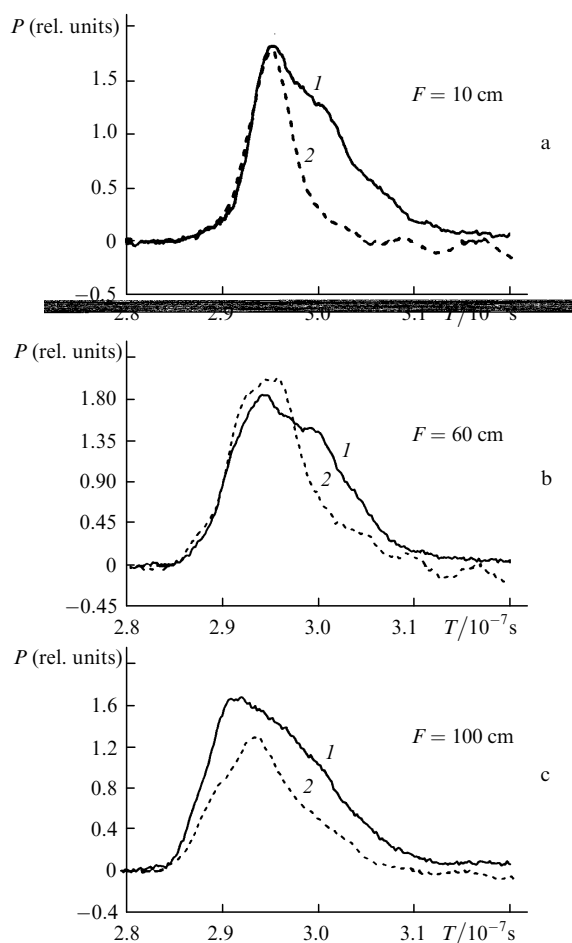


**Figure 2.** Dependences of the reflection coefficient in heptane on the pump intensity for different spectral widths  $\Delta\nu_p$  of the pump line.



**Figure 3.** Near-field distributions of the radiation intensity in the pump beam (a) and in scattered beams (b–d) for different focal lengths of lens (9).

Fig. 4 shows the time dependences of a scattered signal at different focal distances  $F$  of lens (9). One can see that the signal duration decreases with decreasing  $F$ . The signal duration also decreased when the linear absorption coefficient  $\alpha$  of heptane was increased up to  $\sim 0.12$  cm $^{-1}$  (by adding a small amount of acetone). In the setup shown in Fig. 1b, the pump pulse duration was 80 ns, while the duration of scattered pulses did not exceed 15 ns in a broad range of pumping conditions (the pump intensity was varied from  $10^7$  to  $10^{11}$  W cm $^{-2}$  and the pump line width was varied from 0.01 to 24 cm $^{-1}$ ) [6]. The laser used in the setup shown in Fig. 1c produced a train of pump pulses. Under these conditions, stimulated scattering of a train of short pulses was observed during 100 ns.

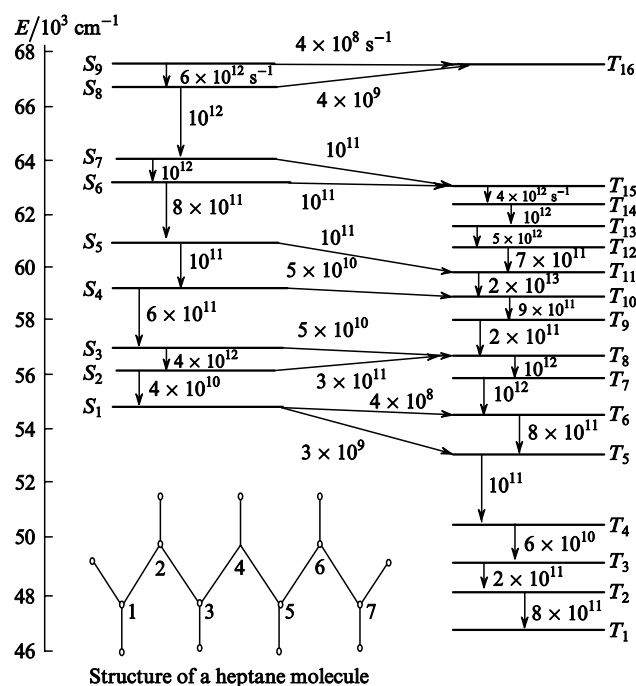


**Figure 4.** Oscillograms of pump pulses (1) and scattered pulses (2) for different focal lengths of lens (9).

The experimental data considered above contain two main results. The first result is that the reflection coefficient upon stimulated scattering decreases with increasing the pump line width much faster than the stimulated scattering threshold increases (for  $\Delta\nu_p = 0.01$  cm $^{-1}$ ,  $I_{th} = 58$  MW cm $^{-1}$ ). Nevertheless, according to the theory, the efficient stimulated scattering can also occur in the case of broadband radiation when a critical pump intensity  $I_{cr} = 4\pi\Delta\nu_p/g$  is achieved ( $g$  is the nonlinear gain) [18]. The second result is that the duration of a reflected pulse does not decrease upon stimulated scattering of pulses of duration above 20 ns. Therefore, under certain conditions, along with stimulated scattering some other process takes place in the interaction of radiation with the medium. In our opinion, this can be photodissociation of molecules upon two-photon absorption of the pump radiation.

It seems that two-photon absorption of radiation from a XeCl laser was first studied in paper [12]. However, the probability of this process has not been accurately calculated so far. In this paper, we calculated the energy level diagram of heptane in order to estimate this probability and to find the relaxation channels of the absorbed energy.

Fig. 5 shows the energy level diagram of the excited electronic states of a heptane molecule and the rate constants for the most efficient photophysical processes (numbers at the arrows). After two-photon absorption of light at 308 nm, the molecule undergoes the transition to the  $S_9$  state (the oscillator strength of the transition is  $f = 0.012$ ). The relaxation of the energy from the  $S_9$  state occurs predominantly due to cascade internal conversion processes occurring successively from the  $S_9$  state to the  $S_0$  state. Then, beginning from the  $S_2$  state, relaxation mainly occurs due to intersystem crossing. It follows from the scheme of photophysical processes that the photodissociation of the heptane molecule upon two-photon absorption will occur predominantly in the triplet channel.



**Figure 5.** Scheme of the excited electronic states of a heptane molecule and the rate constants of photophysical processes.

Tables 1 and 2 present the calculated bond populations for the heptane molecule in the triplet channel. One can see that the C–C bond population decreases most strongly in the  $T_3$  state (Table 1, the  $C_3$ – $C_4$  bond), while the C–H bond population decreases most strongly in the  $T_1$  state (Table 1, the  $C_4$ – $H_{8,9}$  bond).

**Table 1.** Populations of the C–C and C–H bonds of the heptane molecule in excited electronic states  $T_1$ – $T_6$ .

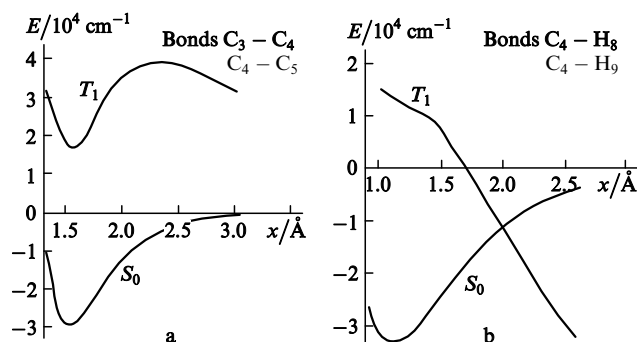
Bonds	State					
	$T_1$	$T_2$	$T_3$	$T_4$	$T_5$	$T_6$
$C_1$ – $C_2$	0.270	0.249	0.274	0.244	0.107	0.296
$C_2$ – $C_3$	0.171	0.152	0.013	0.261	0.084	0.368
$C_3$ – $C_4$	0.109	0.209	–0.107	0.240	0.310	0.345
$C_1$ – $H_1$	0.664	0.653	0.672	0.636	0.597	0.606
$C_1$ – $H_{2,3}$	0.663	0.645	0.714	0.613	0.624	0.571
$C_2$ – $H_{4,5}$	0.604	0.562	0.642	0.568	0.556	0.609
$C_2$ – $H_{6,7}$	0.555	0.569	0.573	0.615	0.637	0.582
$C_4$ – $H_{8,9}$	0.533	0.617	0.551	0.562	0.706	0.612

**Table 2.** Populations of the C–C and C–H bonds of the heptane molecule in excited electronic states  $T_7$ – $T_{15}$ .

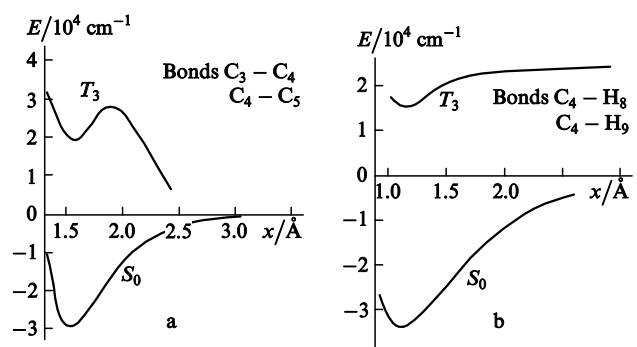
Bonds	State				
	$T_7$	$T_8$	$T_{10}$	$T_{11}$	$T_{15}$
$C_1$ – $H_1$	0.190	0.237	0.360	0.213	0.246
$C_2$ – $C_3$	0.305	0.088	0.346	0.254	0.316
$C_3$ – $C_4$	0.216	0.047	0.368	0.231	0.300
$C_1$ – $H_1$	0.574	0.634	0.525	0.585	0.564
$C_1$ – $H_{2,3}$	0.589	0.676	0.540	0.604	0.577
$C_2$ – $H_{4,5}$	0.623	0.616	0.686	0.615	0.636
$C_3$ – $H_{6,7}$	0.653	0.590	0.584	0.633	0.623
$C_4$ – $H_{8,9}$	0.583	0.586	0.686	0.608	0.633

To find the potential curves in excited electronic states, we performed quantum-chemical calculations of the state energies by varying the lengths of central C–C and C–H bonds, which are weakened upon excitation. The potential curves in the ground state were described by the Morse potential [19], the potential curves of excited electronic states were calculated by the summation of the potential energy in the ground state with the electron-transition energy at each point of the abscissa. The Morse potential was calculated by using the following experimental data: the dissociation energy of the C–C bond was  $D_{C-C} = 352$  kJ mol [20], the vibrational frequency of the bond was  $\nu = 1100$   $\text{cm}^{-1}$  [21], the equilibrium bond length was  $R_{C-C} = 1.53$  Å; the dissociation energy of the C–H bond was  $D_{C-H} = 401$  kJ mol [20], the vibrational frequency of the bond was  $\nu = 2900$   $\text{cm}^{-1}$  [21], and the equilibrium bond length was  $R_{C-H} = 1.11$  Å.

The potential curve describing the  $T_1$  state for the C–C bond has a minimum corresponding to a stable conformation of the molecule (Fig. 6). The C–C bond in the  $T_3$  state can dissociate after overcoming the potential barrier equal to  $\sim 8000$   $\text{cm}^{-1}$  (Fig. 7). The potential curve of the C–C bond in the  $T_3$  state has a barrier equal to  $9000$   $\text{cm}^{-1}$  (Fig. 7), while in the  $T_1$  state the photodissociation occurs without a barrier (Fig. 6). Therefore, the quantum-chemical calculations show that the heptane molecule relaxes for the time of  $\sim 10$  ps after two-photon absorption to the  $T_1$  state,



**Figure 6.** Potential curves of the excited electronic  $T_1$  states of heptane.



**Figure 7.** Potential curves of the excited electronic  $T_3$  states of heptane.

in which the probability of dissociation of the  $C_4$ – $H_8$  and  $C_4$ – $H_9$  bonds is high. The photodissociation of the  $C_3$ – $C_4$  and  $C_4$ – $C_5$  bonds is unlikely because the energy barrier is high.

The analytic expression

$$k \sim 10^{12} \int_{-\infty}^{\infty} \cosh^{-1} \left( \frac{\pi z}{2} \right) \exp \left( \frac{\pi z}{6} \right) \times S_n^2 \left( \delta - \frac{\omega_2^2}{A} + \frac{\omega_2 z}{\sqrt{3}A} \right) dz \quad (1)$$

determining the dissociation rate constant  $k$  for aromatic and aliphatic hydrocarbons and its dependence on the excited-level energy was derived in paper [22]. Here,  $\omega_1 = 3000$   $\text{cm}^{-1}$  is the frequency of valence vibrations of the C–H bond;  $\omega_2 = 1100$   $\text{cm}^{-1}$  is the frequency of deformation vibrations of the C–H bond;  $A = 0.1$  au is the force on the repulsive term acting along valence vibrations of the C–H bond;  $E_0 = 9$  eV is the energy of the  $S_n$  repulsive term at the equilibrium point;  $n = 0$  is the number of a vibrational level of valence vibrations of the C–H bond; and  $[k] = \text{s}^{-1}$ . By knowing the energy of the levels of lower triplet states, we can estimate the rate constant of the hydrogen detachment, which is no less than  $3 \times 10^8$   $\text{s}^{-1}$  for heptane in our case. Therefore, a total time between a two-photon absorption event and the instant of dissociation of C–H bonds in the heptane molecule does not exceed 3 ns.

Our calculations confirm the possibility of photodissociation of molecules during the pump pulse. For the focal length of lens ( $g$ ) equal to 100 mm, the beam diameter of 10 mm, and the beam divergence  $\varphi = 10^{-4}$  rad, the estimated ratio of the number of heptane molecules to the

number of photons in the interaction region is  $10^{-3}$ . Therefore, both linear and nonlinear properties of heptane will substantially change upon photodissociation.

These changes will depend to a great extent on a fraction of energy reflected from a nonlinear medium, which is in turn determined by the intensity, geometry, and the width  $\Delta\nu_p$  of the pump line. When  $\Delta\nu_p$  is comparable with  $\Delta\nu_{Br}$  and a long-focus lens is used, the efficient SBS occurring in front of the beam waist makes it possible to avoid intense two-photon absorption. As  $\Delta\nu_p$  increases, the value of  $I_{cr}$  also increases, resulting in the replacement of SBS by STS. At the same time, a part of the pump energy, which is not involved in STS, is beginning to be spent for photodissociation of molecules. As  $\Delta\nu_p$  is further increased, it is necessary to use a shorter-focus lens to produce the intensity exceeding  $I_{cr}$ .

This reduces a region of nonlinear interaction and, hence, the number of molecules involved in the interaction. In addition, the regions of intense photodissociation and the STS transformation are drawing together. The destruction of a STS grating will result in an increase in the pump energy spent to photodissociation. Therefore, the efficiency of stimulated scattering will decrease beginning from a certain width of the pump line under any conditions.

The reflection of a pulse train observed during 100 ns can be explained by the fact that the rate of recovery of molecules can be as high as the rate of their photodissociation [22]. Therefore, molecules have time to recover during the interval between pump pulses.

Along with photodissociation, the  $T_1$  state can also decay due to phosphorescence and nonradiative relaxation. We have failed to observe any emission in the 250-nm region corresponding to the  $T_1 - S_0$  transition. In the case of heating of the medium, we could not observe any reflection of a pulse train. Therefore, the efficiency of stimulated scattering upon broadband pumping is mainly restricted by photodissociation of molecules.

Thus, we have investigated in this paper the dependence of the efficiency of stimulated scattering of radiation from a XeCl laser in heptane on the pump-beam parameters. We have proposed the mechanism of photodissociation of molecules of the medium, which can strongly affect stimulated scattering. We also studied quantum-mechanically the possibility of photodissociation of the C–C and C–H bonds in a heptane molecule caused by two-photon absorption of light.

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