bility of backscattering over shorter distances, and hence of smaller attenuation.

The degrees of depolarization of different scattering multiplicities are also substantially different. Single scattering is fully polarized, the degree of depolarization of double scattering is $I^z_{z(2)}/I^z_{z(2)} \sim 2\%$, and scatterings of higher multiplicity have polarization degrees $I^z_{z(p)}/I^z_{z(p)} \sim 20\%$. It follows therefore, in particular, that the influence of multiple scattering $I(p)$ manifests itself much earlier in the depolarized component than in the polarized one when the critical point is approached. A distinguishing feature of multiple scattering is also the close character of the angular dependences of the polarized and depolarized components, as illustrated in Fig. 6.

It is of interest to note that although the considered system opalesces very strongly (the beam attenuation over the cell length reached a factor of 500 under the experimental conditions), the extinction coefficient is nevertheless well described by Eq. (6), as seen from Fig. 7, and the obtained value of B is close to that found for this system in Ref. 7.

In conclusion, the authors are deeply grateful to I. L. Fabelinskiĭ and M. A. Anisimov for a discussion of the work.

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Investigation of the interaction of intense laser radiation with sulfur-hexafluoride molecules by the buffer-gas method

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Measurement results are presented for the coefficient of absorption of intense ($\sim 10^7$W/cm^2) Co_2 laser radiation by SF_6 molecules in the presence of noble gases, in the pressure interval up to 40 bar. The variation of the absorption coefficient with change of pressure and of the sort of buffer gas, as well as with the wavelength and intensity of the incident radiation, makes it possible to trace the evolution of the vibrational-state distribution function of the molecules. The character of this function is decided by the competition between the vibrational relaxation processes and laser-radiation absorption. In the high-pressure limit, $P_{He} \gtrsim 20$–40 bar, a two-level interaction was realized for the first time ever between high-intensity laser radiation and SF_6, wherein molecules excited by the light into the state $v = 1$ relax instantaneously via collisions. Reduction of the experimental data yields an estimate of the dependence of the SF_6 molecule decay rate constant on the number of the vibrational level v in collisions with helium atoms. This dependence is approximated by the formula $k(v) \sim k_{10}v^n$ ($n \approx 4.5$, $k_{10} = 2.5 \times 10^{-12}$cm^2/sec). The aggregate of the experimental data confirms the assumption that the interaction of the laser radiation with the SF_6 molecules is linear.

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The interest in the investigation of the mechanism whereby intense IR laser radiation interacts with polyatomic molecules is due, on the other hand, to the rather complicated character of this interaction, and on the other to its possible practical application in selective photochemistry and for isotope separation by lasers. Despite the large number of experimental[1,2] and theoretical[3-5] studies, many details of this process remain unclear. This is due primarily to the lack of the necessary information on the dependence of the degree of interaction of the vibrationally excited polyatomic molecule with the laser-radiation quantum on the degree of the vibrational excitation. In this paper we deduce some information on the mechanism whereby intense laser radiation of wavelength 10.6 μm interacts with SF_6 molecules. We use the buffer-gas method (BGM), which had given good account of itself in laser-chemistry research.[6-8]

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By investigating the absorption of intense laser radiation by polyatomic molecules in the presence of buffer gases (BG) at high pressure it is possible to simulate conditions in which the molecule interactions with the laser radiation compete with vibrational-relaxation processes. This makes it possible, by varying the experimental conditions, to deduce the characteristics of these collisional processes, as well as obtain some information on the character of the interaction between the vibrationally excited molecules and the laser radiation.

The laser radiation source was a pulsed CO_2 laser (TEA excitation) generating 100-nsec pulses with 0.5–3 J per pulse and tunable over the frequencies corresponding to the vibrational-rotational transitions of the *P* branch in the 10.6 μm region. By using a filter, the output energy was maintained constant as the frequency was varied. The investigated gas, SF_6 highly diluted in helium, was fed into the cell and exposed to laser pulses. The energies E_0 and E' of the incident radiation and of the radiation passing through the cell were measured with IMO-2 and KIM calorimeter. The cell length 2.0 cm and the SF_6 pressure 0.3–1.0 Torr were chosen to make the relative absorbed energy equal to 10–15%.

The measurement results are shown in Figs. 1–5, where the reduced laser-radiation absorption coefficient *g* is plotted against the wavelength and energy density of the laser radiation, as well as against the helium pressure. The coefficient *g* was defined as

$$g=-\frac{1}{K_0L}\ln\frac{I_{tr}}{I_0}=\frac{K}{K_0}, \qquad (1)$$

where L is the cell length, K_0 is the seak-signal absorption coefficient at 946 cm^{-1} in SF_6 of the given concentration in the absence of buffer gas, and K is the experimental laser-radiation absorption coefficient. In the determination of the absorbed energy we took into account the experimentally obtained radiation fraction lost to reflection from the optical elements, from the cell, and from the measuring apparatus.

Let us discuss the qualitative features of the presented plots. We note first that, according to Fig. 1, an increase in the BG pressure is accompanied by an increase of the absorption coefficient of the laser radiation, whose wavelength corresponds approximately to the maximum of the linear absorption of the SF_6 molecule. It is natural to attribute this behavior to vibrational relaxation of the strongly excited SF_6 molecule via collisions with the BG atoms. In fact, when intense CO_2 laser radiation acts on SF_6 molecules in the absence of BG, a quasistationary distribution of the molecule vibrational states is established. Although the concrete form of this distribution is determined essentially by the character of the dependence of the laser-photon absorption cross section on the degree of the vibrational excitation of the molecule,[9] it can be stated that this distribution is a smoothly decreasing function. Addition of the BG leads to the appearance of vibrational relaxation that is more effective the shorter the average energy-level spacing in the indicated region of the molecule vibrational spectrum. Since the average level spacing decreases abruptly with increasing vibrational energy of the molecule, one can expect the addition of the

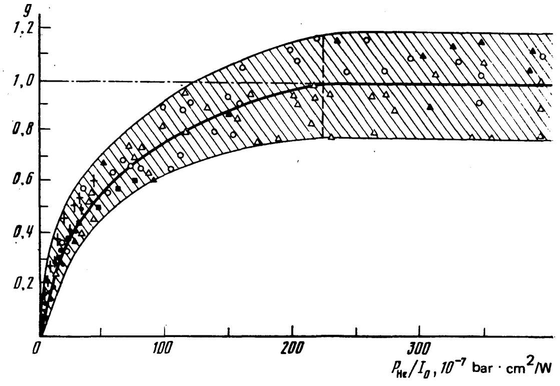

FIG. 1. Dependence of the reduced laser-radiation absorption coefficient *g* on the parameter P_{He}/I_0 for different laser-flux energy densities at 947.7 cm^{-1}: ●) 0.79, ⊘) 0.57, +) 0.45, ▪) 0.25, ○) 0.12, △) 0.09, ▲) 0.06 J/cm^2. P_{He} is the helium pressure in bars; I_0 is the intensity of the incident radiation in W/cm^2. The SF_6 pressure was 0.1–0.4 Torr.

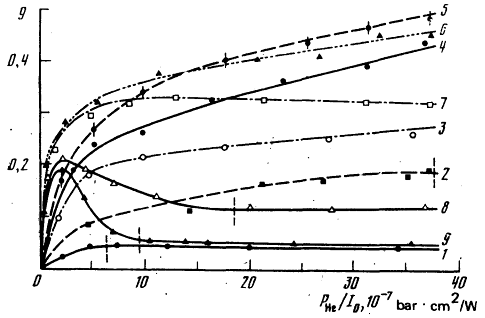

FIG. 2. Dependence of the reduced laser-radiation absorption coefficient *g* on the parameter P_{He}/I_0 for different frequencies. Laser-radiation energy density E_0 = 0.5 J/cm^2, SF_6 pressure 0.3–1.0 Torr. The values of ν are: 1) 952.8, 2) 951.1, 3) 949.4, 4) 947.7, 5) 945.9, 6) 944.1, 7) 940.5, 8) 938.7, 9) 936.8 cm^{-1}.

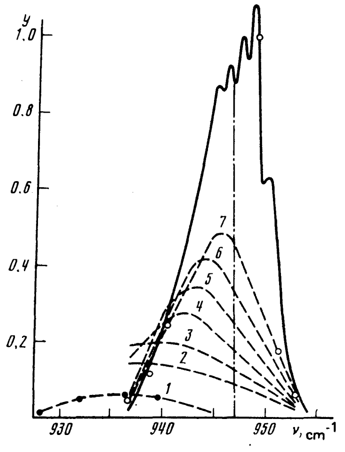

FIG. 3. Spectrum shift of absorption of laser-radiation by sulfur hexafluoride in the presence of helium (E_0 = 0.5 J/cm$_2$). 1) SF_6, 2) SF_6 + 0.5 bar He, 3) SF_6 + 1 bar He, 4) SF_6 + 2 bar He, 5) SF_6 + 3 bar He, 6) SF_6 + 9 bar He, 7) SF_6 + 20 bar He. The solid line shows the position of the linear absorption spectrum of SF_6.[11] The light circles show the experimental values of the reduced absorption coefficient *g*, measured for two-level absorption of the laser radiation (P_{He} = 40 bar).

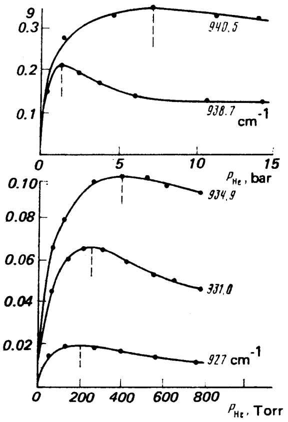

FIG. 4. Dependence of the reduced laser-radiation asorption coefficients at various excitation frequencies on the helium pressure. $E_0 = 0.5$ J/cm^2.

BG to decrease the effective width of the molecule vibrational-state distribution function and hence to increase the number of the ground-state molecules which are mainly responsible for the increased absorption in the region of the maximum linear-absorption cross section ($\nu \approx 946$ cm^{-1}). The vibrational effects manifest themselves most strongly when the lightest buffer gas, helium, is added, and principal attention will be paid in the present paper to results obtained with helium.

Figure 1 shows the reduced laser-radiation absorption coefficient as a function of the ratio of the helium pressure P_{He} to the laser-radiation intensity I_0. It is seen that the results obtained at substantially different values of P_{He} and I_0 turn out to depend, within the limits of experimental error, only on the ratio P_{He}/I_0. Since the effectiveness of the VT-relaxation process depends linearly on the helium pressure, the noted similarity law points definitely to a linear and one-photon interaction between intense laser radiation and SF_6 molecules. In the limit of large ratios $P_{He}/I_0 > 2.3 \times 10^{-3}$ bar $\cdot$ cm^2/W, the plot flattens out, in which case g is close to unity, i.e., the absorption coefficient coincides with the corresponding value $\sigma_0 = 2 \times 10^{-17}$ cm^2 measured in the case of weak radiation. This agreement confirms the conclusion drawn above, that the interaction of the SF_6 molecules with intense laser radiation has a one-photon character. The conclusion agrees also with the character of the dependence, shown in Fig. 3, of the absorption spectrum on the BG pressure. At a helium pressure ~40 bar, the absorption spectrum (light circles) practically coincides with the spectrum obtained in the case of a weak signal (solid line).

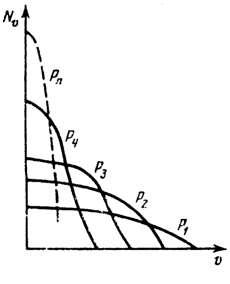

FIG. 5. Qualitative form of molecule vibrational-level distribution function at various He pressures. $P_1 < P_2 < P_3 < P_4 < P_n$.

From the data of Fig. 1 we can deduce the rate constant of the vibrational relaxation of the SF_6 molecule from the level ν_3 ($v = 1$) via collisions with helium atoms. In fact, recognizing that under the considered conditions the interaction of the primary photon with the molecule, just as the VT-relaxation process, has a binary character, it is easy to show that the $g(P_{He}/I_0)$ region in which the derivative of this function undergoes a maximum change corresponds to the condition that the characteristic times of decay of the states (ν_3, $v = 1$) as a result of induced emission and as a result of VT relaxation be equal. It is natural here to expect the principal process of the radiative decay of the considered state to be quadrupole emission

$$SF_6(v_3=1) + \hbar\omega \rightarrow SF_6(v_3=0) + 2\hbar\omega,$$

whose cross section practically coincides with the cross section for the absorption of a photon by an unexcited molecule. This yields an estimate of the VT-relaxation rate constant, obtained by equating the times of the corresponding processes at the point of the maximum change of the derivative of the curve of Fig. 1 [the point $(P_{He}/I_0)^* \approx 230 \times 10^{-7}$ bar $\cdot$ cm^2/W]:

$$k_{VT}^{He} = \left(\frac{I}{N}\right)^{*} \frac{\sigma_0}{\hbar\omega} \approx 2.5 \cdot 10^{-12} \text{ cm}^2 \text{ sec}^{-1} .$$

Figure 2 shows plots of the parameter g vs. the ratio P_{He}/I_0, obtained at various CO_2-laser frequencies. These plots correspond to the SF_6-molecule absorption spectra shown in Fig. 3, obtained at different values of P_{He}/I_0. It is seen that with increasing P_{He}/I_0 ratio the absorption spectrum shifts to the blue side and approaches asymptotically the linear absorption spectrum obtained for a weak signal. The absorption of radiation at frequencies higher than 944 cm^{-1} increases monotonically with increasing P_{He}/I_0, the absorption radiation of frequency lower than 944 cm^{-1} goes through a maximum, and the ratios P_{He}/I_0 corresponding to this maximum decrease with decreasing absorbed-photon frequency.

The foregoing singularities can be explained by bearing in mind the already indicated role of the buffer gas that influences the vibrational-state distribution of the molecules. In fact, in the presence of vibrationally excited molecules the absorption spectrum consists of the linear weak-signal absorption spectrum of the unexcited molecules and of absorption bands of vibrationally excited molecules corresponding to the antisymmetrical ν_3 oscillation mode.$^{1)}$ By virtue of the anharmonicity of the molecular vibrations, the center of each band is shifted in the red direction relative to the center of the linear absorption, by an amount equal to the product of the linear-absorption constant by the number of the vibrational level within each vibration mode. With the absorption spectrum of the SF_6 molecules in a strong field so interpreted, the experimentally observed maxima of the absorption coefficient correspond to the maxima of the populations of those vibrationally excited states which absorb most effectively the radiation of the given frequency (shifted relative to the maximum of the linear absorption).

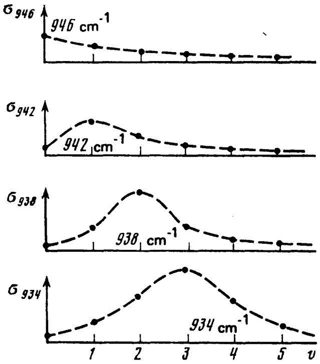

FIG. 6. Qualitative dependence of the cross sections for the absorption of various frequencies on the number of the vibrational state of the excited molecule. It is assumed that the anharmonicity $2X_{33}$ is 4 cm^{-1}.

Within the framework of the interpretation adopted here, the appearance of a maximum on the plot of the population of a given vibrationally excited state vs. the ratio P_{He}/I_0 is explained by the following circumstances. The anharmonicity constant for the ν_3 vibrational mode of the SF_6 molecule is close to 4 cm^{-1}.[10] This means that in the frequency band 927–946 cm^{-1} there can participate at least five excited states corresponding to the ν_3 mode. Each of the $g(P_{He})$ plots shown in Fig. 4 can be regarded as a function that reflects the character of the variation of the population of the corresponding excited state (shown in the figure). Bearing in mind this circumstance, we consider one of the presented curves and attempt to relate the character of its behavior with the above-discussed form of the distribution function of the molecules over the vibrational states of the ν_3 mode.

At small values of P_{He}/I_0, when the formation and decay of a given excited vibrational state of the SF_6 molecule are determined primarily by the interaction of the molecule with the laser radiation, the addition of helium leads to collisional decay of the higher excited vibrational states and to a decrease in the width of the vibrational-state distribution function of the molecules (see Fig. 5). Since the total number of molecules interacting with the laser radiation remains unchanged, the number of molecules in the considered state should increase. The growth of the population of the given state with increasing ratio P_{He}/I_0 will continue until the collisional decay of the given state competes with its radiative decay. The region of the steep descent of the molecule vibrational-state distribution function turns out in this case to be close to the considered vibrational state (see Figs. 5 and 6). Further increase of the ratio P_{He}/I_0 decreases the population of the considered excited state, which tends to zero in the limit as $P_{He}/I_0 \to \infty$. The absorption of radiation of the given frequency then tends to a value characteristic of linear weak-signal absorption.

The latter is confirmed by the results shown in Fig. 3, where the reduced absorption coefficients g corresponding to two-level absorption of the laser radiation are marked (light circles) on the SF_6-molecule weak-signal absorption spectrum obtained with a monochromator in the absence of buffer gases.[11] The agreement between the spectra confirms the foregoing qualitative explanation of the results.

Assuming that the cross section for the absorption of the laser radiation increases linearly with the number of the vibrational state corresponding to the given vibration mode, we can, using the data of Fig. 4, estimate the rate constant of the collisional decay of the ν_3 vibrational-rotational states with $v = 2, 3, 4, 5$. By the same reasoning as used above to estimate the effectiveness of the decay of the state $v = 1$, we equate the rates of the radiative and collisional decays of the indicated states at the gas pressure where the corresponding $g(P_{He})$ curves have a maximum. This yields the sought constants, namely 5.6×10^{-11}, 3.5×10^{-10}, 1.3×10^{-8}, 3.5×10^{-9}, and 7.9×10^{-9} cm^3/sec for the states with $v = 2, 3, 4, 5, 6$.

With account taken of the already cited value of the rate constant of the relaxation of the SF_6 molecule from the first level excited by the He atoms, the obtained data can be represented by the empirical relation $k(V) \propto k_{10} v_n$, where $n \approx 4.5$ and $k_{10} \approx 2.5 \times 10^{-12}$ cm$^3 \cdot$ sec^{-1}. The steep growth of the collisional decay rate constant with increasing level number agrees with our notions concerning the character of formation of a quasicontinuum on the upper vibrational states. In fact, with increasing number of the vibrational state, a sharp decrease takes place in the average distance between the neighboring levels, and it is this distance which determines the effectiveness of the vibrational relaxation.

We note in conclusion that the proposed method can be used to estimate the VT-relaxation constants of various polyatomic molecules on buffer gases.

1) In this crude qualitative model no account is taken of the role of the thermal bands and of the vibrational states belonging to oscillation modes other than the optical deformational vibration. The adequacy of this approximation is confirmed by the mutual consistency of the results obtained by different methods of reducing the experimental data.

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Two-quantum resonance excitation of two-level systems by stochastic fields

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The two-quantum excitation of a two-level system by broad-band radiation is investigated theoretically and experimentally. It is shown that the character and efficiency of the radiation's action can differ very greatly for fields that have different statistics. It is found that correlation between the harmonics of the spectrum can give an excitation efficiency not inferior to that of a monochromatic field at any level of excitation. Intraspectral correlation was produced experimentally by heterodyning, and it was shown that an originally inefficient signal having the statistics of complex Gaussian noise can be converted into an efficient correlated signal without any essential change of the spectrum, power, and intensity of the fluctuations as compared with the original signal. The action of the correlated field has special features combining those of monochromatic and broad-band nonmonochromatic excitation. In particular, the excitation spectrum of the correlated field is sharply resonant. The resonance part of the spectrum shows a paradoxical behavior: It becomes narrower and narrower as the width of the spectrum of the exciting field is increased.

PACS numbers: 42.50. + q

The study of the behavior of resonance systems in stochastic fields is of interest in various branches of physics. Such research is particularly significant for quantum radiation physics and nonlinear optics, because often the nonmonochromaticity of the field acting on resonant atomic-molecular and spin systems cannot be eliminated under actual conditions.

Experience in research on one-quantum and stepwise processes in classical resonant systems characterized by a single natural frequency has brought about a certain inertia in our ideas, with the supposition that under conditions close to resonance systems will be the more strongly excited, the narrower the spectrum of the applied radiation for a given intensity. It is intuitively assumed that the behavior of systems in stochastic fields becomes more and more like that found with monochromatic excitation, the narrower the spectrum of the nonmonochromatic field is made.

It is not hard to give examples of phenomena that do not fit into the framework of these ideas. It is well known[1] that under certain conditions nonmonochromatic fields can excite a resonance system $k!$ times more intensely than monochromatic fields of the same power (here k is the multiplicity of the many-photon resonance). Another example[2]: The broadening of the transition line in the quadratic dynamic Stark effect is greater the narrower the spectrum of the nonmonochromatic excitation. Both of these phenomena are caused by the fluctuations of the excitation's intensity and occur when the perturbation of the system is weak and the saturation effects are negligible. Moreover, these phenomena are brought about by the action of radiation with a narrow spectral band with an upper limit on its width imposed by definite conditions.[1,2]

Although these examples do correct the usual ideas about resonance phenomena in nonmonochromatic fields, it is still hard to expect monochromatic and broad-band stochastic radiations to be closely similar in their efficiencies and the nature of their effects on a system, at comparable intensities and without limitations in principle on the width of the excitation spectrum. In fact, if we consider, for example, a two-quantum process of resonance excitation of a two-level system by broad-band radiation (see Fig. 1), it can be seen that the main effect is given by the spectral region $\omega_0 + \omega_1 \approx \omega_{21} \pm \gamma_2$, where γ_2 is the line width of the transition, and ω_0 and ω_1 are the frequencies of the harmonics of the excitation, which run through all values in the spectrum. But since the main part of the radiation's intensity is concentrated in a band of width $\sim\Delta$, it is evident that for a given intensity the larger Δ, the smaller the excitation efficiency will be. Therefore it would seem that in any many-quantum resonance process broad-band radiation could not achieve the efficiency of a monochromatic field. This sort of argument leads to the conclusion that also the spectrum of the excitation in the process in question cannot be noticeably narrower than the pumping spectrum when $\Delta \gg 2$.

Nevertheless these conclusions are not absolutely correct. In this two-quantum process the action of broad-band radiation can be made no less efficient than monochromatic radiation. Furthermore there will then be a sharp resonance with a width considerably smaller than Δ. It will be shown later that the broad-band effect becomes both efficient and selective when its statistics satisfy definite requirements.

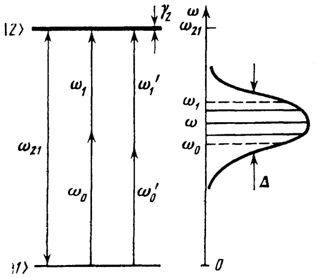

FIG. 1. Scheme of two-quantum excitation of a resonant system by nonmonochromatic radiation. To the right is shown the position of pairs of mutually complementary harmonics in the spectrum of the exciting radiation.

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