

form of the cross section. To explain the anomalous yield of the reaction $\text{Ni}^{64}(\gamma, p)\text{Co}^{63}$ it is necessary to propose the presence, besides the bremsstrahlung spectrum of the gamma quanta, also of a narrow (on the order of 1 keV) gamma line with energy close to the kinetic energy of the accelerated electrons, and with an intensity equal to the intensity of the bremsstrahlung spectrum in the region 0.2 - 0.4 MeV from the upper boundary.

No such additional line could be observed in the hitherto-performed measurements of the bremsstrahlung spectrum, since these measurements were performed either with an energy resolution not better than 100 keV, or in steps $\Delta E_{\gamma m}$ much larger than the width of the proposed line.

In a study of the yield of photonuclear reactions, this line can appear in the gamma spectrum only in those cases when the cross section near the threshold consists of individual narrow peaks. Apparently the large difference between the densities of the single-particle levels of the shell even-even nucleus Ni^{64} and the odd-odd Cr^{53} causes the unusual structure of the yield curve to be observed only for the first of these nuclei. The appreciable shift of the start of the yield curve of the reaction $\text{Ni}^{64}(\gamma, p)\text{Co}^{63}$ relative to the threshold, compared with the reaction $\text{Cr}^{53}(\gamma, p)\text{V}^{52}$, is apparently due to the same factor.

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INVESTIGATION OF REACTIONS OF EXCITED IODINE ATOMS WITH THE AID OF A PHOTODISSOCIATION LASER

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The photodissociation iodine laser operating with CF_3I molecules in the near infrared ($\lambda = 1.315 \mu$) can be used as a convenient device for the investigation of the kinetics of reactions of atomic iodine. As is well known [1], in the photolysis of CF_3I there are produced only excited atoms I^* (the state $5^2\text{P}_{1/2}$).

The radiative lifetime of the state $2^2\text{P}_{1/2}$ is about 0.1 sec. It is therefore possible to choose conditions (low pressures or low pump levels) such that the entire atomic iodine is in the excited state¹⁾ during a sufficiently long time interval ($\Delta t \sim 10^{-3}$ sec). In the generation regime, however, from the instant of formation of the laser field, owing to stimulated transitions, the working volume contains both excited atoms I^* and unexcited ones I. Thus, an investigation of the photolysis of CF_3I in the generation regime and without generation makes it possible to separate, to a certain degree, reactions in which the atoms

¹⁾This follows, in particular, from experiments with a Q-switched iodine laser [2].

I* and I take part.

In the experiment we determined the temporal dependence of I_2 production by photolysis of CF_3I from the absorption at the wavelength $\lambda = 4650 \text{ \AA}$. The pressure was $P(CF_3I) = 0.1 \text{ atm}$; the decomposition of the CF_3I at the employed pumping did not exceed 1.5%. Under these con-

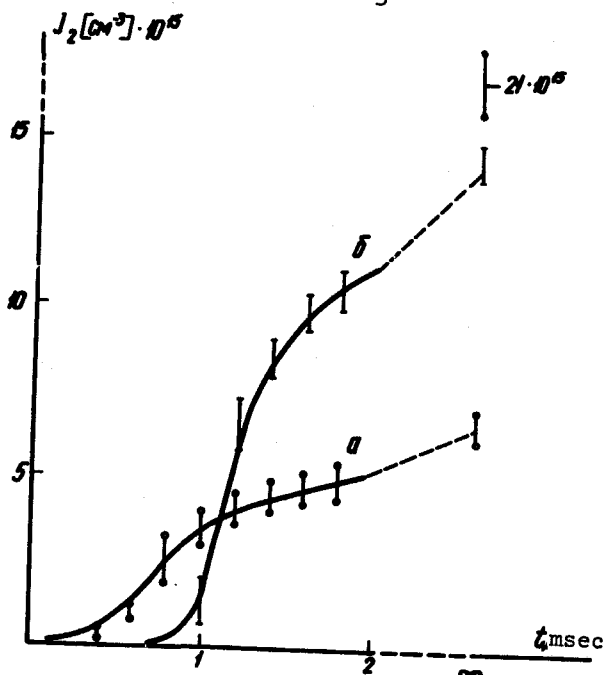


Fig. 1. Plot of production of $I_2(t)$, $E_{\text{pump}} = 445 \text{ J}$, $P(CF_3I) = 0.1 \text{ atm}$; curve *b* - without generation, curve *a* - with generation; * - final amount of I_2 in mixtures with NO. The calculated curves (solid lines) correspond to the following values of the constants: $k_1 = 5 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$; $k_3 = 6.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$; $k'_3 = 3 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$; $k_6 = 4.3 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$.

ditions, the temperature remained practically constant ($\Delta T \leq 100^\circ\text{C}$).

Two series of experiments were performed at each value of the pump: a) in the generation regime, b) without generation, i.e., under conditions of ordinary photolysis. The final number of molecules I_2^∞ was determined by the iodometry method. In addition we measured the final amount of I_2 in mixtures of CF_3I with NO with concentration ratios 1:0.3, 1:1, and 1:2 at a constant CF_3I partial pressure of 0.1 atm. It is known that NO molecules are good "absorbers" of CF_3 radicals. The addition of NO contributes therefore to the elimination of interaction between atomic iodine and the CF_3 radicals. The results of the experiment are shown in Fig. 1. As seen from this figure, the production curves $J_2(t)$ in regimes *a* and *b* differ greatly. The main qualitative feature is the intersection of curves *a* and *b*. Curve *a* first lies above *b*, but at large times their ratio is reversed, and the final concentration

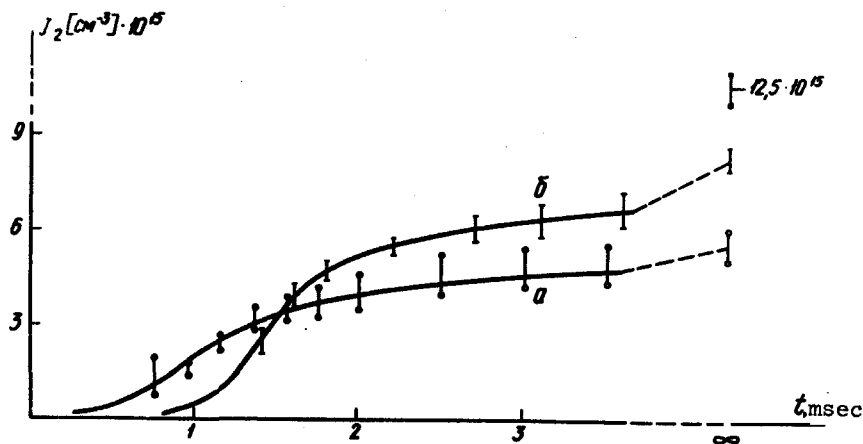


Fig. 2. Plot of production of $I_2(t)$, $E_{\text{pump}} = 210 \text{ J}$, $P(CF_3I) = 0.1 \text{ atm}$; curve *b* - without generation, curve *a* - with generation, * - final amount of I_2 in mixtures with NO. The calculated curves (solid lines) correspond to the following values of the constants: $k_1 = 5 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$; $k_3 = 4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$; $k'_3 = 4 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$; $k_6 = 7 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$.

2) According to [3], the absorption cross section of I_2 at this wavelength is independent of the temperature, accurate to $\sim 7\%$, in the interval $400 - 1300^\circ\text{K}$.

I_2^∞ is larger in the regime without generation. Noticeable production of I_2 is observed in this regime only after the lapse of a relatively long time Δt_d after the pump is turned off. In the interpretation of the experimental data we considered the following reactions of the atoms I and I*, of the radicals CF_3 , and of the molecules I_2 : $I + I + M \xrightarrow{k_1} I_2 + M$; $I + I^* + M \xrightarrow{k_1'} I_2 + M$; $I^* + I^* + M \xrightarrow{k_1''} I_2 + M$; $I^* + CF_3I \xrightarrow{k_2} I_2 + CF_3$; $CF_3 + I \xrightarrow{k_3} CF_3I$; $CF_3 + I^* \xrightarrow{k_3'} CF_3I$; $CF_3 + CF_3 \xrightarrow{k_4} C_2F_6$; $I^* + I_2 \xrightarrow{k_5} I + I_2$; $I^* + CF_3I \xrightarrow{k_6} I + CF_3$; $CF_3 + CF_3I \xrightarrow{k_7} C_2F_6 + I$; $CF_3 + CF_3I \xrightarrow{k_7'} C_2F_6 + I^*$ (M = third body).

The rate constants of some of these reactions are known from the literature [1, 4, 5]: $k_4 = 3.9 \times 10^{-11}$, $k_5 = 5 \times 10^{-12}$, and $k_6 = 3.5 \times 10^{-16}$ cm³/sec. The constants of the remaining reactions must be determined or estimated from experiment. In the general case the choice of the constants (and the preference of one reaction over another) is ambiguous. In our case, however, the time dependences of $I_2(t)$ in regimes a and b are characterized to such an extent by distinguishing features, that any leeway is practically eliminated. In addition, in choosing the experimental conditions special attention was paid to maximum separation of the process of interest in time.

Thus, by the time formation of I_2 begins, there are already no free CF_3 radicals in the working volume. This excludes the reaction $CF_3 + I_2 \rightarrow CF_3I + I$, which can play an important role in other cases. From the value of Δt_d in regime b it is easy to obtain an upper limit for the rate constants of the reactions with the atoms I* (k_1'' , k_2 , k_6 , k_7). Since the constant k_5 is known, we can separate from the $I_2(t)$ curves the section $t > t_c$ ($[I_2]$ larger than a certain critical value), when the entire atomic iodine is in the ground state, and determine k_1 from this section. The main qualitative feature of the $I_2(t)$ curves in regimes a and b, namely their point of intersection, can be explained only with the aid of the inverse-recombination reactions (the constants k_3 and k_3') provided k_3 is much larger than k_3' . The value of k_3' is determined by the difference between the final concentrations I_2^∞ in pure CF_3I in regime b and in mixtures with NO, while the constant k_3 is determined by the difference between I_2^∞ for regimes a and b. Indeed, in regime b the atoms I (unexcited) appear only after the vanishing of the radicals CF_3 .

The final values of the constants of interest to us were determined by trial and error during the course of the computer integration of the corresponding systems of equations for the concentrations (in regime a - with allowance for the laser field). The following

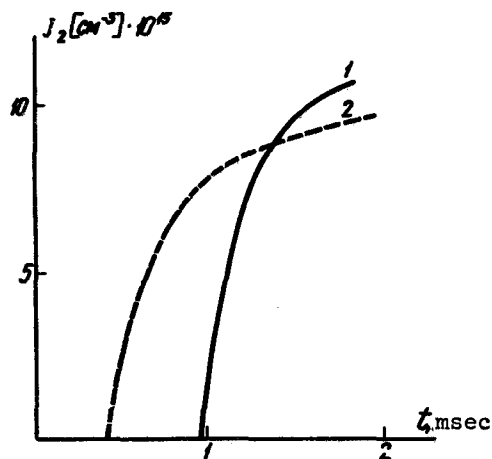


Fig. 3. Plot of production of $I_2(t)$ in the regime without generation; $E_{\text{pump}} = 445$ J, $P(CF_3I) = 0.1$ atm; curves 1 and 2 pertain to different degrees of purification of the working medium, with curve 2 denoting an insufficiently purified medium.

results were obtained: $k_1 = 5 \times 10^{-32}$ cm⁶/sec, $k_1' \leq 2 \times 10^{-33}$ cm⁶/sec, $k_1'' \leq 10^{-33}$ cm⁶/sec. $k_2 \leq 10^{-17}$ cm³/sec, $k_3 = (4 - 6.5) \times 10^{-11}$ cm³/sec, $k_3' = (3 - 4) \times 10^{-12}$ cm³/sec, $k_6 = (4.3 - 7) \times 10^{-17}$ cm³/sec, $k_7 \leq 3 \times 10^{-6}$ cm³/sec. 3) It was impossible to estimate the constant k_7' , since the experimental results are highly insensitive to inclusion of this reaction in the analysis [6].

A detailed description of the work will be published later.

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REPOPULATION OF HIGHLY-EXCITED VIBRATIONAL LEVELS IN A COLD LATTICE

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We consider a molecular crystal consisting, e.g., of diatomic molecules. The molecules exchange vibrational energy and this process is more probable than the conversion of the intramolecular energy into lattice energy, i.e., into phonons. One of us [1] considered the influence of anharmonicity on the lifetime of highly-excited vibrational levels in molecular crystals, and noted a strong narrowing of the energy bands for such excitations. States in which second vibrational levels (obtained, as it were, by sticking of two-single-quantum excitations) are excited were considered by Jortner and Rice [2] and later by Agranovich [3]. In the present article we consider a different aspect, connected with the fact that the number N of the vibrational quanta (abbreviated "vi-quanta") can be regarded as approximately conserved, and one can seek a stationary state at a given lattice temperature T_1 and at a given¹⁾ value of N .

The subject of our study is the distribution of the molecules over the vibrational states. By virtue of the anharmonicity, the energy of the two-quantum state is lower than the energy of two single-quantum states. A similar relation holds also for higher states. This can be expressed with the aid of the inequality

$$\Delta E_r = E_{r-1} + E_1 - E_r - E_0 > 0, \quad r > 1, \quad (1)$$

where E_r is the energy of the anharmonic oscillator. In the case of a Morse potential it is given by (in a system of unifs in which $\Omega = \hbar = 1$)

3) The constants k_3 and k_3' are given under the assumption that the corresponding reactions are binary. One cannot exclude the possibility of participation of a third body.

1) Approximate conservation of the total number of intermolecular quanta is possible, since nonradiative transitions with change of the number of vi-quanta are connected with the production of a large number of phonons N_p and are therefore highly unlikely. N_p is approximately equal to $\Omega/\omega_d \sim 20 - 30$, where Ω is the value of the vi-quantum ($\sim 2^3 - 3 \times 10^3$ cm⁻¹) and ω_d is the Debye frequency of the crystal ($\sim 10^2$ cm⁻¹). Thus, the only process leading to a change in the number of vi-quanta is their emission. The corresponding time is $t_p \approx 10^{-2} - 1$ sec for molecules having a dipole moment (CO, NO, HCl) and $t_p = 10^6 - 10^7$ sec [4] for molecules having no dipole moment (O₂, N₂, H₂).