Multiphoton IR excitation and dissociation of CF_3I: The experiment and model

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Multiphoton absorption and dissociation of CF_3I by laser radiation are experimentally investigated. A semiempirical model of an excitation of CF_3I is proposed. This model is based on an earlier experimental demonstration of the existence of two ensembles in the molecular-gas excitation process. Good agreement between the results of measurements and those of calculations is obtained. The comparison of the theory and the experiment yields the average anharmonicity constant Fermi-interaction constants of CF_3I as well as the dependence of an important quantity that characterizes the excitation process—the fraction of molecules excited to high vibrational levels—on both the frequency and the laser radiation energy flux density.

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1. INTRODUCTION

Multiphoton excitation and dissociation of polyatomic molecules by high-power IR laser radiation (see the reviews[1,2]) is presently intensively investigated in many laboratories. Despite the appreciable number of experimental and theoretical studies, no existing complete theoretical model of the phenomenon accounts for all the existing reliable experimental data; the mechanism of the phenomenon is only qualitatively understood. The difficulty of the theoretical approach is due primarily to the lack of spectroscopic data on the high vibrational levels of polyatomic molecules (intramode and intermode anharmonicities, cross sections of the vibrational transitions, rotational constants, etc.). It can therefore be assumed that a semiempirical approach, using the experimentally measured quantities as the parameters of the theoretical model, provides at present the best approximation.

In the theoretical description of the process of IR photoexcitation of a polyatomic molecule it is customary to distinguish arbitrarily between three stages of the process: 1) passage by the molecule through several lower discrete levels, 2) excitation in the quasicontinuum, and 3) dissociation of the overexcited molecule. The greatest difficulties lie in the description of the first stage, since the complete spectrum of the vibrational-rotational transitions between the lower levels in a strong IR field is not known. The second stage can be simulated with good justification by a sequence of resonance transitions, and has been described by rate equations formulated in Refs. 3 and 4. Finally, the decay of the molecule that has absorbed an energy ε higher than the dissociation energy D can be described with the aid of the statistical theory of unimolecular decay (the RRKM theory).

The uncertainty in the description of the excitation of the molecule during the first stage hinders greatly the theoretical analysis of the succeeding excitation stages. Nonetheless, it is feasible in principle to construct a model that describes qualitatively correctly the behavior of the molecule in the quasicontinuum. This is made possible, as will be shown below, by the concept of the fraction q of the molecules that become involved in the vibrational-excitation process. The parameters of the model can be the experimentally measured average absorbed energy $\bar{\varepsilon}$ and of the dissociation yield β, as well as their dependences on the characteristics of the IR exciting radiation.

The present paper deals with the following: a) experimental investigation of the parameters of the IR photoexcitation and dissociation of the CF_3I molecule, and b) development of a semiempirical model of excitation of the CF_3I molecule on the basis of these experiments. We begin with a brief description of the experimental procedure and proceed next to an exposition of the results of the measurements of $\bar{\varepsilon}$ and β (Sec. 2). The key point of the paper is Sec. 3, where the attributes by means of which the calculated curves must be compared with the experimental ones are formulated. In Sec. 4 are given the fundamental equations of the model and a physical treatment of the molecular constant in whose terms the transition cross sections can be expressed. The results of the theory and their comparison with experiment are given in Sec. 5, while Sec. 6 is devoted to a discussion of the results.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The principal quantities measured in the present study of the CF_3I molecule are the average vibrational energy $\bar{\varepsilon}$ absorbed by the molecule and the dissociation yield β. The experimentally measured parameters on which the semiempirical model is based must meet certain requirements. First, these parameters must pertain only to the initial excited molecule. This means that it is necessary either to exclude or to take accurate account of the successive dissociation of the products as well as of all their secondary chemical reactions, particularly recombination. In addition, an extremely important role is played by the accuracy of the measurements of both the parameters themselves and of the characteristics of the exciting radiation. These requirements serve as the basis in the mea-

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surement of $\bar{\varepsilon}$ and β.

To excite and dissociate the CF_3I molecule we used radiation from an atmospheric-pressure pulsed CO_2 laser with selection of the vibrational-rotational lines. The spectral width of the emission line did not exceed $0.03\ cm^{-1}$, and the pulse duration at half-height was 80 nsec. The laser radiation was collimated into the cells with CF_3I with the aid of a long-focus mirror telescope. For a more accurate determination of the energy density of the radiation in the cell, we measured the distribution of the energy over the cross section of the spot in two directions, using moving slit diaphragms (Fig. 1). The measurement of the absorbed energy of the laser radiation was made in a CF_3I cell 150 cm long with the aid of radiation thermocouples. The accuracy of the measurement of the absolute values of the energy was not worse than 10%.

The dissociation of CF_3I molecule was effected in a stainless-steel cell with NaCl windows. The cell contained a lateral stub to freeze out the molecular iodine produced as a result of the dissociation of the CF_3I. The dissociation yield β was determined by measuring the change of the coefficient of IR absorption of CF_3I, using an IKS-24 infrared spectrometer. The procedure used to measure the dissociation yield will be described below (see also Ref. 5). The accuracy with which β was determined was not worse than 5%. The CF_3I pressure in the cells was constant at 0.2 Torr, and the cell wall temperature was +20°C.

Multiphoton absorption. The CF_3I molecule was excited in the vibrational band ν_1, the linear-absorption spectrum of which is shown in Fig. 2 (dashed). The most important quantitative characteristic of the multiphoton excitation process is the absorbed energy $\bar{\varepsilon}$ per molecule in the irradiated volume. The value of $\bar{\varepsilon}$ was determined by calorimetry of the laser-pulse energy absorbed in the CF_3I. Figure 2 shows also the frequency dependences of $\bar{\varepsilon}$ for the CF_3I, measured at two different laser-radiation energy densitites: $\Phi = 0.1\ J/cm^2$ (curve 2) and $\Phi = 1.0\ J/cm^2$ (curve 1). The multiphoton-absorption band width exceeds the linear-absorption band width and increases with increasing radiation-energy density. In addition, the multiphoton-absorption spectra reveal a certain structure that varies with Φ.

Figure 3 shows the dependence of $\bar{\varepsilon}$ on the IR pulse energy Φ, measured for CF_3I at the frequency $\omega_{las} = 1074.65\ cm^{-1}$ corresponding to the Q branch of the ν_1 band of the CF_3I molecule. With increasing Φ, the value of $\bar{\varepsilon}$ first increases, and then saturates at Φ

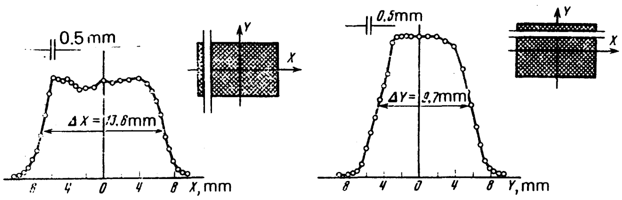

FIG. 1. Distribution of the energy (in relative units) in the cross section of the CO_2 laser beam.

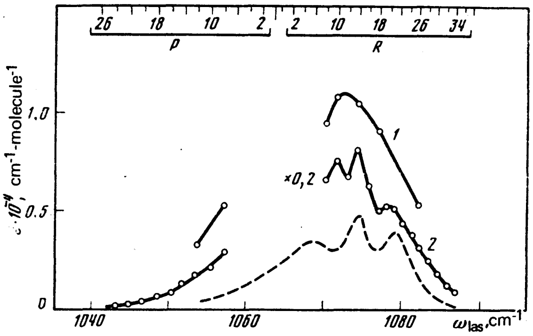

FIG. 2. Frequency dependence of the absorbed energy $\bar{\varepsilon}$ per CF_3I molecule: 1—$\Phi = 1\ J/cm^2$. 2—$\Phi = 0.1\ J/cm^2$; $p_{CF_3I} = 0.2$ Torr. The dashed curve shows the linear absorption spectrum of the ν_1 band.

$> 4\ J/cm^2$, with $\bar{\varepsilon}_{sat} \approx 20{,}000\ cm^{-1}$. The saturation of $\bar{\varepsilon}$ is due to the fact that, as will be shown later, at $\Phi > 2\ J/cm^2$ an appreciable fraction of the CF_3I molecules dissociates during the time of the pulse. We note also the fact that, as shown by measurements, at $\Phi > 2\ J/cm^3$ the value of $\bar{\varepsilon}$ is practically independent of the pulse duration τ (which ranges from 80 to 500 nsec), and depends only on the laser pulse energy (at fixed ω_{las}).

Multiphoton dissociation. As shown in Ref. 6, the primary act in IR photo dissociation of the CF_3I molecule is the detachment of an iodine atom

$$CF_3I + n\hbar\omega \rightarrow CF_3 + I. \tag{1}$$

The end products are the result of the secondary reactions

$$CF_3 + CF_3 + M \rightarrow C_2F_6 + M, \tag{2}$$

$$CF_3 + I + M \rightarrow CF_3I + M, \tag{3}$$

$$I + I + M \rightarrow I_2 + M, \tag{4}$$

where M is a third body (atom, molecule, or radical) or else the cell wall. The reaction (1) determines the primary dissociation yield β, i.e., the fraction of the molecules in the irradiated volume, which have dissociated under the influence of the IR pulse in the absence of the secondary reactions (2)–(4). The aggregate of the reactions (1)–(4) determines the observed dissociation yield β^{obs}, i.e., the fraction of the CF_3I molecules by which the initial concentration of the CF_3I molecules was decreased after the end of the action of reaction (1)–(4) and after chemical and thermal equilibrium was established. The value of β^{obs} was determined from the decrease of the CF_3I pressure

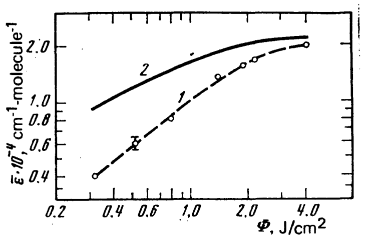

FIG. 3. Dependence of the absorbed energy per molecule of the laser-pulse energy density at $\omega_{las} = 1074.65\ cm^{-1}$; 1—experiment, $p_{CF_3I} = 0.2$ Torr; 2—calculation.

using the standard relation

$$p/p_0=(1-\Gamma\beta^{\text{obs}})^N,$$

where p_0 and p are the partial pressures of CF_3I before and after the irradiation, respectively; N is the number of radiation pulses; $\Gamma=v/V$, where v and V are respectively the irradiated volume and the total volume of the cell. In no case did p/p_0 exceed 50%.

Figure 4 shows the measured dependence of β^{obs} at a CF_3I pressure 0.2 Torr on the laser-radiation energy density at $\omega_{\text{las}}=1074.65$ cm^{-1}. Just like $\bar{\varepsilon}$, the quantity β^{obs} at $\Phi>2$ J/cm^2 is practically independent of the radiation-pulse duration. The reaction (3) plays an essential role in the formation of the end products, therefore $\beta^{\text{obs}}<\beta$.

To determine the primary dissociation yield β we used the following experimental procedure. Oxygen was added to the CF_3I in the irradiated cell to serve as an acceptor for the CF_3 radicals, and the dependence of the CF_3I dissociation yield β_{O_2} on the oxygen pressure was measured. With increasing oxygen pressure, the value of β_{O_2} first increased, reaching a maximum at $p_{O_2}=1.5$ Torr, and then started to decrease slowly. The increase of β_{O_2} was due to the effective binding of the radical CF_3 (the result is F_2CO) and suppression of the reactions (2) and (3). The decrease of β_{O_2} at $p_{O_2}>1.5$ Torr is due to partial deactivation of the vibrationally excited CF_3I molecules by the O_2 molecules in the course of the irradiation.

To take the deactivation into account, we measured also the dependence of the CF_3I dissociation yield on the pressure of a neutral buffer, nitrogen. It turned out that at O_2 and N_2 pressures higher than 1.5 Torr the quantity β_{O_2}/β_{N_2} reaches a constant value. This means, first, that O_2 and N_2 deactivate the vibrational excitation of the CF_3I to practically equal degrees, and in addition, the value $(\beta_{O_2}/\beta_{N_2})_{\max}=1.63$ shows by how many times β^{obs} is smaller than β. Since, as shown by measurements, $(\beta_{O_2}/\beta_{N_2})_{\max}$ is practically independent of the radiation energy density Φ, we can, now that we have the dependence of β^{obs} on Φ, determine the dependence of the primary dissociation yield β on Φ. Figure 4 shows the dependence of β on Φ at $\omega_{\text{las}}=1074.65$ cm^{-1}. At $\Phi=4.7$ J/cm^2 we have $\beta=0.98$, i.e., almost all the molecules in the irradiated volume dissociate under the influence of the IR laser pulse.

An important characteristic of the process is the quantum efficiency of the dissociation

$$\varphi=D\beta/\bar{\varepsilon}, \tag{5}$$

which determines the relative fraction of the absorbed IR energy consumed in the dissociation of the molecules. Figure 5 shows from the Φ dependence of the primary quantum efficiency calculated from the measured Φ dependences of β and $\bar{\varepsilon}$. At $\Phi=4.0$ J/cm^2 we have $\varphi=0.9$, i.e., 90% of the absorbed energy goes to dissociation of the CF_3I molecules. Figure 6 shows the dependence of φ on the laser-emission frequency at a fixed energy density $\Phi=1.0$ J/cm^2. It is seen that the quantum efficiency of the dissociation at this value of Φ first increases when the excitation frequency is shifted towards longer wavelengths, reaches a maximum in the region of the maximum of the frequency dependence of the absorbed energy ($\nu\approx1072$ cm^{-1}), and then remains practically unchanged.

3. ANALYSIS OF OBSERVED DATA

The values of the averaged absorbed energy per molecule $\bar{\varepsilon}$ and of the primary dissociation yield β, measured for CF_3I, as functions of the radiation energy density Φ, can be used as the basis for a comparison with the theoretical model.

The difficulties encountered in the development of a complete theory were noted in the introduction and are connected with the description of the molecule excitation in the region of the lower energy levels. There exists, however, an experimental fact that points to the feasibility of constructing a semiempirical model that operates with a description of the molecule excitation only in the region of the quasicontinuum. Thus, it was shown in Ref. 7 for the AsO_4 molecule and in Ref. 8 for the SF_6 molecule that IR photoexcitation produces two ensembles of molecules: "cold" unexcited molecules and "hot" molecules excited to high vibrational states. Finally, ignoring the existence of two ensembles leads to a patent contradiction between the values of $\bar{\varepsilon}$ and β obtained also from our experimental results. In fact, for example, at $\Phi=0.3$ J/cm^2 the average energy ab-

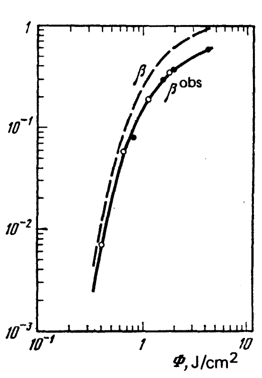

FIG. 4. Experimental dependence of the dissociation yield on the laser-pulse energy density Φ, measured for CF_3I and $\omega_{\text{las}}=1074.65$ cm^{-1}: β^{obs}—observed dissociation yield, β—primary dissociation yield; E Torr.

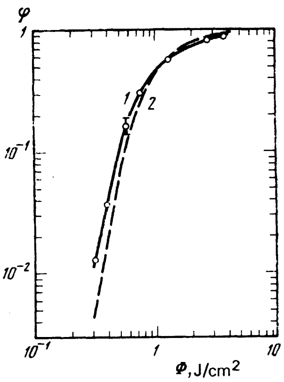

FIG. 5. Dependence of the quantum efficiency of the dissociation on the laser-pulse energy density at $\omega_{\text{las}}=1074.65$ cm^{-1}: 1—experiment, $p_{CF_3I}=0.2$ Torr; 2—calculation.

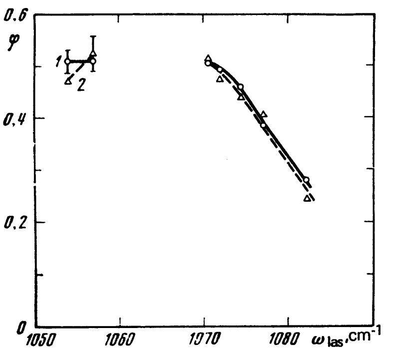

FIG. 6. Frequency dependence of the quantum efficiency of dissociation at $\Phi = 1$ J/cm^2: 1—experiment, $p_{CF_3I} = 0.2$ Torr; 2—calculation.

sorbed by the molecule is $\bar{\varepsilon} \approx 3000$ cm^{-1}, corresponding to a summary Boltzmann population $\sim 3 \times 10^{-7}$ of the levels lying above the dissociation boundaries, whereas the dissociation yield amounts to $\beta \sim 10^{-3}$. This contradiction can be "corrected" only by assuming that a certain fraction $q < 1$ of the molecules takes part in the excitation process and has a relatively high average excitation level $\bar{\varepsilon}_q = \bar{\varepsilon}/q$.

The theoretical model that considers molecule excitation only over the quasicontinuum levels should describe correctly the distribution for the upper ensemble. We note, however, that this assumption does not take into account the possibility of gradual involvement of the molecules in the process of excitation into the quasicontinuum furing the laser pulse, but the very existence of two ensembles indicates that this involvement is realistic (see also Sec. 6).

Under the assumption made we arrive at the following relation between the theoretical quantities and the experimentally observed ones:

$$\varepsilon_{\text{exp}}/q = \varepsilon_{\text{theor}} \quad \beta_{\text{exp}}/q = \beta_{\text{theor}} \tag{6}$$

From this, according to (5), we obtain a relation for the quantum efficiencies

$$\varphi_{\text{exp}} = \varphi_{\text{theor}} \tag{7}$$

which does not depend on the still unknown quantity q.

Thus, the comparison of our model with experiment will be based on the dependences of the quantum efficiency φ both on the energy density and on the laser frequency. As will be shown below, good agreement between the theoretical and experimental dependences of φ can be reached by varying only two molecular constants that have a clear physical meaning but whose experimental determination is quite difficult. Having reached agreement between the experiment and calculated dependences of φ we determine, first, these constants and, second, the dependences of the factor $q = \bar{\varepsilon}_{\text{exp}}/\bar{\varepsilon}_{\text{theor}}$ on the density and on the frequency of the laser radiation.

4. THEORETICAL MODEL

To describe the excitation of the CF$_3$I molecule we shall use the kinetic-equation system formulated in Refs. 3 and 4. This system of equations, which will be cited below, is meaningful only for the quasicontinuum region of high vibrational states, where cascade resonance transitions are possible in principle because of the large density of the vibrational levels.[1)] This kinetic-equation model, however, is being more and more frequently used for the description of the entire process, with an aim at interpreting experiments in which the absorbed energy of the molecule certainly exceeds the energy needed to excite it into the quasicontinuum (see Refs. 3, 10–12). Such a description is used in the present paper.

Thus, let the molecule start with a certain state of energy E_0. Because of the requirement of energy conservation in the course of interaction with the IR field, the states that are populated have energies E_n (reckoned from E_0) equal to the energy of n radiation quanta (see Fig. 7 as well as Refs. 9). Of course, the width of the spectral interval of the populated states in the vicinity of the energy E_n is finite, even if the exciting radiation is strictly monochromatic, and is determined by the rates of the induced transitions $\sigma_{n-1,n}I$ and $\sigma_{n,n+1}I$, where σ are the transition cross sections and I is the radiation intensity (in photons/cm$^2\cdot$sec). The variables that describe the excitation process are chosen to be the summary populations z_n of the levels lying in the vicinities of the resonances. The kinetic equations for the populations z_n are of the form

$$\frac{dz_n}{dt} = \sigma_{n-1,n}I\left(z_{n-1} - \frac{\rho_{n-1}}{\rho_n}z_n\right) - \sigma_{n,n+1}I\left(z_n - \frac{\rho_n}{\rho_{n+1}}z_{n+1}\right) - W_n z_n. \tag{8}$$

Since the densities of the vibrational levels in the vicinities of the successive resonances are not equal to one another but, on the contrary, increase quite rapidly with increasing n, the rates of the direct and inverse transitions are not equal, a fact taking into account in (8) by the factors ρ_{n-1}/ρ_n and ρ_n/ρ_{n+1} (ρ_n is the density of the vibrational states of the molecule corresponding to the energy E_n). The rates W_n in Eq. (8) describe the decay of states lying above the dissociation boundary ($W_n = 0$ for states below this boundary).

The unknown quantities for the molecule in Eqs. (8) are the cross sections of the successive transitions. For comparison with experiment (for example, in

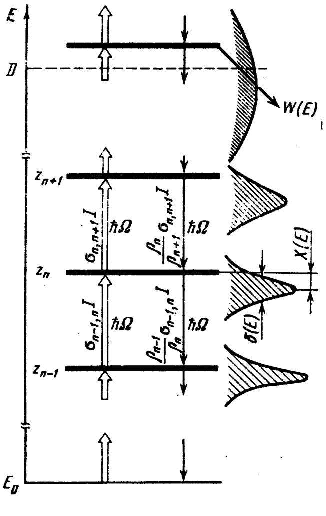

FIG. 7. Illustration explaining the theoretical model of the excitation of the CF$_3$I molecule.

Refs. 3, 10, 12) they have chosen previously more or less realistic phenomenological dependences of the cross section on the number of the transition. The shortcomings of this approach are quite obvious, since the selected cross sections for the different frequencies of the radiation are not connected in any way with one another, whereas physically a connection should exist. In the present paper we express the cross sections for all the radiation frequencies in terms of only two parameters that have in the case of the molecule a clear physical meaning.

We start from the fact that in the harmonic approximation an arbitrary excited vibrational level $|a\rangle$ of the CF_3I molecule, characterized by a set of vibrational quantum numbers $|n_1, n_2, \ldots, n_6\rangle$, is connected with a dipole-allowed transition near the laser frequency $\omega_{\rm las} \sim 1050\ldots1080$ cm^{-1} with a state $|b\rangle$ with a set of quantum numbers $|n_1+1, n_2, \ldots, n_6\rangle$. Anharmonicity leads to a shift of this transition, and also to its broadening as a result of the fact that the harmonic wave functions ψ_a and ψ_b corresponding to the states $|a\rangle$ and $|b\rangle$ contribute to the large number of closely located "correct" eigenstates of the exact Hamiltonian of the molecule. The mixing of the harmonic states proceeds via Fermi resonances. The CF_3I molecule has four particularly close Fermi resonances, three of the three-frequency type and one of the four-frequency type:

$$\begin{gathered} 2\nu_5-\nu_1\approx 5\ \text{cm}^{-1}, \quad \nu_2-2\nu_6\approx 10\ \text{cm}^{-1}, \\ \nu_3+\nu_6-\nu_5\approx 11\ \text{cm}^{-1},\ 2\nu_2-\nu_3-\nu_4\approx 11\ \text{cm}^{-1}. \end{gathered} \tag{9}$$

The vibrational frequencies of the molecule are given in the Table. If the matrix elements $V_{\alpha\beta}$ of the corresponding interaction operators

$$\begin{gathered} \hat V_1=\alpha_1\hat x_5^2\hat x_1, \quad \hat V_2=\alpha_2\hat x_5\hat x_6^2, \\ \hat V_3=\alpha_3\hat x_3\hat x_5\hat x_6, \quad \hat V_4=\alpha_4\hat x_2^2\hat x_3\hat x_4 \end{gathered} \tag{10}$$

exceed the characteristic resonance defect ~5–10 cm^{-1}, then complete mixing of the harmonic states takes place within the limits of an energy interval of the order of $2\langle V_{\alpha\beta}\rangle$.[16] As to the contribution of a given harmonic state to states located at distances $\Delta \gg \langle V_{\alpha\beta}\rangle$, this contribution (the square of the modulus of the amplitude) in accordance with the perturbation theory is proportional to Δ^{-2}. This asymptotic behavior corresponds to the Lorentz contour introduced in Ref. 11 to describe the absorption of the molecule in the quasicontinuum. In the present paper we also approximate the contour of the absorption from a given vibrational state by a Lorentz contour (see Fig. 7). To specify completely the Lorentz contour of absorption from a given vibrational state, it suffices to know two quantities—the transition frequency ν at the center of the contour and the half-width δ of the contour. Obviously, both ν and δ are functions of the vibrational energy E.

As indicated above, the interval in which the harmonic states are mixed because of the Fermi interaction amounts to $2\langle V_{\alpha\beta}\rangle$. The width $2\delta(E)$ of the contour of transitions from a state with energy E is obviously a sum of the mixing interval of the harmonic states in the vicinity of the energy E and the mixing interval in the vicinity of the energy $E+\omega_{\rm las}$, so that

$$\delta(E)\approx\langle V_{\alpha\beta}(E)\rangle+\langle V_{\alpha\beta}(E+\omega_{\rm las})\rangle. \tag{11}$$

As to the function $\langle V_{\alpha\beta}(E)\rangle$, it should correspond to the dependence, on the vibrational energy, of the matrix elements of the operators (10) responsible for the Fermi interaction. Since the principal role in the formation of the quasicontinuous contour of the transitions is made by the three-frequency Fermi resonances, the function $\langle V_{\alpha\beta}(E)\rangle$ can be represented in the form

$$\langle V_{\alpha\beta}(E)\rangle\approx V_0(E/\omega_{\rm las})^{3/2}, \tag{12}$$

where V_0 is a constant that characterizes on the average the Fermi interaction energy.

It is natural to define the transition frequency $\nu(E)$ at the center of the Lorentz contour in terms of the average anharmonic shift, which is proportional to the vibrational energy. Using anharmonicity constants expressed in the customarily employed spectroscopic terms, we arrive at the equation

$$\nu(E)\approx\nu_1-x_0E/\nu_1, \tag{13}$$

where

$$x_0=\sum_{i=1}^{6}x_{i1}(\nu_1/\nu_i)(1+\delta_{i1})$$

has the meaning of the "average" anharmonicity constant. We note that averaging of the anharmonicity constant (just as of the Fermi-interaction constant) has a perfectly natural physical justification, inasmuch as for the strongly excited states of the molecule the most probable combinations of the vibrational quantum numbers are those corresponding to equipartition of the vibrational energy over all the modes.

Thus, the cross section of absorption from a state with energy E at the frequency $\omega_{\rm las}$ can be represented in the form

$$\sigma(E)=\frac{4\pi\omega_{\rm las}}{3\hbar c}\langle\mu^2(E)\rangle\frac{\delta(E)}{\delta^2(E)+[\omega_{\rm las}-\nu(E)]^2}, \tag{14}$$

where $\delta(E)$ and $\nu(E)$ are determined by Eqs. (11)–(13), while $\langle\mu^2(E)\rangle$ is equal to the squared dipole moment, integrated over the Lorentz contour and averaged over the states in the vicinity of the energy E. This quantity remains undetermined in (14). To determine $\langle\mu^2(E)\rangle$ we use the sum rule for the squares of the dipole moments, which in our case takes the form

$$\rho(E)\langle\mu^2(E)\rangle=[\rho_0(E)+2\rho_1(E)+3\rho_2(E)+\ldots]\mu_1^2, \tag{15}$$

where μ_1 is the vibrational dipole moment of the mode ν_1; ρ_0 is the density of the vibrational states with energy E and with the occupation n_1 of the mode ν_1 equal to zero, ρ_1 is the density of the vibrational states with energy E and $n_1=1$, etc. From (15) we can easily determine the function $\langle\mu^2(E)\rangle$. There are many good approximations for the calculation of the density of

TABLE I.

	Frequency, cm^{-1}					
	$\nu_1(1)$	$\nu_2(1)$	$\nu_3(1)$	$\nu_4(2)$	$\nu_5(2)$	$\nu_6(2)$
Molecule: CF_3I:	1075,2 [13]	741 [14]	286 [14]	1185 [14]	540 [14]	265 [14]
Complex:	1087 [15]	703 [15]	–	1251 [15]	512 [15]	120 *

The asterisk marks the value obtained by us.

the vibrational states. We have used the Witten-Rabinovitch approximation (see, e.g., Ref. 17). The function $\langle\mu^2(E)\rangle$ determined for the molecule CF_3I is shown in Fig. 8. The numerical value of the vibrational dipole moment of the ν_1 mode of the CF_3I molecule was determined by us from measurements of the intensity of the absorption band ($S=2.4\pm0.1$ cm^{-2} Torr^{-1}) and amount to (according to Ref. 18) $\mu_1=0.39$ D. Thus, the unknown parameters in the formulas for the cross sections are only the averaged anharmonicity and Fermi-interaction constants x_0 and V_0, respectively, a variation of which should in fact be used to compare experiment with theory.

Our calculation has so far disregarded rotation. Since the selection rule $\Delta K=0$ with respect to the projection of the angular momentum on the molecule axis holds for the ν_1 band of the CF_3I molecule, the contour, averaged over K, of the molecule absorption from the excited vibrational-rotational state consists, strictly speaking, of a superposition of three Lorentz contours corresponding to the transitions in the P, Q, and R branches. A rigorous allowance for the rotations leads to a substantial increase of the number of equations. In the stage of merely fitting the varied parameters, we confined ourselves to the system (18) for a molecule with a rotational quantum number $J_0=50$, taking all three branches into account, but neglecting the variation of J. States with this rotational quantum number have the largest total population at $T=293$ K.

The statements made above apply equally well to the thermal bands. In the parameter-fitting stage, we took into account the thermal bands by an averaging procedure, assuming that the molecule starts not from the ground state but from an energy level $E_0\approx400$ cm^{-1} equal to the average vibrational energy of the gas at $T=293$ K.

Of course, the chosen values of J_0 and E_0 bring the model close to the real situation. Tests made on the integration of the complete set of equations, with account taken of the distribution over the rotational levels as well as of the initial distribution over the vibrational levels, yielded small differences (<3%) from the calculated values of $\bar{\varepsilon}$ and β.

We arrive thus at the final formula, which we have used in Eq. (3), for the cross section of the successive transitions:

$$\sigma_{n,n+1}=\frac{4\pi\omega_{las}}{9\hbar c}\langle\mu^2(E_n)\rangle\delta(E_n)\sum_{j=-1}^{1}\{\delta^2(E_n)+[\omega_{las}-\nu(E_n)-2BJ_0j]^2\}^{-1},$$

$$E_n=E_0+n\omega_{las}. \tag{16}$$

Here, as before, the functions δ and ν are defined by Eqs. (11)–(13); $B=0.05$ cm^{-1} is the rotational constant of the CF_3I molecule. The dependence of the cross section on the number of the transition at the frequency 107.65 cm^{-1}, which corresponds to the tabulated value of the $R(14)$ line of the CO_2 laser, is shown in Fig. 8.

The rates of the molecular decay in Eqs. (8) were calculated by us within the framework of the RRKM theories (see, e.g., Ref. 17):

$$W_n=\frac{1}{c}\frac{Q(E_n)}{\rho(E_n)}, \tag{17}$$

where $\rho(E_n)$ is the molecule state density expressed in centimeters, and $Q(E_n)$ is the number of states of the activated complex from the molecule dissociation energy to the energy E_n. We can again use the Witten-Rabinovitch approximation,[17] the use of which in the calculation of Q and ρ calls for knowledge of the following constants: the frequencies of the molecule, the frequencies of the activated complex, and the molecule dissociation energy. The values used by us for the frequencies of the molecule CF_3I and of the activated complex corresponding to the dissociation of the molecule into the radical CF_3 and the atom I are given in the Table. The dissociation energy known to us is[10]

$$D=18865\pm1000\ \text{cm}^{-1}. \tag{18}$$

The value of D in the indicated limits is, strictly speaking, the third variable parameter of the model.

As a result of numerical integration of Eqs. (8) we get the theoretical values $\bar{\varepsilon}_{theor}$ and β_{theor}. The quantity β_{theor} consists of the dissociation yield during the laser pulse and the dissociation yield after the laser pulse. The second term is equal to the summary relative population of the levels located above the dissociation boundary. We have thus disregarded the influence of the collision processes.

The calculation results are compared with experiment is using the values of φ, in accordance with the arguments advanced in Sec. 3.

5. COMPARISON OF THE CALCULATION RESULTS WITH EXPERIMENT

The most sensitive to the choice of the parameters x_0, V_0 and D turned out to be the frequency dependence of the quantum efficiency φ. The best agreement between φ_{theor} and φ_{exp} for the entire frequency dependence corresponds to the following parameter values:

$$x_0=3.8\pm0.2\ \text{cm}^{-1},\ V_0=0.73\pm0.03\ \text{cm}^{-1},\ D=18300\ \text{cm}^{-1}. \tag{19}$$

The deviations of x_0 and V_0 are presented under the assumption that the principal experimental error is due to the possible ≈10% error in the measurement of the energy density of the laser pulse. The value of the dissociation energy D in (19) is an upper-bound

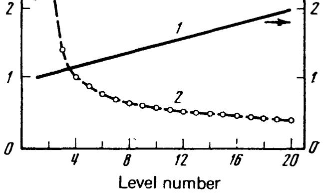

FIG. 8. Dependence of the mean squared dipole moment $\mu^2_{n-1,n}$ (1) and of the transition cross section $\sigma_{n-1,n}$ (2) on the number of the vibrational level.

estimate. The lower-bound estimate agrees with the lower bound of (18).

The theoretical values of φ at an energy density $\Phi = 1$ J/cm^2 and at various laser frequencies are shown in Fig. 6. Figure 9 shows the values of the factor q, calculated from the ratio $\bar{\varepsilon}_{\rm exp}/\bar{\varepsilon}_{\rm theor}$. It is seen that the fraction of the excited molecules is maximal in the frequency region close to the Q branch, and decreases by several times only on the far wings of the absorption band.

Using the obtained values of the parameters (8) we calculate the functions $\bar{\varepsilon}_{\rm theor}(\Phi)$ (Fig. 3) and $\beta_{\rm theor}(\Phi)$ at the frequency 1074.65 cm^{-1}. The corresponding function $\varphi_{\rm theor}(\Phi)$ shown in Fig. 5 agrees within the limits of experimental error with the experimental dependence for the section $\Phi > 0.7$ J/cm^2 of the plot.

The calculated and experimental functions $\bar{\varepsilon}(\Phi)$ make it possible to obtain the dependence of the factor q on the laser-pulse energy density at the frequency 1074.65 cm^{-1} (see Fig. 10).

The obtained dependences of the factor q for the CF$_3$I molecule on the frequency and on the radiation energy density can be compared with the analogous dependences (Figs. 9 and 10) previously obtained in Ref. 20. The method used in Ref. 20 to determine the factor q is based on the assumption that the principal physical parameter that determines the dissociation yield is the average energy $\bar{\varepsilon}_q = \bar{\varepsilon}_{\rm exp}/q$ of the molecules of the excited ensemble. (In the case, for example, of a Boltzmann distribution, this parameter is obviously the temperature of these molecules). In addition, it was assumed that the dependences of q and of $\beta_q \equiv \beta_{\rm exp}/q$ on Φ is much weaker for q than for β_q. Curve 1 of Fig. 9 was obtained on the basis of the experimental dependence of the quantum dissociation efficiency $\varphi_{\rm exp}$ on the excitation frequency. It is convenient to use precisely this dependence, since φ is independent of q. We used here an additional assumption, that the function $\beta_q(\bar{\varepsilon}_q)$ is universal and independent of $\omega_{\rm las}$.[2)] Using the values β_q and e_q determined in Ref. 20 for $\omega_{\rm las} = 1074.65$ cm^{-1}, we can obtain the value of $\varphi = \varphi(\bar{\varepsilon}_q)$, which is likewise independent of $\omega_{\rm las}$. Equating the values of φ and $\varphi_{\rm exp}$ for different $\omega_{\rm las}$ we can determine from $\varphi(\bar{\varepsilon}_q)$ the value of $\bar{\varepsilon}_q$. Hence, knowing $\bar{\varepsilon}_{\rm exp}$, we have determined the factor $q = \bar{\varepsilon}_{\rm exp}/\bar{\varepsilon}_q$ for different excitation frequencies.

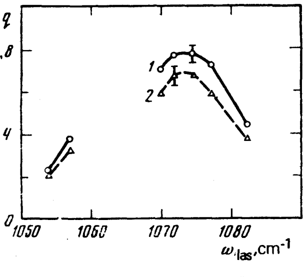

FIG. 9. Frequency dependence of the factor $q = \bar{\varepsilon}_{\rm exp}/\bar{\varepsilon}_{\rm theor}$: 1—obtained on the basis of the results of Ref. 20, 2—obtained from a comparison of the experimental and theoretical data; $\Phi = 1$ J/cm^2.

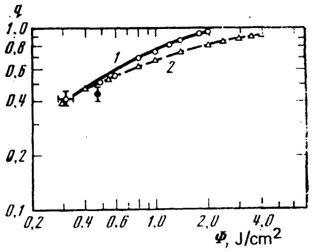

FIG. 10. Dependence of the factor q on the laser-pulse energy density at $\omega_{\rm las} = 1074.65$ cm^{-1}: 1—obtained in Ref. 20, 2—obtained from a comparison of the experimental and theoretical dependence of the absorbed energy on the laser-pulse energy density; ●—value obtained on the basis of the data of Ref. 21.

A comparison of the values of q obtained in Ref. 20 and on the basis of our present calculation shows that the maximum difference does not exceed 20%. In addition, at $\Phi = 47$ J/cm^2, the results agree well with the value $q = 0.47$ measured by the method of double IR-UV resonance.[21]

Figure 5 shows a noticeable difference between the experimental and calculated functions at $\Phi < 0.7$ J/cm^2. It can be shown that one of the cause of this difference is the substantial contribution of collisional dissociation after the termination of the pulse. To this end we compare the vibrational distribution produced under the influence of the IR pulse with the Boltzmann distribution for the same absorbed energy. This comparison is shown in Fig. 11 for $\Phi = 0.4$ and 1 J/cm^2. For the first of these values of Φ the Boltzmann populations of the levels above the dissociation boundary are substantially larger than the calculated ones. For the second value of Φ, the Boltzmann populations of the first few levels above the dissociation boundary are smaller than the calculated ones. After the end of the laser pulse it is necessary to take into account the vibrational-relaxation process, which has two competing tendencies. On the one hand, this process tends to establish a Boltzmann distribution in the upper subsystem. On the other hand, because of exchange of vibrational energy with the lower sub-

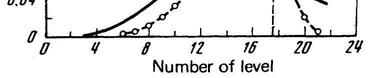

FIG. 11. Vibrational energy distribution functions at $\omega_{\rm las} = 1074.65$ cm^{-1}: a) $\Phi = 0.4$ J/cm^2, b) $\Phi = 1$ J/cm^2. Curves 1—calculated distribution functions under IR laser excitation; 2—Boltzmann distribution functions at the same absorbed energies. The vertical dashed lines indicates the CF$_3$I dissociation limits.

system, the vibrational energy of the upper subsystem decreases. Obviously, the contribution of the collisional dissociation can be quite appreciable if the relation between the Boltzmann and calculated distributions takes the form shown in Fig. 11a. However, when the relation between the Boltzmann and calculated distributions takes the form of the curves in Fig. 11b, the collisions apparently cannot lead to a substantial decrease of the dissociation yield, inasmuch as even at ~1000 cm^{-1} above the dissociation limit the rate of the monomolecular decay is already larger than the rate of the vibrational relaxation under the experimental conditions.

6. DISCUSSION

The characteristics of the multiphoton IR excitation and of the dissociaition of the CF_3I, which were measured in the present study, and the semiempirical excitation model based on these measurements, are in good agreement. The choice of the molecule was successful for several reasons. First, dissociation of CF_3I produces the relatively simple radical CF_3, which absorbs weakly the exciting radiation (unlike, for example, the SF_6 molecule and the radical SF_5). Second, it was possible to take into account relatively simply the recombination of the radicals and to determine the primary dissociation yield. Third, because of the relatively low dissociation limit of CF_3I, we were able to obtain a near-unity dissociation yield without focusing the laser beam, so that the interpretation of the results is much simpler.

The theoretical model assumed in the present paper does not differ in principle from those used before. The only difference lies in the choice of the cross sections of the transitions in the quasicontinuum, which in our opinion is physically fully justified (see Sec. 4). The distribution function is also close in form to those obtained previously. We emphasize once more that what is new in principle is the approach itself to the comparison of the experimental and calculated results (see Sec. 3). In fact, in the preceding studies[3, 10-12] no account was taken of the fact that the molecules at the low levels can interact differently with the laser pulse. In the present paper we have attempted to take this into account by using as the basis experimental facts[7, 8] that point to the existence of two ensembles of molecules in the course of their excitation. Good agreement was obtained between the measurement results and the calculation results. We note that this agreement was obtained both for the frequency dependences and for the dependences on the laser-pulse energy density.

Our investigations have also made it possible to determine so important a characteristic as the fraction of the molecules excited into high vibrational states, and obtain the dependence of q on both the frequency and on the laser-pulse energy. We call attention to the slow dependence (Fig. 10) of the factor q on the laser-pulse radiation density. For values of q close to unity, we have the relation

$$(1-q) \propto \exp(-\Phi/\Phi_0) \tag{20}$$

for both curve 1 and curve 2 of Fig. 10. This behavior of the factor q can apparently not be explained within the framework of the theoretical models that attribute the passage of the molecule through the system of low levels to field broadening. The most advanced model from this point of view, based on the "seepage" effect,[22] yields the relation

$$(1-q) \propto \exp[-(\Phi/\Phi_0)^n], \tag{21}$$

where n is the number of laser quanta needed for the excitation of the molecule into the quasicontinuum. Estimating the lower limit of the quasicontinuum at

$$E_{\text{lim}} \sim \omega_{\text{las}} (V_0/\Delta_{\text{Fermi}})^{3/2}$$

[this estimate follows directly from (12)], we obtain, taking (9) and (19) into account, $n \gtrsim 5$. We arrive thus at a clear cut difference between (20) and (21).

In conclusion, we call attention once more to an important feature of the model assumed in the present paper. We have actually assumed that the distribution of the populations in the upper ensemble of molecules is described by the solution of Eqs. (8) with initial conditions $z_n(0) = \delta_{n0} q$, where q is constant. Actually the factor q can vary during the pulse. In the case when the change of q is determined by the density of the passing energy, the model can be easily refined by using a successive approximation method. Taking the obtained solution as a zeroth approximation, we can introduce in the next approximation a term proportional to $dq/d\Phi$ in the first equation of (8), and this term can be estimated from the $q(\Phi)$ dependence obtained in the zeroth approximation, etc. The resultant correction, however, is not large since the zeroth approximation has already yielded (see Fig. 10) a slow dependence of the factor q on the laser-pulse energy density Φ.

It should also be noted that the value of the factor q can in principle be determined not by the transmitted energy, but by the intensity of the laser pulse. In this case the molecules can be excited from definite initial states into the quasicontinuum within a time much shorter than the pulse duration, and the subsequent change of q can be neglected.

It appears that for further development of the considered model we need new theoretical and experimental studies that explain the very physical nature of the factor q. The quantities and relations obtained in the present paper can serve as one of the criteria for the still nonexistent calculation, capable of accounting for the available experimental data, of the excitation of the lower vibrational levels of the molecules.

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1) For the change from the description with the aid of the Schrödinger equation to the description with the aid of kinetic equations see Ref. 9.

2) It appears that one can make also a more general assumption, that the distribution function $F(\mathcal{E}_q)$ does not depend on the excitation frequency within the limits of one vibrational band, from which follows automatically the universality of the function $\beta_q(\varepsilon_q)$. As shown by calculations of the excitation dynamics, in our case the distribution function at various frequencies and at the same value $\mathcal{E}_{\text{theor}} = 10^4$ cm^{-1} hardly differ from one another. In the general case, however, the

conditions for the validity of this assumptions have not been made clear.

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Effect of geometry and field intensity on the profiles of saturated-absorption resonances in low-pressure molecular gases

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It is shown theoretically that a unique interaction between the impact and field or transit broadening mechanisms makes the collision line shift dependent on the intensity and the geometry of the field. It is found in the particular case of the $\lambda = 3.39\ \mu\text{m}$ methane transition that the mechanism affects appreciably the reproducibility of the frequency. The joint influence of recoil and field and transit broadenings on the line shift is also considered. It is shown that allowance for transit effects alters the dependence of the line shift on the field intensity because of the recoil effect.

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1. INTRODUCTION

Modern nonlinear-spectroscopy methods can attain a very accurate agreement between the frequency of a laser and the frequency of the molecular transition. The experiments that have demonstrated the possibility of developing a high-grade unified laser frequency and length standard by this method[1] initiated an intense study of the causes that restrict the accuracy of the reproducibility of the molecular-transition frequency by such a standard. A rather large number of papers have been devoted to a theoretical investigation of the influence of collisions under specific conditions of very low absorbing-gas pressures,[2] saturation-field geometry,[3] quadratic Doppler effect,[4,5] and a number of other factors on the profile of the saturated-absorption resonance. Particular attention was paid to an improvement of the influence of the magnetic hyperfine structure of