Strong vibrational overexcitation above the dissociation limit and the monomolecular decay of the large molecule $(CF_3)_3CI$ in an infrared laser field

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Infrared multiphoton overexcitation above the dissociation limit of the polyatomic molecule $(CF_3)_3CI$ was investigated experimentally in the field of a CO_2 laser pulse. Resonance multiphoton ionization of the I atom, produced as a result of photodissociation in the ground state $5p(^2P_{3/2})$ or the excited state $5p(^2P_{1/2})$, was used to investigate the kinetics of the monomolecular decay of overexcited $(CF_3)_3CI$ molecules when collisions could be neglected. Calorimetric measurements showed that more than twofold vibrational overexcitation of $(CF_3)_3CI$ above the dissociation limit was achieved. The experimental data were then used to determine the monomolecular decay rate k and the parameters of the distribution function for the overexcited molecular ensemble, namely, the mean energy $\bar{\varepsilon}$ and the distribution width δ. The measured values of k and δ are compared with theoretical predictions.

1. INTRODUCTION

Vibrationally highly-excited molecules are of fundamental importance because this type of excitation produces a change in the nature of vibrational motion as the energy of the molecule increases, i.e., regular motion is replaced by stochastic motion.[1] There is, therefore, considerable interest in methods that can be used to produce vibrationally highly-excited molecules. Infrared multiphoton excition (MPE) of polyatomic molecules by a strong laser field[2] is one of the most readily accessible methods of this kind. It is well-known[2] that, even when collisions can be neglected, most of the polyatomic molecules that absorb energy from the IR field can be overexcited above the dissociation limit D, and can then dissociate. However, the degree of vibrational overexcitation that can be attained is very dependent on the number s of vibrational degrees of freedom of the molecule.

Considerable overexcitation above the dissociation limit of a "small" polyatomic molecule with $s \simeq 10$–15 vibrational degrees of freedom is impossible. This conclusion is based on the quasiequilibrium theory[3] of monomolecular decay (RRKM theory), which relies on the assumption of a statistical equilibrium distribution of vibrational energy in the isolated molecule (i.e., the molecule "forgets" how it was excited). The decay of the overexcited molecule occurs as a result of fluctuations when sufficient energy has been concentrated on the bonds to be broken.[4] It follows that the smaller the number of degrees of freedom, the faster will this fluctuation occur for a fixed degree of overexcitation. The rate of decay $k(\varepsilon)$ of a small polyatomic molecule (ε is the vibrational energy) exceeds, even for a low degree of overexcitation, the rate of excitation in an IR field attained experimentally, and the molecule decays. This behavior of small polyatomic molecules, predicted by the RRKM theory, is confirmed by experimental studies of the average energy absorbed in IR MPE[2,5] and by measurements of the internal energy distribution among rotational, translational, and vibrational degrees of freedom of the byproducts IR multiphoton dissociation of such molecules.[6–8]

A "large molecule" with $s \gtrsim 30$ vibrational degrees of freedom can be substantially overexcited by an IR laser field ($\varepsilon > 2D$). We shall show this by using simple estimates based on the RRKM theory. A molecule will absorb energy from the field until its monomolecular decay rate $k(\varepsilon)$ becomes comparable with its rate w of excitation in the IR field. We shall use the quasiclassical RRKM approximation[3]:

$$k(\varepsilon)=\bar{\omega}\,[(\varepsilon+\varepsilon_0{}^+-D)/(\varepsilon+\varepsilon_0)]^{s-1}, \qquad (1)$$

where

$$\bar{\omega}=\prod_{i=1}^{s}\omega_i\Big/\prod_{i=1}^{s-1}\omega_i{}^+,$$

ω_i and ω_i^+ are the vibrational frequencies of the molecule and the activated complex, respectively, and ε_0 and ε_0^+ are the zeroth vibrational energies of the molecule and the complex, respectively. For large polyatomic molecules ($s \gg 1$)

$$\varepsilon_0=\frac{1}{2}\sum_{i=1}^{s}\hbar\omega_i\approx\varepsilon_0{}^+=\frac{1}{2}\sum_{i=1}^{s-1}\hbar\omega_i{}^+,$$

so that, putting $k(\varepsilon) = w$, we find from (1) that

$$\varepsilon+\varepsilon_0=D[1-(w/\bar{\omega})^{1/(s-1)}]^{-1}. \qquad (2)$$

For typical IR MPE using a pulsed CO_2 laser, the IR intensity is $I \simeq 10^8$ W/cm^2 (Ref. 2). If we take the typical cross section for vibrational transitions in a highly-excited molecule to be $\sigma \simeq 10^{-18}$–10^{-19} cm^2 (Ref. 2), we find that $w = \sigma I/\hbar\omega_{IR} \simeq 10^9$ s^{-1}. It then follows immediately from the above definition of the frequency factor $\bar{\omega}$ that its typical value is of the same order as the frequency of molecular vibrations: $\bar{\omega} \simeq 10^{13}$ s^{-1}. Substituting these values of w and $\bar{\omega}$ in (2), and taking $s - 1 = 30$, we find that $\varepsilon + \varepsilon_0 = 3.8D$. This estimate shows that a large polyatomic molecule can be highly overexcited above the dissociation limit in the IR MPE process.

There is some indirect experimental evidence at present for the substantial overexcitation of $(CF_3)_3CI$ ($s = 36$);

Ref. 9), anthracene ($s = 66$; Ref. 10), and benzylamine ($s = 45$; Ref. 11) above the dissociation limits. However, we know of no experiments demonstrating a high degree of overexcitation ($\varepsilon > 2D$) under IR MPE in large molecules.

In this paper, we report the results of direct experimental studies of strong vibrational overexcitation above the dissociation limit and of the decay of a large molecule in an IR laser field when collisions between the molecules can be neglected. The particular molecule chosen for these investigations was $(CF_3)_3CI$. We have actually observed the monomolecular decay of this molecule in real time. This was achieved by the photoionization method described in Section 3. The method is based on selective (in the initial states) multiphoton ionization of I atoms. We have also carried out direct measurements of the energy absorbed from the IR field when, only a small fraction of the molecules dissociates during the laser pulse. The experimental results are presented in Section 4. They were used to determine, first, the average degree of excitation of the molecules $\bar{\varepsilon}$ (Section 4), which, under our conditions of IR MPE, was greater by a factor of 2.4 than the dissociation energy of $(CF_3)_3CI$. Second, we determined the rate of monomolecular decay, $k(\varepsilon)$, of isolated molecules (Section 5) and, third, we found the width δ of the distribution function of the ensemble of overexcited molecules (Section 5). We have shown that, for an average degree of overexcitation $\bar{\varepsilon} = 2.4D$, practically the entire distribution function of the vibrationally excited ensemble of molecules is confirmed to the region $\varepsilon > 1.9D$. Comparison between the decay rates for isolated $(CF_3)_3CI$ molecules with the predictions of RRKM theory, given in Section 6, shows that the two are in agreement. The measured dependence of the mean energy absorbed per molecule, $\bar{\varepsilon}(\Phi_{IR})$, on the IR energy density is used in Section 7 to deduce a theoretical estimate for the distribution width δ^{th}, which agrees with the measured width determined from real-time observations of the monomolecular decay of $(CF_3)_3CI$.

2. APPARATUS

A block diagram of the apparatus is shown in Fig. 1a. The working frequency of the CO_2 laser was $\omega_{IR} = 947.7$ cm^{-1} (10P16 line). The energy per IR pulse was 1 J, the pulse width at half maximum was 100 ns, and the full width was 300 ns. This IR radiation was first attenuated by CaF_2 plates and then focused by spherical ($f = 150$ cm) and cylindric ($f = 12$ cm) NaCl lenses in the space between the collecting electrodes of an ionization chamber. The energy of each IR pulse was measured by a pyroelectric detector. The distribution of the IR field in the focal plane (Fig. 1b) was measured by scanning with the pyroelectric detector in two directions. The detector aperture was defined by a 20-μm slit. The IR radiation produced the vibrational excitation of $(CF_3)_3CI$.

An XeCl excimer laser ($\lambda = 308$ nm, $\varepsilon_{XeCl} = 30$ mJ) was used to pump the dye laser (rhodamine C) consisting of a master oscillator and an amplifier. The dye laser was assembled in accordance with the standard scheme.[12] Radiation from the dye laser was frequency doubled by a KDP crystal. The second harmonic was then focused by a quartz lens ($f = 4.5$ cm) at the center of the IR caustic. The IR and UV rays lay in the horizontal plane, and the angle between them was 60°. The energy of the frequency-doubled UV pulse was up to 100 μJ, the width at half height was 8 ns, and the width of the spectrum was 1 cm^{-1}. The second harmonic was tuned to the two-photon resonance $5p(^2P_{3/2}) - 6p(^2D_{5/2})$, $\lambda_1 = 3046.7$ Å (Ref. 13) of the three-photon ionization of the I atom in the ground state or the two-photon resonance $5p(^2P_{1/2}) - 6p(^4D_{1/2})$, $\lambda_2 = 3040.3$ Å (Ref. 13) of the three-photon ionization of excited atoms I*. (We note that, when the UV frequency was detuned from resonance, the number of photoions produced in this way fell by a factor of more than 1000.) The size of the UV caustic (diameter 2.5×10^{-3} cm, length 0.5 cm) was much smaller than typical dimensions of inhomogeneities in the IR field, which, together with the nonlinear mechanism used to detect the atoms, ensured that the diagnostic procedure was well localized. The energy of each UV pulse was measured at exit from the ionization chamber by a pyroelectric detector. This UV radiation was used as the diagnostic probe for undecayed $(CF_3)_3CI$ molecules or their decay products (the I atoms).

The delay between the exciting IR pulses and the probing UV pulses was measured to within ± 10 ns for each laser shot. This was done by measuring the delay between the CO_2 and XeCl current pulses with the Ch3-34 frequency meter.

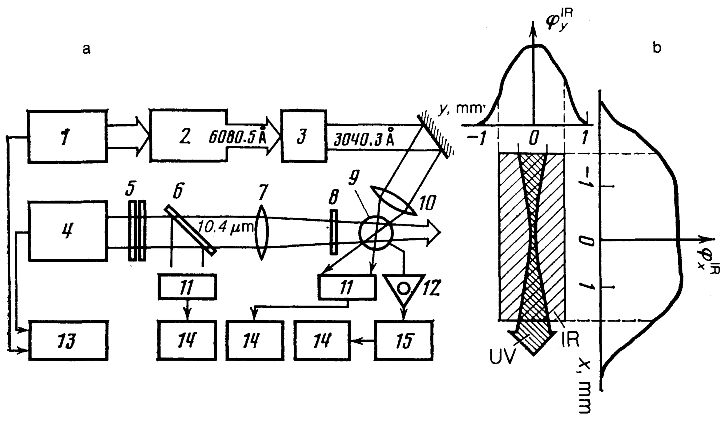

FIG. 1. a) Block diagram of the apparatus: 1—XeCl excimer laser; 2—dye laser; 3—KDP crystal; 4—CO_2 laser; 5—CaF_2 absorbers; 6—NaCl plate; 7—NaCl lens, $f = 150$ cm; 8—cylindric NaCl lens, $f = 12$ cm; 9—ionization chamber; 10—quartz lens, $f = 4.5$ cm; 11—pyroelectric detector; 12—head amplifier; 13—Ch3-34 frequency meter; 14—V4-17 pulse voltmeters; 15—U2-6 amplifier. b) Section through the IR caustic.

Absolute calibration of the delay-measuring system was made against the S8-12 oscillograph and fast IR and UV photodetectors (FPU-500 and FK-19, respectively).

The photoion current was measured in the ionization chamber filled with $(CF_3)_3CI$ at a pressure of 10^{-3} Torr. The chamber was refilled frequently enough to avoid the accumulation of photochemical byproducts. The photoions were collected by applying a potential difference of 30 V to the chamber electrodes (2-cm diameter plates). The ion signal was first amplified by a head amplifier mounted directly on the ionization chamber, and then by the U2-6 amplifier. After pulse-shaping, (time constant $100\,\mu s$), the signal was recorded by the pulse voltmeter V4-17.

The average degree of excitation of the $(CF_3)_3CI$ molecules was determined from the measured absorption of the IR pulse (100 ns). These measurements were carried out in a cell ($l = 14$ cm) filled with $(CF_3)_3CI$ at a pressure of 0.1 Torr. The pressure in the cell was determined in two stages. Coarse pressure monitoring was performed with the VDG-1 manometer. The precise value of the pressure ($\pm 3\%$) was determined using the Specord 75IR spectrometer to record the IR transmission spectrum of a gas introduced at the same pressure into a monitoring cell. The energy of the IR pulse was measured with thermocouple probes at entry and exit of the main chamber ($l = 14$ cm). The lateral size of the IR beam was 0.8×0.8 cm and the beam was uniform to within 5% over the cell length.

It is important to note that the conditions under which all these measurements were performed were such that collisions between the molecules during each measurement could be neglected. Actually, the value of the characteristic gas-kinetic collision parameter was $(p\tau_{col}) = 50$ ns·Torr (Ref. 14). When the monomolecular decay process was observed, the total pressure in the chamber was less than 3×10^{-3} Torr. Under these conditions, the average time between collisions, $\tau_{col} \gtrsim 10\,\mu s$, is much greater than the time taken to observe the decay ($1\,\mu s$). During measurements of the energy absorbed from the IR field, the collision time was $\tau_{col} \simeq 500$ ns ($p = 0.1$ Torr), which is also appreciably greater than the laser pulse length ($\tau_{IR} = 100$ ns).

3. PHOTOIONIZATION METHOD OF DETECTING THE DECAY OF THE IODIDES

Since all iodides RI (R is an organic or fluoroorganic radical) have a similar mechanism of photolysis in the A-band,[15] the method we have used to detect the $(CF_3)_3CI$ decay is suitable for all iodides. We shall demonstrate its utility by taking $(CF_3)_3CI$ as an example.

First, we make the following important remarks. The lowest-lying dissociation channel of the vibrationally overexcited $(CF_3)_3CI$ molecules is the decay into the $(CF_3)_3C$ radical and the I atom in the ground electronic state $5p(^2P_{3/2})$ (the energy necessary to break the C–I bond lies near $D = 19\,000$ cm^{-1} for all known iodides[16]). When the molecule decays with the formation of the atomic iodide with I* in the lowest electronically excited state $5p(^2P_{1/2})$, a further 7603 cm^{-1} of energy is necessary.[13] Decay channels involving the breaking of the C–C or C–F bonds lie higher still along the energy scale.[16] We shall show that vibrationally-overexcited $(CF_3)_3CI$ molecules dissociate along the lowest-lying energy channel. Using (1), we find that, when $\varepsilon = 2.5D$ (this degree of overexcitation was attained in our experiments), the rate of decay of $(CF_3)_3CI$ molecules along the channel involving the formation of I* was lower by a factor of 1000 than the decay rate along the lowest-lying energy channel (we used $\varepsilon_0^+ = 11\,000$ cm^{-1} and $D = 19\,000$ cm^{-1}; Ref. 17). The great majority of all the vibrationally overexcited molecules are thus seen to decay along the channel

$$(CF_3)_3CI + n\hbar\omega_{IR} \xrightarrow{\beta(t)} (CF_3)_3C + I(^2P_{3/2}), \tag{3}$$

where $\beta(t)$ is the decay probability as a function of time t.

The second harmonic of the dye laser was used as the diagnostic probe for $(CF_3)_3CI$ decays. The frequency of this UV radiation was tuned to the two-photon resonances $5p(^2P_{3/2}) - 6p(^2D_{5/2})$ ($\lambda_1 = 3046$ Å) or the $5p(^2P_{1/2}) - 6p(^4D_{1/2})$ ($\lambda_2 = 3040.3$ Å) resonances of three-photon ionization of the iodine atom (Fig. 2). We shall show that, in the first case (λ_1), we detected the decay products of the molecule, i.e., the I atoms, whereas, in the second case (λ_2), we detected undissociated molecules. Both wavelengths used lay in the A absorption band of the $(CF_3)_3CI$ molecule.[15] When a photon of this UV radiation is absorbed, the corresponding electron localized on the C–I bond undergoes a transition from a bonding to a dissociating molecular orbital[15] (see also Fig. 2), and the molecule decays along the channels

$$(CF_3)_3CI + \hbar\omega_{UV}\, C \begin{array}{ll} \overset{5\%}{\nearrow} (CF_3)_3C + I\,(^2P_{3/2}) & \quad (4a) \\ \underset{95\%}{\searrow} (CF_3)_3C + I^*\,(^2P_{1/2}) & \quad (4b) \end{array} .$$

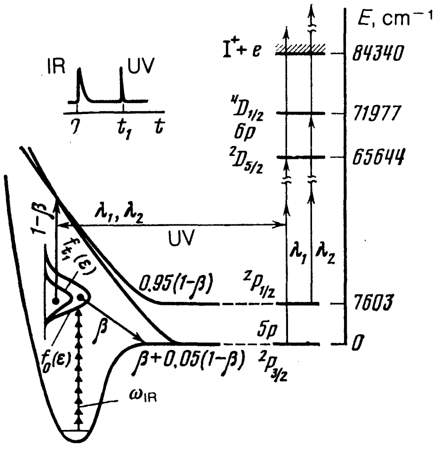

FIG. 2. Photoionization diagnostics of the monomolecular decay of $(CF_3)_3CI$. Molecules that are vibrationally excited by the IR field decay along the lowest-lying energy channel (3) [$\beta(t)$ is the dissociation yield at time t]. Undecayed molecules [their fraction is $1 - \beta(t)$] absorb the UV photon and decay preferentially (95%) along channel (4b) with the formation of excited ($^2P_{1/2}$) iodine atoms. Under these conditions, selective photoionization of the initial states of the unexcited I atoms can be used to detect the appearance of this product of the monomolecular decay of $(CF_3)_3CI$, whereas photoionization of the excited atoms I* can be used to determine the concentration of undecayed molecules (see text).

The I* quantum yield during UV photolysis of $(CF_3)_3CI$ at $\lambda \simeq 3000$ Å was shown by our measurements to be 95%. Since only a small fraction of the molecules (5%) decays along channel (4a), and if the conditions are such that the dissociation yield of the vibrationally overexcited molecules is $\beta \gtrsim 5\%$ [channel (3)], selective (in the initial states of the atom) ionization of I can be used to detect the appearance of this decay product of $(CF_3)_3CI$. This selective ionization is performed by returning the second harmonic of the dye laser to the above two-photon resonance ($\lambda = 3046.7$ Å).

Since excited iodine is not produced in the decay of vibrationally overexcited $(CF_3)_3CI$ molecules, the measured concentration of I* produced in the UV photolysis of $(CF_3)_3CI$ can be used to determine the concentration of molecules that have not decayed [molecules that have not decayed along channel (3) will decay along channel (4) under the influence of the UV radiation; see Fig. 2]. These measurements were performed by tuning the second harmonic of the dye laser to the two-photon ionization resonance of excited iodine ($\lambda_2 = 3040.3$ Å). Thus, the UV radiation performs two functions in the detection of undecayed molecules: first, they take part in the UV photolysis of $(CF_3)_3CI$ and, second, they ionize the I* atoms produced as a result.

We now emphasize one important feature of the above method of detecting $(CF_3)_3CI$. Since UV photolysis is accompanied by a transition in the A-band from the bound state of the molecule with a discrete energy spectrum to a repulsive state with a continuous energy spectrum (Fig. 2), the A-band of the iodides has a considerable homogeneous width. Even for the small vibrationally unexcited molecules CH_3I and CF_3I, the homogeneous width of the absorption band amounts to 4000 cm^{-1} (Refs. 18 and 19). UV absorption from the vibrationally-excited levels causes broadening of the A-band.[20] As we pass from CH_3I and CF_3I to the more polyatomic iodides, the A-band should not narrow because, in such molecules, a larger number of vibrational quantum numbers can change when a UV photon is absorbed. In fact, the absorption spectrum of $(CF_3)_3CI$ is somewhat wider that that of CF_3I (Ref. 15). In view of the foregoing, we may conclude that, when absorption is highly saturated near the center of the A-band, all the molecules undergo UV photolysis independently of their initial vibrational state. In our experiments, the UV energy density in the focus corresponded to a tenfold saturation of the UV photolysis of $(CF_3)_3CI$.

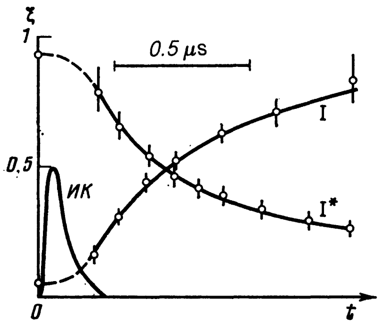

FIG. 3. Photoionization measurements yielding the probability ξ of formation of atomic iodine in ground and excited states under the combined action of exciting IR and probing UV pulses illuminating $(CF_3)_3CI$ as a function of the delay t between the laser pulses. $\xi_I = \beta(t) + 0.05[1 - \beta(t)]$; $\xi_{I}^{*} = 0.95[1 - \beta(t)]$, where $\beta(t)$ is the probaiblity of decay along channel (3). $\Phi_{IR} = 3.8$ J/cm², $\omega_{IR} = 947.7$ cm^{-1}, $P_{(CF_3)_3CI} = 10^{-3}$ Torr, $\lambda_1 = 3046.7$ Å (I), $\lambda_2 = 3040.3$ Å (I*).

Figure 3 shows the photoion signal at $\lambda_1 = 3046.7$ Å (I) and $\lambda_2 = 3040.3$ Å (I*) as a function of the delay t between the exciting IR and the probing UV laser pulses. The photoionization signals shown in Fig. 3 are given in units of the probability of formation of atomic iodine in the ground or excited state when both laser pulses act on the $(CF_3)_3CI$. Since all the molecules in our experiment that have not decayed along channel (3) are dissociated by the probing UV radiation, the probability of formation of unexcited and excited atoms is given by $\xi_I = \beta(t) + 0.05[1 - \beta(t)]$ and $\xi_{I*} = 0.95[1 - \beta(t)]$ respectively. Without going into detail of the absolute calibration of the photoionization method, we shall briefly indicate how this calibration was carried out. The sensitivity of detection of the unexcited I atoms was determined when, at the time of arrival of the probing UV pulse, all the molecules had already decayed along channel (3) (for $t = 1$ μs and Φ_{IR} between 8 and 25 J/cm², the photoionization signal due to unexcited atoms was saturated, whereas the signal due to excited atoms was absent). The sensitivity of detection of excited atoms was determined from the fact that, first, all the molecules decayed under the influence of the leading edge of the UV pulse (tenfold saturation of photolysis) and, second, the photoionization signal due to unexcited atoms for $\Phi_{IR} = 0$ amounted to 0.05 of the signal for $\Phi_{IR} = 25$ J/cm². Figure 3 demonstrates the fact that the detection of intact $(CF_3)_3CI$ molecules and their decay products is complementary. In subsequent measurements, we used the detection of the initial molecules.

4. EXPERIMENTAL DATA

Figure 4 shows the measured fraction $F = 1 - \beta$ of undecayed $(CF_3)_3CI$ molecules as a function of the delay between the exciting IR and probing UV laser pulses under different conditions of excitation. Each point in Fig. 4 is an average over 10–30 measurements. The indicated error is the root mean square deviation. It is clear from these experimental data that, for $\Phi_{IR} = 3$ J/cm², most of the molecules decay during the time of observation ($\simeq 1$ μs), so that practically all the molecules are overexcited above the dissociation limit under these experimental conditions. We note that the observation time has an upper bound that is set by the expansion time which, under our conditions, is 10 μs.

It is clear from Fig. 4 that the slope of the experimental $F(t)$ curve increases with increasing Φ_{IR}. This was, in fact, expected because the rate of monomolecular decay, $k(\varepsilon)$, is shown by RRKM [see (1)] to increase with increasing energy ε, which, in turn, increases with increasing Φ_{IR}. It is clear from these results that the experimental points do not lie on an exponential curve: the rate of decay of the overexcited molecular ensemble decreases with decreasing number of undecayed molecules. It is quite natural to relate this nonex-

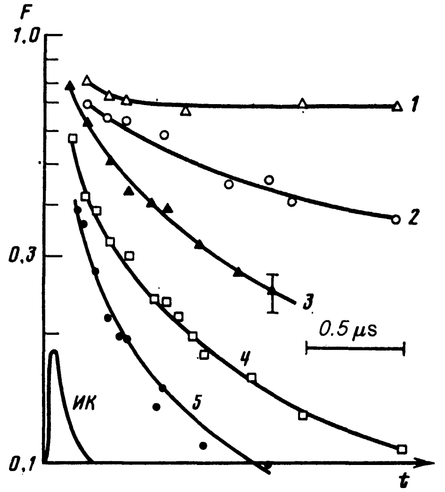

FIG. 4. Measured fraction of decayed molecules $F=[(CF_3)_3CI]/[(CF_3)_3CI]_{\Phi_{IR}=0}$ as a function of the delay between the exciting IR and probing UV laser pulses: 1—$\Phi_{IR}=2.3$ J/cm^2 ($\bar{\varepsilon}_1=2.21D$); 2—$\Phi_{IR}=3.0$ J/cm^2 ($\bar{\varepsilon}_2=2.37D$); 3—$\Phi_{IR}=3.8$ J/cm^2 ($\bar{\varepsilon}_3=2.53D$); 4—$\Phi_{IR}=5.1$ J/cm^2; 5—$\Phi_{IR}=5.8$ J/cm^2, $\tau_{IR}=10^{-7}$ s, $\tau_{UV}=8\times10^{-9}$ s, $\omega_{IR}=947.7$ cm^{-1}, $P_{(CF_3)_3CI}=10^{-3}$ Torr.

ponential dependence to the fact that the ensemble of molecules was excited in a nonmonoenergetic manner by the IR radiation, and there was a distribution with a finite width. Actually, using (1) ($\varepsilon_0^+\simeq\varepsilon_0=11\,000$ cm^{-1}, $D=19\,000$ cm^{-1}), we find that the rate of decay of molecules with energy $\varepsilon=2.4D$ is higher by a factor of four than that for molecules with energies lower by only 10%. Since molecules with a large store of vibrational energy are shown by (1) to decay more rapidly, the rate of decay averaged over the ensemble will decrease as the number of undecayed molecules decreases.

Figure 5 shows the measured average energy absorbed in IR MPE of $(CF_3)_3CI$ as a function of the IR energy density. We note particularly that, for $\Phi_{IR}\lesssim4$ J/cm^2, the energy is absorbed by the molecules and not by the decay products. Actually, under these excitation conditions, most of the molecules do not decay during the irradiation time (see Fig. 4), and the decay products of the small fraction of dissociating molecules can absorb only a negligible amount of the energy carried by the trailing edge of the IR pulse. Curve 1 of Fig. 4 is thus seen to correspond to the average degree of overexcitation $\bar{\varepsilon}_1=(2.21\pm10\%)D$, curve 2 corresponds to $\bar{\varepsilon}_2=(2.37\pm10\%)D$, and curve 3 to $\bar{\varepsilon}_3=(2.53\pm10\%)D$. Curves 4 and 5 were obtained when an appreciable fraction of the molecules decayed during the exciting laser pulse, and the resulting radicals $(CF_3)_3C$ could absorb energy from the IR field. This complicates the determination of the average degree of excitation of the initial molecules from the measured absorption under these conditions.

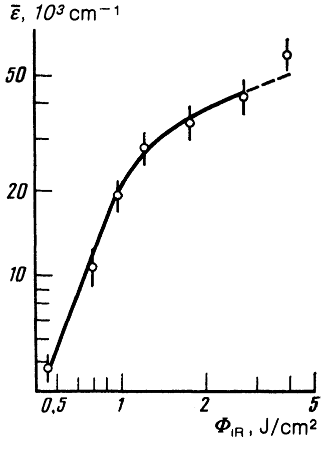

FIG. 5. Mean energy absorbed by the molecule as a function of the IR energy density: $\tau_{IR}=10^{-7}$ s, $\omega_{IR}=947.7$ cm^{-1}, $P=0.1$ Torr.

5. DETERMINATION OF THE DECAY RATE *k* AND WIDTH δ OF THE DISTRIBUTION FUNCTION OF OVEREXCITED MOLECULES FROM EXPERIMENTAL DATA

When the ensemble of molecules is nonmonoenergetically overexcited above the dissociation limit, different decay rates $k(\varepsilon)$ correspond to different energies ε. The total number of molecules decreases in accordance with the expression

$$n(t)=n_0\int_0^\infty f_0(\varepsilon)\exp[-k(\varepsilon)t]\,d\varepsilon, \qquad (5)$$

where n_0 and f_0 are, respectively, the number of molecules and the distribution function at the initial time. It is clear from physical considerations that the decay curve $n(t)$ of a nonmonoenergetic ensemble should depend not only on the rate of decay near the distribution maximum k_0, but also on the distribution width δ. In fact, the greater the width δ, the greater is the change in the decay rate $k(\varepsilon)$ as ε is varied within the width of the distribution function $f_0(\varepsilon)$ and, consequently, the greater the observed difference from exponential decay.

Let us determine the mean rate of decay and the distribution width from the above experimental data. To do this, we expand $\ln k(\varepsilon)$ near $\bar{\varepsilon}$ (the maximum of the distribution function):

$$\ln k(\varepsilon)\approx\ln k_0+(k'/k_0)(\varepsilon-\bar{\varepsilon}), \qquad (6)$$

$$k_0=k(\tilde{\varepsilon}),\qquad k'=[dk/d\varepsilon]_{\varepsilon=\tilde{\varepsilon}}.$$

From (5) and (6), we have

$$\frac{n(t)}{n_0}\approx F_{\delta k'/k_0}(k_0t)=\int_{-\infty}^{+\infty}dx\,f_{00}(x)\exp\left\{-k_0t\exp\left(\frac{\delta k'}{k_0}x\right)\right\}, \qquad (7)$$

$$x=\frac{\varepsilon}{\delta},\ \delta=\left[\int_0^{+\infty}(\varepsilon-\tilde{\varepsilon})^2f_0(\varepsilon)\,d\varepsilon\right]^{1/2},\ f_{00}(x)=\delta^{-1}f_0[(\varepsilon-\tilde{\varepsilon})/\delta],$$

where δ is the variance of the distribution $f_0(\varepsilon)$ and f_{00} is the shifted distribution function with unit variance ($\bar{x}=0$, $\overline{x^2}=1$). Thus, for a fixed shape of the distribution function $f_{00}(x)$ of the overexcited ensemble, the decay of the molecules is described by (7), which contains the parameter $\delta k'/k_0$. The magnitude of this dimensionless parameter is a measure of the variation of the rate of decay over the width δ of the distribution function $f_0(\varepsilon)$.

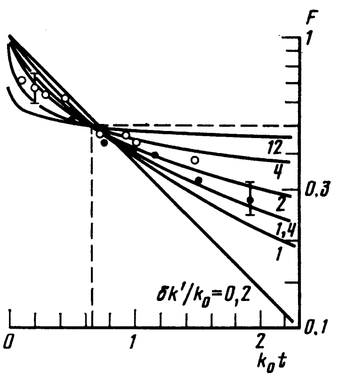

FIG. 6. The one-parameter family $F_{\delta k'/k_0}(k_0t)$ (7), obtained for the Gaussian distribution function. The experimental points are as follows: ○—$\bar{\varepsilon}_2 = 2.37D$, $k_0 = 1.0\times10^6$ s^{-1}; ●—$\bar{\varepsilon}_3 = 2.53D$, $k_0 = 2.6\times10^6$ s^{-1}.

The one-parameter family of curves $F_{\delta k'/k_0}(k_0t)$ was calculated for two model distribution functions, namely, the Gaussian function

$$f_{00}^{(1)}(x) = (2\pi)^{-1/2}\exp(-x^2/2), \tag{8}$$

and the rectangular function

$$f_{00}^{(2)}(x) = \begin{cases} 1/2\cdot3^{1/2}, & |x|<3^{1/2} \\ 0, & |x|>3^{1/2} \end{cases}. \tag{9}$$

Calculations show that, despite the considerable difference between the two models, the curves $F_{\delta k'/k_0}^{(1),(2)}(k_0t)$ differ very little from one another ($|F^{(1)} - F^{(2)}| \lesssim 0.03F$) in the most interesting region $0.2 \leqslant F \leqslant 0.8$.

Figure 6 shows the one-parameter family $F_{\delta k'/k_0}(k_0t)$, calculated for the distribution (8). It is clear from this figure that, independently of the dependence on $\delta k'/k_0$, all the $F_{\delta k'/k_0}(k_0t)$ curves reach the 0.5 level in more or less the same time $k_0t_{0.5} = 0.65$. This enables us to determine k_0 from the experimental data: $k_0 = 0.65/t_{0.5}$. Figure 7 shows the decay rate determined in this way. The indicated uncertainties represent, first, the spread of the experimental points and, second, the fact that the initial instant of time could not be determined because of the finite time taken to excite the molecules in the IR field.

To determine the width δ of the distribution function, we plot the experimental points obtained for $\bar{\varepsilon}_2 = 2.37D$ and $\bar{\varepsilon}_3 = 2.53D$ on the k_0t, F plane. It is clear from Fig. 6 that these points lie on the theoretical curve $F_{\delta k'/k_0}(k_0t)$ for $\delta k'/k_0 = 3 \pm 1(\bar{\varepsilon}_2 = 2.37D)$ and for $\delta k_0'/k_0 = 1.7 \pm 0.3(\bar{\varepsilon}_3 = 2.53D)$. Using (1) to calculate k'/k_0, we find that $\delta_2 = (9 \pm 3)\times10^3$ cm$^{-1} = 0.47D$ in the first case, and $\delta_3 = (6 \pm 1)\times10^{-3}$ cm$^{-1} = 0.32D$ in the second. For comparison, we reproduce the width of the Boltzmann distribution for the two energies: $\delta_2^{\mathrm{B}} = 10.1\times10^3$ cm^{-1} and $\delta_3^{\mathrm{B}} = 10.6\times10^3$ cm^{-1}. [We note that (1) yields the same result for k'/k as the more accurate calculation based on the inversion of the partition function (Section 6). At the same time, the use of (1) to calculate the function $k(\varepsilon)$ itself leads to appreciable errors.]

Thus, in our experiment, practically all the molecules (and not only the molecules whose energies were close to the average over the ensemble) were significantly overexcited above the dissociation limit. Actually, the degree of excitation of molecules whose energy was within the width of the distribution function was significantly greater than the dissociation energy: $\varepsilon_2 = (2.37 \pm 0.47)D$ and $\varepsilon_3 = (2.53 \pm 0.32)D$.

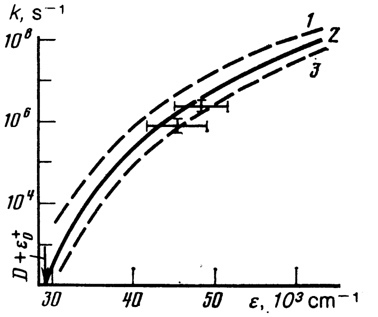

FIG. 7. Rate of monomolecular decay $k(\varepsilon)$ of $(CF_3)_3CI$, calculated for $D_1 = 18\,000$ cm^{-1} (1), $D_2 = 19\,000$ cm^{-1} (2), $D_3 = 20\,000$ cm^{-1} (3). The experimental points were obtained from the kinetic curves (Fig. 4).

6. COMPARISON OF EXPERIMENTAL DECAY RATES WITH THE PREDICTIONS OF THE RRKM THEORY

Figure 7 shows the rate $k(\varepsilon)$ for the $(CF_3)_3CI$ molecule, calculated from the RRKM theory.[3] The total number N and the density ρ of vibrational states that were necessary for the determination of $k(\varepsilon)$ were calculated by inverting the partition function. The inverse Laplace transformation was performed in the first approximation of the method of steepest descents.[3] The following parameters of the molecule and of the activated complex were used in the calculation. The frequencies of 33 vibrations of the $(CF_3)_3CI$ molecule were taken from Ref. 17, but anharmonism was not taken into account. We assumed that all three torsional vibrations of the CF_3 groups in the molecule and in the activated complex became free internal rotations for the above high degrees of overexcitation. The frequency of the doubly-degenerate bending vibration of the I atom in the activated complex was reduced by a factor of two (65 cm^{-1}) as compared with the frequency of the analogous vibrations in the molecule (130 cm^{-1}). The remaining 30 vibrational frequencies of the activated complex [coupled to the vibrations of the $(CF_3)_3CI$ molecule] were assumed to be equal to the frequencies of the corresponding vibrations in the molecule. The C–I bond energy lies in the region of 19 000 cm^{-1} ($\pm$ 1000 cm^{-1}) for all the known iodides.[16] This value of D was used in our calculations.

It is well-known that, for molecules with a large number of degrees of freedom ($s \gtrsim 20$), and high degree of overexcitation above the dissociation limit ($\varepsilon - D \gtrsim (0.5 - 1)\varepsilon_0^+$, where ε_0^+ is the energy of zeroth vibrations of the activated complex), the first approximation of the method of steepest descents yields $k(\varepsilon)$ to within a figure on the order of 1%.[3] The conditions imposed on the polyatomic molecule and the degree of over excitation were readily satisfied in our case ($s = 36$, $\varepsilon - D = 3\varepsilon_0^+$).

Comparison of the experimental decay rates of isolated $(CF_3)_3CI$ molecules with the predictions of the RRKM theory based on the assumption of an equilibrium statistical distribution of vibrational energy, independently of the method used to excite the molecules, shows that there is good agreement between experiment and theory to within the experimental uncertainty and the uncertainty in the parameters of the activated complex and the molecule.

7. COMPARISON OF THE EXPERIMENTAL WIDTH OF THE DISTRIBUTION OF OVEREXCITED MOLECULES WITH ESTIMATES BASED ON THE APPROXIMATE THEORY OF MPE

We shall show how the experimental dependence of the mean energy absorbed per molecule, $\bar{\varepsilon}(\Phi_{\rm IR})$, on the IR energy density can be used to estimate the width of the distribution function of the excited molecules, and will then compare this estimate with the experimental width δ deduced from the kinetic curve (Fig. 4 in Section 5). We shall do this using the kinetic equations for evolution of the distribution function in the quasicontinuum[21]:

$$\hbar\omega_{\rm IR}\, df_n/dt = -(\sigma_{n,\,n+1}+\sigma_{n,\,n-1}) I f_n + \sigma_{n-1,\,n} I f_{n-1} + \sigma_{n+1,\,n} I f_{n+1}, \qquad (10)$$

where f_n is the fraction of molecules with energy $\varepsilon_n = n\hbar\omega_{\rm IR}$ and $\sigma_{n,n\pm1}$ are the microscopic cross sections for absorption and stimulated emission in states with energy ε_n. The information contained in the distribution function f_n is, however, too detailed for our purposes because we need to determine only the width δ of the distribution f_n. It was shown in Ref. 22 that this width can be determined with sufficient precision without solving (10). Actually, let us define the mean energy by

$$\bar{\varepsilon} = \hbar\omega_{\rm IR}\sum_{n=0}^{\infty} n f_n \qquad (11)$$

and the distribution width δ by

$$\delta^2 = \sum_{n=0}^{\infty} (n\hbar\omega_{\rm IR} - \bar{\varepsilon})^2 f_n . \qquad (12)$$

The equations for $\bar{\varepsilon}$ and δ^2 can now be obtained by differentiating (11) and (12) and substituting (10) for $\hbar\omega_{\rm IR}\, df_n/dt$ on the right-hand side:

$$\frac{d\bar{\varepsilon}}{dt} = \sum_{n=0}^{\infty} \sigma(\varepsilon_n) I f_n, \qquad (13)$$

$$\frac{d\delta^2}{dt} = \sum_{n=0}^{\infty} [2(n\hbar\omega_{\rm IR} - \bar{\varepsilon})\sigma(\varepsilon_n) + \Sigma(\varepsilon_n)] I f_n, \qquad (14)$$

where

$$\sigma(\varepsilon_n) = \sigma_{n,\,n+1} - \sigma_{n,\,n-1}, \qquad (15)$$

$$\Sigma(\varepsilon_n) = \sigma_{n,\,n+1} + \sigma_{n,\,n-1}. \qquad (16)$$

The quantity $\sigma(\varepsilon_n)$ is the differential absorption cross section. If we suppose that f_n has a sharp enough maximum, we can expand $\sigma(\varepsilon)$ and $\Sigma(\varepsilon)$ into series around $\bar{\varepsilon}$. The high-order terms in these expansions provide only a small contribution to the final results,[22] and we shall therefore confine our attention to the first two terms. The resulting closed system for $\bar{\varepsilon}$ and δ^2 can be integrated:

$$d\bar{\varepsilon}/d\Phi_{\rm IR} = \sigma(\bar{\varepsilon}), \qquad (17)$$

$$\delta^2 = \hbar\omega_{\rm IR}\,\sigma^2(\bar{\varepsilon}) \int_0^{\bar{\varepsilon}} d\varepsilon\, \frac{1+2n_R(\varepsilon)}{\sigma^2(\varepsilon)}, \qquad (18)$$

where $n_R(\varepsilon)$ is the average population of the resonance (i.e., excited by the laser) mode of the molecule at energy ε. In deriving (18), we used the following ratio of absorption to stimulated emission probabilities that ensues from the principle of detailed balance:

$$\sigma_{n,\,n-1}/\sigma_{n-1,\,n} = n_R/(n_R+1) \approx \sigma_{n,\,n-1}/\sigma_{n,\,n+1}. \qquad (19)$$

To estimate δ from (18), we first find $\sigma(\varepsilon)$ from the experimental function $\bar{\varepsilon}(\Phi_{\rm IR})$ (Fig. 5) with the aid of (17) (in practice, we differentiated the smooth curve that approximates the experimental points). Taking $n_R \simeq \varepsilon/s$, we find from (18) that $\delta_2^{\rm theor} = 6\times10^3$ cm^{-1} $(0.32D)$ for the mean degree of excitation $\bar{\varepsilon}_2 = 2.37D$ and $\delta_3^{\rm theor} = 5\times10^3$ cm^{-1} $(0.26D)$ for $\bar{\varepsilon}_3 = 2.53D$. Comparison with the experimental width obtained from real-time measurements of the fraction of undecayed molecules shows good agreement between theory and experiment [$\delta_2 = (9\pm3)\times10^3$ cm^{-1} and $\delta_3 = (6\pm1)\times10^3$ cm^{-1}]. We note, however, that the accuracy of the estimate based on (17) and (18) is not high because these calculations rely on the differentiation of the experimental function $\bar{\varepsilon}(\Phi_{\rm IR})$, which itself is determined with limited precision.

8. CONCLUSIONS

Our results lead us to the following conclusions.

1. Large molecules such as $(CF_3)_3CI$ $(s = 36)$ can be highly overexcited $(\varepsilon > 2D)$ by IR MPE in the field of a pulsed CO_2 laser $\Phi_{\rm IR} \gtrsim 3$ J/cm^2, $\tau_{\rm IR} = 100$ ns), and the entire distribution function of the molecules is then found to lie well above the dissociation limit.

2. The rate of decay of isolated $(CF_3)_3CI$ molecules agrees (to within experimental error and the uncertainty in the parameters of the molecule and the activated complex) with the predictions of the RRKM theory based on the assumption of an equilibrium statistical distribution of the vibrational energy of the molecule, which is independent of the method used to excite the molecule.

3. Real-time observations of the decay of an overexcited ensemble of molecules can be used to determine the width of the distribution function of the ensemble. The distribution width obtained in this way for the $(CF_3)_3CI$ molecules overexcited by an infrared field is in agreement (to within experimental error) with the estimate deduced from the dependence of the mean absorbed energy $\bar{\varepsilon}(\Phi_{\rm IR})$ using the approximate theory of MPE.[22]

Our results suffer from the following shortcomings that can, nevertheless, be removed.

1. The range of lifetimes of overexcited molecules that we have observed is limited at the lower end by the length of the laser pulses and, at the higher end, by expansion. This

range can be substantially extended in either direction. It is possible to produce 10-ns IR pulses by the standard method of plasma truncation of the CO_2 laser pulse,[23] and to extend the range into the region of shorter lifetimes. Long lifetimes can be measured using molecular-beam techniques.[24]

2. IR MPE produces nonmonoenergetic excitation of molecules above the dissociation limit, which reduces the precision of the comparison beween experiment and the RRKM theory. A monoenergetic distribution of molecules above the dissociation limit can, in principle, be produced by exciting higher overtones[25] or by electronic relaxation during the excitation of electronic states.[26]

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[1]G. M. Zaslavskiĭ, Stokhastichnost' dinamicheskikh sistem (Stochasticity of Dynamic Systems), Nauka, Moscow, 1984.

[2]V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov, and E. A. Ryabov, Multiple Photon IR Laser Photophysics and Photochemistry, Gordon and Breech, London, Paris, New York, 1985.

[3]P. J. Robinson and K. A. Holbrook, Unimolecular Reaction, Wiley, New York, 1972; H. Eyring and S. M. Lin, Basic Chemical Kinetics, Wiley, New York, 1980.

[4]L. D. Landau, Soobr. Trudov (Collected Papers), Nauka, Moscow, 1969.

[5]V. N. Bagratashvili, V. S. Dolzhikov, and V. S. Letokhov *et al.*, Zh. Eksp. Teor. Fiz. **77**, 2238 (1979) [Sov. Phys. JETP **50**, 1075 (1979)].

[6]A. S. Sudbo, P. A. Schulz, and E. R. Grant, *et al.*, J. Chem. Phys. **70**, 912 (1979).

[7]H. Reisler, F. Kong, A. M. Renlund, and C. Wittig, J. Chem. Phys. **76**, 997 (1982).

[8]B. H. Rockney and E. R. Grant, J. Chem. Phys. **79**, 708 (1983).

[9]V. N. Bagratashvili, V. N. Burimov, and L. E. Deev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **35**, 155 (1982) [JETP Lett. **35**, 189 (1982)].

[10]V. N. Bagratashvili, M. V. Kuz'min, V. S. Letokhov, and A. N. Shibanov, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 92 (1983) [JETP Lett. **37**, 112 (1983)].

[11]H. Reisler, F. B. T. Pessine, and C. Wittig, Chem. Phys. Lett. **99**, 388 (1983).

[12]F. P. Schaefer (Ed.), Dye Lasers, Springer, 1974 [Russ. transl., Mir, 1976].

[13]Atomic Energy Levels, ed. by C. E. Moore, NBS Circular, Washington, 1958.

[14]B. F. Gordiets, A. I. Osipov, and L. A. Shelepin, Kineticheskie protsessy v gazakh i molekulyarnye lazery (Kinetic Processes in Gases and Molecular Lasers), Nauka, Moscow, 1980.

[15]A. M. Pravilov, Kvantovaya, Elektron. (Moscow) **8**, 1397 (1981) [Sov. J. Quantum Electron. **11**, 847 (1981)].

[16]Energiya razryva khimicheskikh svyazei. Potensialy ionizatsii i srodstvo k elektronu (Chemical Bond energies. Ionization Potentials and Electron Affinities), ed. by V. N. Kondrat'ev, Nauka, Moscow, 1974.

[17]H. Bürger and G. Pawelke, Spectrochim. Acta A **35**, 559 (1979).

[18]M. Shapiro and R. Bersohn, J. Chem. Phys. **73**, 3810 (1980).

[19]G. N. A. van Veen, T. Beller, A. E. de Vries, and M. Shapiro, Chem. Phys. **93**, 277 (1985).

[20]I. N. Knyazev, Yu. A. Kudryavtsev, N. P. Kuz'mina, and V. S. Letokhov, Zh. Eksp. Teor. Fiz. **76**, 1281 (1979) [Sov. Phys. JETP **49**, 650 (1979)].

[21]M. Quack, J. Chem. Phys. **69**, 1282 (1978); **70**, 1068 (1979).

[22]M. V. Kuzmin, Chem. Phys. **81**, 199 (1983).

[23]C. R. Quick Jr., J. J. Tice, T. A. Fischer, and C. Wittig, Chem. Phys. Lett. **62**, 435 (1979).

[24]V. M. Apatin and G. N. Makarov, Pis'ma Zh. Eksp. Teor. Fiz. **38**, 120 (1984) [JETP Lett. **38**, 141 (1984)].

[25]F. F. Crim, Ann. Rev. Phys. Chem. **35**, 659 (1984).

[26]A. A. Egseev, V. M. Krivtsun, and G. A. Kuritsyn *et al.*, Zh. Eksp. Teor. Fiz. **87**, 111 (1984) [Sov. Phys. JETP **60**, 64 (1984)].

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