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# Intermolecular and intramolecular distribution of vibrational energy under multiphoton excitation by IR laser radiation

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The vibrational distribution produced in molecular gases by IR laser pulses is investigated by high-time-resolution Raman spectroscopy. Quantitative data are obtained and interpreted regarding an ensemble of molecules excited during the IR pulse under both collisionless conditions and conditions involving collisions with buffer-gas particles. The energy threshold at which the vibrational energy becomes randomly distributed among the vibrational modes (becomes randomized) during the interaction with the IR pulse is determined for the $SF_6$ and $CF_3I$ molecules. A possible mechanism for randomization of the vibrational motion in $SF_6$ is considered.

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## 1. INTRODUCTION

A major question in the study of multiphoton excitation of molecules by IR irradiation (see Ref. 1) is the nonequilibrium vibrational distribution produced in a molecular gas as a result of interaction with a pulsed IR field. Here, there are two problems whose solution is extremely important for an understanding of the multiphoton excitation process. First of all, the question concerning the form of the vibrational energy distribution function of the molecules in the gas is of interest, i.e., the form of the intermolecular vibrational energy distribution. Secondly, it is important to know the distribution of absorbed energy among the different vibrational degrees of freedom of the molecule, i.e., the form of the intramolecular vibrational energy distribution.

A variety of approaches are used to study the vibrational energy distribution: various semiempirical models[2,3] have been developed and direct experiments have been performed. In the latter case, it was possible to progress rather far using spectroscopic methods of probing the excited states. Thus, in experiments with $OsO_4$ (Ref. 4) and $SF_6$ (Ref. 5), it was shown with the IR probe method that the distribution produced in multiphoton excitation consists of two molecular ensembles: excited molecules in a vibrational quasicontinuum, and unexcited molecules. The fraction $q$ of molecules in the upper ensemble was measured. An analogous conclusion concerning the existence of ensembles of "hot" and "cold" molecules was drawn from a study of multiphoton absorption and dissociation of $CF_3I$ (Ref. 6), and on the basis of UV probing of $SF_6$

molecules.[7] Nevertheless, many unresolved questions remained; among these, the most important one concerns the physical reason for the $q$ factor (i.e., for the splitting of molecules into two ensembles), and the dynamics of formation of the ensemble of hot molecules during the laser pulse.

Regarding the question of the intramolecular energy distribution in multiphoton excitation, the situation here is very complicated. This question has recently been the subject of numerous discussions. Usually it is assumed[8] that for a sufficiently high level of excitation, close to the dissociation threshold, the energy distribution is that of statistical equilibrium. This is due to the random, stochastic nature of the vibrational motion in the molecule.[9] At the same time, for a sufficiently low level of excitation, the motion is described well by the normal-coordinate approximation and selective excitation of individual modes is possible in principle. Intermediate cases involving "local" modes[10] and partial, incomplete randomization[11] are also possible.

Current theoretical criteria[9] for the energy threshold above which the motion is randomized allow only a rough estimate of the threshold. Therefore direct experiments making possible direct determination of the randomization limit are necessary. This is important not only for understanding the specific process of multiphoton excitation of molecules. The results are important also from the point of view of clarifying the general conditions under which the description of the behavior of a quantum system with many degrees of freedom can be statistical.

The study of the enumerated unresolved questions of multiphoton excitation of molecules is the subject of this work. The experimental method chosen for the investigations is based on probing the excited molecules using spontaneous Raman light scattering. The principal advantages of this technique are rather obvious. Here we may count on a much simpler interpretation of the observed spectra than, for example, in the IR probe method; this is because in Raman scattering the direct and inverse vibrational transitions are spectrally separated, in contrast to IR absorption, in which they are mixed. The direct- and inverse-transition spectra are located in the Stokes and anti-Stokes region, respectively. The latter circumstance makes it possible to use the Raman scattering signal in the anti-Stokes region for a direct study of the distribution of absorbed energy among the different modes of the excited molecules.

The results of preliminary experiments involving Raman probing of molecules in multiphoton excitation, in particular some results of a study of the randomization effect, are presented in our previous papers.[12,13] In this paper, we give a complete exposition of the results and their interpretation. As objects of study we chose the molecules $SF_6$ and $CF_3I$; quite a large amount of data is available concerning the multiphoton excitation process in these molecules. In Secs. 2 and 3 we describe the experimental apparatus, the measurement technique, and the interpretation of the measurements. Then in Secs. 4 and 5 we present the results of the experimental investigation of the evolution of the vibrational energy distribution and of the randomization effect. Section 6 is devoted to a theoretical analysis of the randomization mechanism. Finally, in Sec. 7 we discuss the results.

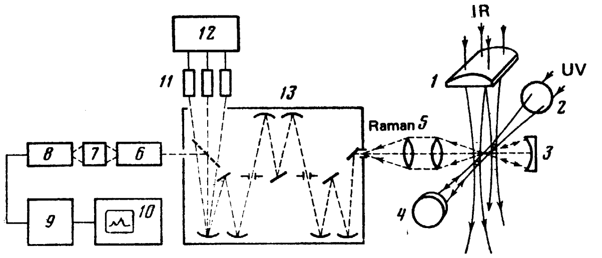

FIG. 1. Block diagram of the experimental apparatus: (1) cylindrical lens; (2) spherical lens; (3), (4) mirrors; (5), (7) objectives; (6) image converter; (8) isocon television tube; (9) signal processor unit; (10) multichannel storage; (11) photomultiplier; (12) signal counter; (13) triple spectrograph.

## 2. EXPERIMENTAL APPARATUS AND MEASUREMENT TECHNIQUE

For the investigation of the Raman spectra in multiphoton excitation of $SF_6$ and $CF_3I$ molecules by IR irradiation, we used an apparatus whose schematic is given on Fig. 1. The apparatus consists of the following basic elements: pulsed $CO_2$ laser, ruby laser with frequency doubling; a cell with the tested gas; and a photoelectric recording system composed in turn of two systems—a three-channel system and a multichannel system.

The multiphoton IR excitation of molecules was accomplished by $CO_2$ laser irradiation with pulse duration $\tau_{IR} = 15 \pm 3$ ns at half maximum. The radiation frequencies were selected close to the positions of the $Q$ branches of the $\nu_1$ vibrations of the $CF_3I$ molecule and the $\nu_3$ vibrations of the $SF_6$ molecule, and were respectively 1074.65 and 947.75 $cm^{-1}$. In order to obtain a Raman signal, the second harmonic emission of a ruby laser was used at a wavelength of $\lambda_{probe} = 3472$ Å; this pulse of controllable delay $\tau$ was passed through a cell with the tested gas following the $CO_2$ laser pulse. The pulse length was $\tau_{UV} = 20$ ns, energy 50 mJ. The measurements were carried out in crossed laser beams, focused inside the gas cell. The $CO_2$ laser spot dimensions at the focus of the cylindrical lens were: length 7 mm and width 1 mm. The recorded beam intersection region has the dimensions: length 3 mm and diameter 0.2 mm. Mirrors 3 and 4 were used to amplify the Raman signal. The delay $\tau$ between the end of the IR pulse and the beginning of the UV pulse was produced by a synchronization system and was fixed accurate to 15 ns. The experiments were carried out at a pulse repetition frequency 1 Hz.

It is well known that the magnitude of the useful signal in Raman probing is small due to the small cross section of the process ($\sim 10^{-30}$ $cm^2/sr$). The necessity for operating at low pressures (<1 mm Hg) in order to realize the collisionless regime increased the measurement difficulty. Furthermore, according to the conditions of the experiment, broad portions of the spectrum needed to be recorded. In this case, even using a double spectrograph cannot solve the problem of suppression of radiation at the unshifted frequency. Therefore, in the apparatus described, a triple-monochromator spectrograph was used to provide the required suppression of the scattered light.

The Raman radiation was focused at the entrance slit of the spectrograph. The relative aperture of the spectrograph was 1:5.3, the transmission was 4%, the working region of the spectrum was 250–800 nm. The spectrograph could be operated with both subtractive and additive dispersion. With subtractive dispersion, two stages are used as the pre-monochromator with zero dispersion, resulting in a reciprocal linear dispersion $L = 0.74$ nm/mm and a resolution $\delta\lambda = 0.15$ nm. For additive dispersion, $L = 0.25$ nm/mm, and $\delta\lambda = 0.05$ nm.

The experiments with Raman probing of molecules were usually carried out in one of two regimes. In regime I, a Raman spectrum of width up to 10 nm could be recorded with resolution down to 0.05 nm. In regime II, the integrated intensity of the spectrum was measured in each of the three adjacent sections with overall width to 10 nm.

To record the Raman spectra in regime I, a multichannel television photon-counting system was used. The system consisted of (see Fig. 1) a three-stage image converter with an electrostatic shutter 6, which was optically matched by wide-aperture objective 7 to a high-sensitivity isocon television tube 8. The gain of the system was sufficient to record individual photoelectrons. A blocking pulse on the photocathode of the isocon suppressed the noise of the ungated stages of the image converter. The spectral lines, in the form of individual scintillations corresponding to single photoelectrons, were located parallel to the television scan lines. The information accumulated on the isocon target after each laser pulse was read after one frame (20 ms), sent to the signal processor unit 9, and were recorded successively line-by-line in the memory channels of a multichannel storage 10. In the processor unit, the video pulses corresponding to single-electron scintillations, were discriminated according to the upper and lower level and normalized. The basic parameters of the system are: the working field, 5×15 mm; the number of resolved spectral elements, 80; the memory channel capacity, $10^5$; one noise count per $10^3$ accumulation cycles.

In regime II, the recording was accomplished using a three channel photon counting system consisting of three photomultipliers 11 and a signal counter 12. All three channels were gated by pulses of length to 20 ns. Usually, the useful Raman signal was recorded by the central photomultiplier, and the side tubes could be used for recording the background in the adjacent sections of the spectrum. The maximum counting rate of the system is 50 MHz, the number of noise counts is 1 per $10^5$ measurement cycles. In the reduction of the results, the error in the measurement of the Raman signal was defined as $\delta I/I = N^{-1/2}$ ($N$ is the number of counts). In measurements in the anti-Stokes region, the background signal was determined in the absence of radiation from the $CO_2$ laser and then subtracted from the value of the accumulated Raman signal.

The apparatus constructed made it possible to measure the Raman signal with the pressure of the tested gases $SF_6$ and $CF_3I$ reduced to $10^{-2}$ mm Hg.

## 3. FEATURES OF DIAGNOSTICS OF VIBRATIONALLY-EXCITED MOLECULES BY THE RAMAN SPECTROSCOPY METHOD

The simplest examination of the diagnostics of vibrationally excited molecules by the Raman spectroscopy method may be carried out using the harmonic approximation. If $\nu_i^R$ is a Raman-active mode of the molecule, and $\sigma_{01}$ is the Raman cross section in the $v_i = 0 \rightarrow v_i = 1$ transition in this mode, then the Raman cross section for transitions between the levels $(v_i - 1)\nu_i^R$ and $v_i\nu_i^R$ is equal to $v_i\sigma_{01}$ and does not depend on the other quantum numbers.[14] We shall assume that the energy distribution in the mode $\nu_i^R$ is described by the populations $Z_v$. Then we find that the integrated intensity of the anti-Stokes signal $I_{AS}^i$ is proportional to the energy $\bar{\varepsilon}_i$ stored in the mode $\nu_i^R$:

$$I_{AS}^i \propto \sum_{v_i} Z_{v_i}\sigma_{v_i,v_i-1} = \sigma_{01}\sum_{v_i} v_i Z_{v_i} = \sigma_{01}\bar{\varepsilon}_i/h\nu_i^R, \tag{1}$$

$$\bar{\varepsilon}_i = \sum_{v_i} h\nu_i^R\, v_i Z_{v_i}.$$

It is easy to see that $I_{AS}^i$ does not depend on the form of the distribution of $Z_{v_i}$. A simple relation can also be obtained for the intensity of the Stokes signal $I_S^i$:

$$I_S^i \propto \sigma_{01}(1 + \bar{\varepsilon}_i/h\nu_i^R). \tag{2}$$

Real molecules have anharmonic vibrations which grow proportionally to the increase in the vibrational quantum numbers $v_i$. Therefore a question arises concerning the possibility of separating from the spectrum the Raman signals in the different modes, taking into account the fact that the Raman spectrum of vibrationally excited molecules will be broadened and shifted toward the red due to the vibrational distribution and anharmonicity. However, it is known that the IR absorption spectra[5,15] and IR fluorescence spectra[16] of vibrationally hot molecules, despite the shift and the broadening, retain the structure of individual modes. Experiment has shown that Raman spectra also retain their mode structure even in strong vibrational excitation of the molecules. We cite Fig. 2 in Ref. 12, on which is presented a section of the spectrum in the anti-Stokes region obtained upon multiphoton excitation of $CF_3I$ molecules. It is easy to see that the modes $\nu_2$ and $\nu_5$ are clearly resolved, although shifted relative to their harmonic position, and that their intensities can be measured independently.

A second question concerns the applicability of the simple relations (1) and (2) for the vibrational distribution on multiphoton excitation of real molecules. This relation may be perturbed due to the anharmonic in-

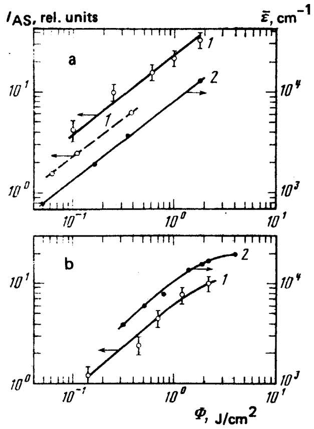

FIG. 2. The integrated intensity $I_{AS}$ of the anti-Stokes Raman scattering (curves 1) and the average energy $\bar{\varepsilon}$ absorbed by the molecule (curves 2) as a function of the energy density of the laser radiation Φ: a) $SF_6$, b) $CF_3I$. The values of $\bar{\varepsilon}$ are obtained on averaging over all the molecules of the irradiated volume. The solid lines are the measurements for $p = 1$ mm Hg, $\tau = 0.5\,\mu s$; the dashed line is for $p = 0.1$ mm Hg, $\tau = 40$ ns.

teraction (the dependence of the Raman cross section on $\lambda_R$ gives an insignificant contribution). In order to check this, we compared the dependences of the integrated anti-Stokes signal for different modes on the laser energy density with the analogous dependences of the absorbed energy measured by the method of direct calorimetry in our previous papers.[3,5] The corresponding dependences are given in Fig. 2. In this case, part of the Raman probe experiments were carried out under such conditions ($p\tau = 0.5\ \mu s \cdot$ mm Hg) that as a result of collisional exchange the equilibrium energy distribution over the modes of the excited molecule could be assumed. As is seen from Fig. 2, the dependences of the anti-Stokes signals and of the energy absorbed by the molecule are similar, i.e., $I_{AS} \propto \bar{\varepsilon}$. This result shows that, to within experimental error, Eq. (1) is valid, and by measuring the integrated intensity of the anti-Stokes signal we can directly measure the energy stored in the probed mode. Such a simple interpretation of the Raman signal opens up good possibilities for studying many aspects connected with the multiphoton excitation process. Several of these possibilities have been realized, as will be shown below.

In conclusion, we note that Eq. (1) is applicable to the obvious case in which we may neglect direct excitation of the molecules to the next electronic state as a result of the absorption of UV radiation. For this it is necessary that the quantity $(\varepsilon_i + h\nu_{probe})/h$ be appreciably less than the characteristic frequency of the electronic transition $\nu_{el}$:

$$\varepsilon_i + h\nu_{probe} < h\nu_{el}. \tag{3}$$

This condition is certainly satisfied for $SF_6$ molecules, which are transparent down to the vacuum ultraviolet region.[17] The situation is more complex for $CF_3I$. The molecule has a continuous absorption band with $\lambda_{max} = 265$ nm.[17] For sufficiently strongly vibrationally excited $CF_3I$ molecules, the condition (3) may no longer be satisfied and continuous resonant Raman scattering will occur. As a result, both the form of the dependence $I^i = I^i(\varepsilon_i)$ and the Raman spectrum itself may be changed. The effect of this process on $I_{AS}^i$ under our experimental conditions was not appreciable. Nevertheless, it may be one of the reasons why a "pedestal" arises in the Raman spectrum in $CF_3I$. There is no such pedestal in $SF_6$.

## 4. VIBRATIONAL ENERGY DISTRIBUTION IN THE AN ENSEMBLE OF MOLECULES IN MULTIPHOTON EXCITATION

The first problem is to measure the vibrational energy distribution function in the interaction of the molecules with IR radiation. The use of the Raman probe method makes it possible to study the distribution function, its formation, and its subsequent time evolution.

One possibility is connected with recording the Raman signal in the Stokes region—not the integrated value but rather its spectrum. In this case, in contrast to the anti-Stokes Raman scattering, the signal is produced both by the excited and by the unexcited molecules. This method was realized in experiments with $SF_6$. A multichannel system was used to record the Raman spectra. On Fig. 3 we present sections of the Raman spectrum, each obtained by accumulation of 2000 pulses. The pressure of $SF_6$ was 2 mm Hg everywhere. In the absence of a pulse from the $CO_2$ laser (Fig. 3a), we observe a single peak with center at 775 cm$^{-1}$, which agrees well with the position of the $\nu_1$ mode of the $SF_6$ molecule. The width of the peak is determined by the spectral resolution, which amounted to $\delta\nu_R \approx 10$ cm$^{-1}$.

Irradiation of $SF_6$ by $CO_2$ laser pulses substantially changes the shape of the Raman spectrum (Fig. 3b). In the spectrum we observe two maxima which are easily

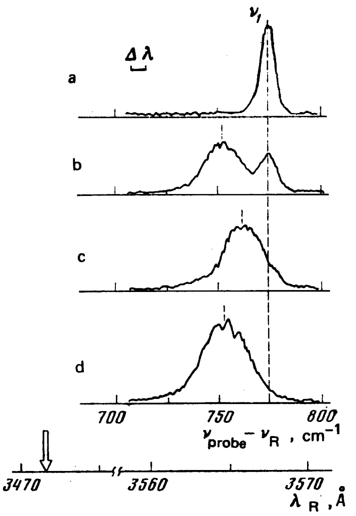

FIG. 3. Section of the spectrum of the Stokes signal for Raman scattering in $SF_6$: a) without irradiation by a $CO_2$ laser, Φ = 0; b) Φ = 0.5 J/cm$^2$, $\tau = 50$ ns; c) Φ = 0.5 J/cm$^2$, $\tau = 3\,\mu s$; d) Φ = 0.5 J/cm$^2$, $\tau = 50$ ns, $p_{Xe} = 120$ mm Hg. Below the arrow is shown the position of the probing UV radiation $\lambda_{probe}$. The $SF_6$ pressure was $p = 2$ mm Hg everywhere.

interpreted. The first maximum, unshifted in frequency, is produced by molecules which did not interact with the $CO_2$ laser pulses and remained in the initial vibrational state. The second maximum corresponds to the molecules which are vibrationally excited in multiphoton excitation. Due to the anharmonicity of the vibrations, the Raman spectrum of these molecules is shifted toward the red relative to the position of the $\nu_1$ frequency. The distinct dip in the Raman spectrum on Fig. 3b is direct evidence of the presence of a dip in the vibrational energy distribution function of the $SF_6$ molecules. This result confirms the existence of two ensembles of molecules (vibrationally excited and unexcited) after the IR pulse passes through and confirms the analogous conclusion drawn earlier[5] for $SF_6$ on the basis of IR-IR double resonance experiments.

Analysis of the spectrum on Fig. 3b makes it possible to determine also the fraction $q$ of excited molecules. Comparing the amplitudes of the unshifted peak on Figs. 3a and 3b (its magnitude is proportional to the number of unexcited molecules), we obtain $q=0.56$ and $\Phi=0.5$ J/cm², which agrees well with the measured $q=0.6$ (Ref. 5).

On increasing the time between the IR and the UV pulses, the shape of the vibrational distribution function changes; this leads to a transformation of the Raman spectrum. This is quite obvious in Fig. 3c, which shows the Raman spectrum at 3 $\mu$s after the $CO_2$ laser pulse. We observe only one maximum, located approximately in the middle between the peaks in Fig. 3b. Such a transformation of the spectrum is due to the $V-V$ exchange process, as a result of which the two ensembles ultimately blend into one. Of course, in this case the average energy of the excited molecules is reduced, and it is this which leads to the shift of the Raman spectrum on Fig. 3c. Here we note especially that the evolution of the spectrum on Fig. 3b to the shape on Fig. 3c is not at all connected with any intramolecular redistribution of the energy. As has been shown[12] (see also Sec. 5), under our experimental conditions an equilibrium distribution of the absorbed energy over all the $SF_6$ molecules is produced even in the multiphoton excitation process itself.

Collisions with the buffer gas during the IR pulse also lead to a change in the form of the vibrational distribution function. In this case, the signal from the excited molecules grows while that from the unexcited molecules decreases. At a sufficiently high buffer-gas pressure, there is no unshifted peak at all, as is seen from Fig. 3d, which shows the Raman spectrum following addition of Xe at 120 mm Hg ($\tau=50$ ns). Such a behavior of the Raman spectrum allows us to conclude that collisions with the buffer gas increase the number of molecules participating in the multiphoton excitation process. At sufficient buffer pressure, after a time $\tau_{IR}$ all the $SF_6$ molecules manage to take part in the absorption. The latter follows from the fact that the magnitude of the signal from the excited molecules on Fig. 3d, as was to be expected, is about twice as great as that presented on Fig. 3b.

Another important result follows from Fig. 3d: namely, the position of the Raman spectrum of the excited molecules is not shifted in the presence of the buffer gas. This implies that under the experimental conditions ($p\tau=6\ \mu s\cdot$mm Hg), collisions with the buffer do not lead to an appreciable change in the average energy of the molecules in the upper ensemble. The $V-T$ and $V-R$ relaxation may then be neglected by virtue of its low rate. Thus, for example, our measurement by the Raman probe method of the rate of $V-T, R$ relaxation of $CF_3I$ molecules by xenon gave a value of 440 $\mu s\cdot$mm Hg. Consequently, only collisions with a change in rotational state of the molecule (characteristic rate $p\tau\approx100$ ns $\cdot$ mm Hg) can be responsible for the evolution of the spectrum on Fig. 3d. In this case, it is essential that the rotational relaxation, by enrolling in the multiphoton excitation process new molecules in the initial vibrational state, does not exert an appreciable influence on their subsequent excitation by the field. This very important conclusion follows directly from the fact that the average energy of the excited molecules is independent of the pressure of the buffer under conditions in which we may neglect $V-T, R$ relaxation.

This role of the rotational relaxation provides still another method for determining the fraction of excited molecules $q$ from measurement of the dependence of the integrated Raman signal on the pressure of the buffer gas. We have shown[13] that addition of the buffer gas leads to an initial increase in the Raman signal $I_{AS}$, and then to saturation. The observed growth in the signal is connected only with the increase in the number of molecules participating in the multiphoton excitation. Saturation is reached upon excitation of all the molecules. Therefore the ratio of the saturated signal to its magnitude in the absence of the buffer is equal to $q$. The values of $q$ measured by this method are presented on Fig. 4a. Furthermore, the value of $q$ obtained from the decrease in the Stokes Raman signal from the unexcited $SF_6$ molecules is indicated. On this same figure are presented the values of $q$ which

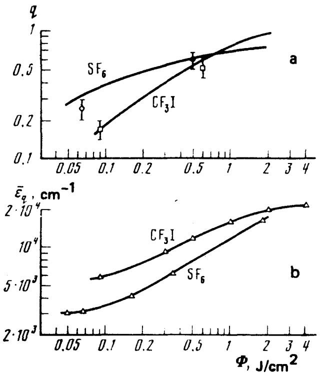

FIG. 4. Dependence of (a) the fraction of excited molecules of $SF_6$ and $CF_3I$ and (b) the average energy of these molecules, on the energy density of the $CO_2$ laser pulse. On Fig 4a, the solid lines are data from Refs. 5, 6; ●, ○—$SF_6$, □—$CF_3I$ (○, □ are the measurements from the anti-Stokes Raman scattering, ● from the Stokes Raman scattering).

were measured for $SF_6$ and $CF_3I$ previously.[5,6] As is evident, the values of $q$ obtained by different methods agree well with one another. A somewhat larger value of $q$ obtained for $SF_6$ in Ref. 5 at $\tau_{IR} = 10^{-7}$ s and at small $\Phi$ is due to the contribution of rotational relaxation under the conditions of these experiments.

The value of the factor $q$ makes it possible to determine the true level of excitation of the molecules—not simply the energy calculated for all the molecules, but the average energy $\bar{\varepsilon}_q = \bar{\varepsilon}/q$ of only the excited molecules. Using the $q$ values obtained in this work, and also the results of measurements of the absorption in multiphoton excitation of $SF_6$ (Refs. 5, 18) and $CF_3I$ (Ref. 3), we obtained the corresponding $\bar{\varepsilon}_q$ for these molecules as functions of $\Phi$. They are given on Fig. 4b. A characteristic of these plots is the slow initial growth of the level of excitation of the molecules. For $SF_6$, this is the region $\bar{\varepsilon}_q \approx 3000$ cm$^{-1}$.

The results given on Figs. 4a and 4b are essential for the understanding the multiphoton excitation process. They give an idea of how the excitation occurs. Thus, from these data it follows in particular that the monotonic power-law character usually observed in $SF_6$ for the absorption function $\bar{\varepsilon} = \bar{\varepsilon}(\Phi)$ is not produced in the region $\Phi < 0.1, \ldots 0.15$ J/cm$^2$ by an increase in the level of excitation $\bar{\varepsilon}_q$, but rather is determined primarily by the increase in the number of excited molecules. For high values $\Phi (\Phi > 0.4-0.5$ J/cm$^2$ for $SF_6)$, the increase in absorption is still primarily connected with the increase in the level of excitation, since $q$ changes slowly here.

The important role of the factor $q$ in multiphoton excitation of molecules determines the necessity for studying the process of its formation. The plots of $q$ vs. $\Phi$ presented on Fig. 5 were measured at constant pulse durations; therefore it is not obvious *a priori* which determines the character of the dependence, the energy of the pulse or its intensity. It is therefore of interest to determine the kinetics of its formation during the time of the laser pulse. Using the Raman probe method, we carried out such measurements for $CF_3I$.

The $CF_3I$ molecules were probed at different instants $\tau$ of the IR pulse, the shape of which is given on Fig. 5a. (Such a shape was obtained by special selection of the working mixture of the $CO_2$ laser). At the same points, the value of the factor $q$ was measured by the method described above upon addition of buffer gas. The saturated Raman signal $I_{AS}^{sat}$ was recorded for $p_{Xe} = 120$ mm Hg. Under these conditions at $\tau \geqslant 400$ ns, the deactivation of the molecules due to $V-T$, $R$ relaxation becomes already substantial. In order to take into account its contribution, the measured value of $I_{AS}^{sat}$ was increased by the factor $\exp(kp_{Xe}\tau)$, where $k^{-1} = 440$ $\mu$s · mm Hg is the independently measured value of the deactivation rate constant. The values of $q$ determined in such a manner at different instants of the pulse are given in Fig. 5d. The corresponding values of $\bar{\varepsilon}_q$ are given on Fig. 5c. It is obvious that the value of $q$ increases monotonically during the course of the entire pulse. Knowing the density of the pulse energy passing through the gas up to the probing instant (Fig. 5b), it is easy to obtain the plots of $q$ and $\bar{\varepsilon}_q$ vs. $\Phi$. The curves obtained agree well with those measured[6] at constant pulse length $\tau_{IR} = 10^{-7}$ s.

These results show that the magnitude of the factor $q$, at least for $CF_3I$, is determined primarily by the transmitted energy of the pulse, and not by its intensity. This conclusion is confirmed, in our opinion, also by the results of a special experiment. The $CF_3I$ molecules were probed on excitation by pulses of length $\tau_{IR} = 15$ ns and $\tau_{IR} = 100$ ns. The energy density was the same in both cases: $\Phi = 0.34$ J/cm$^2$. In the first case, we obtained $q = 0.42 \pm 0.1$ and in the second case $q = 0.31 \pm 0.06$. Thus, it is obvious that close values of $q$ are obtained for a six to sevenfold difference in pulse intensity.

## 5. INTRAMOLECULAR ENERGY DISTRIBUTION IN MULTIPHOTON EXCITATION. RANDOMIZATION EFFECT

In Sec. 3 we showed that the integrated anti-Stokes signal $I_{AS}$ is proportional to the energy stored in the probed mode. Two obvious possibilities for the study of the intramolecular distribution follow from this

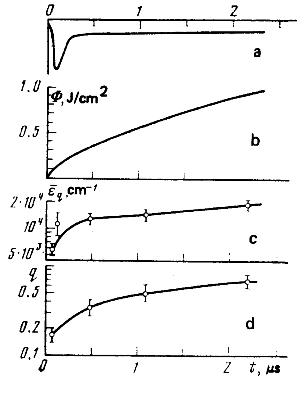

FIG. 5. The dynamics of excitation of $CF_3I$ during the laser pulse: a) the shape of the $CO_2$ laser pulse; b) the distribution of the transmitted energy with respect to time; c) the level of excitation of the molecules for different $\tau$; d) the factor $q$ for different $\tau$. The pressure of $CF_3I$ was $p = 0.05$ mm Hg.

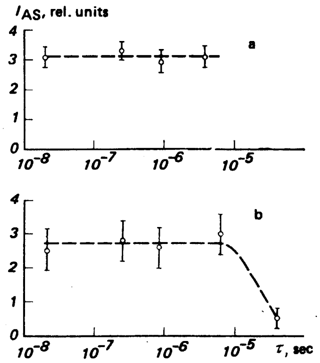

FIG. 6. Dependence of the integrated signal $I_{AS}$ of the anti-Stokes Raman scattering of the time $\tau$ between the IR and the UV pulses: a) $CF_3I$; probing of the mode $\nu_2$, $p = 0.1$ mm Hg, $\Phi = 0.09$ J/cm$^2$; b) $SF_6$; probing of the mode $\nu_2$, $p = 0.1$ mm Hg, Hg, $\Phi = 0.06$ J/cm$^2$.

circumstance. The first is connected with the observed evolution of the magnitude of the Raman signal $I_{AS}$ with time. It is clear that if Raman probing lags the excitation by a time $\tau$ which exceeds the characteristic time of intermode collisional energy exchange, then the integrated Raman signal will be proportional to the equilibrium energy in the mode $\nu_i^R$. Measuring the dependence of $I_{AS}$ on $\tau$, we can quantitatively determine by how much the energy distribution over the modes produced in the multiphoton excitation process itself differs from the equilibrium distribution. The characteristic $I_{AS}(\tau)$ dependences for different modes $\nu_i^R$ of the $SF_6$ molecules and $CF_3I$ molecules are given on Fig. 6 (see also Ref. 12). Within experimental error, we could not detect a change in the signal with time, when varying $\tau$ from 0–15 ns up to several microseconds. At pressures of 0.1–0.5 mm Hg, this corresponds to going from a region where we may neglect the collisional exchange to a region where this process is significant. The decrease of the signal at $\tau > 5$ μs is connected with diffusion from the excitation region. This is confirmed by experiments at $p = 10$ mm Hg, in which the signal did not change up to several tens of microseconds. We also assume that the experiments were carried out under conditions of collisionless excitation of the molecules by IR radiation, since $p\tau_{IR} \leqslant 1.5–6.5$ ns · mm Hg. The measurements of $I_{AS}$ as a function of pressure are also evidence in favor of this. It turned out that for $\Phi = 0.97$ J/cm² and $\tau = 0–15$ ns, $I_{AS}$ is linearly dependent on the pressure of the $SF_6$ in the pressure range $p = 0.1\ldots1$ mm Hg. The results given on Fig. 6 therefore provide a basis for stating that, within the measurement error, no redistribution of energy stored in the molecule among its vibrations occurs; i.e., the distribution is at equilibrium or at least close to it.

Here we should point out the following. The conclusion drawn is based on the independence of the Raman signal $I_{AS}$ of the time over a large range of $p\tau (0 < p\tau \leqslant 1\ldots2$ μs · mm Hg). However, collisions lead not only to an equilibrium distribution of the internal energy of the molecule over its vibrations, should such not have existed before. As was shown in Sec. 4, in multiphoton excitation two ensembles are formed: of excited and of unexcited molecules. Therefore on collisions the average energy of the excited molecules may decrease so much as to make substantial quantum character of the heat capacity of the vibrational degrees of freedom. Consequently, this value of the energy stored in the mode may change, even if an equilibrium intermode distribution is maintained. However, in our experiments, even at the lowest levels of excitation this effect for the probed mode $\nu_1$ should not exceed 20% for $SF_6$. The accuracy in the measurements of $I_{AS}$ in this case did not exceed ±15%; therefore this effect was not yet noticed. Nevertheless, it imposes certain limits on the possibilities of the technique employed.

Information concerning the character of the intramolecular energy distribution is also obtained by comparing the results of direct calorimetry of the energy absorbed in multiphoton excitation with the results of Raman probing. Such a comparison of $\bar{\varepsilon} = \bar{\varepsilon}(\Phi)$ and $I_{AS} = I_{AS}(\Phi)$ has already been carried out in Sec. 3 under conditions in which the energy distribution in the molecule at the instant of probing should be at equilibrium by virtue of the collisional intermode exchange. On Fig. 2a are given also the values of the Raman signal on probing the $SF_6$ molecules at an instant $\tau$ when the intermode exchange in collision may be neglected ($p\tau < 4$ ns · mm Hg). Here, too, we observed the proportionality $I_{AS}^{\text{no coll}} \propto \bar{\varepsilon}$. Since simultaneously $I \propto I_{AS}^{\text{coll}}$, this is again evidence that collisions after the IR pulse do not lead to a change in the character of the distribution of the energy absorbed by the molecule among its vibrational degrees of freedom.

From all the results presented above, it follows unambiguously that under the conditions of the experiments with multiphoton excitation of $SF_6$ and $CF_3I$ molecules, states are formed which correspond to a statistical equilibrium distribution of the energy absorbed among all or at least the majority of the vibrations of these molecules. This proves that the stochastic character of the vibrational motion in the molecules under consideration sets in already during the interaction with the IR radiation.

The results make it possible to estimate the randomization threshold. The minimum energy density of the $CO_2$ laser pulse in these experiments at which the Raman signal was reliably recorded (the signal/noise ratio was 6:1) was 0.06 J/cm² for $SF_6$ and 0.09 J/cm² for $CF_3I$. From the known values of the absorbed energy $\bar{\varepsilon}$ (see Fig. 2) and also of the fraction of excited molecules $q$, we can determine the average absorbed energy for the molecules excited to the upper ensemble, $\bar{\varepsilon}_q = \bar{\varepsilon}/q$. If we add to this value the initial average vibrational energy at a temperature of 293°K, then we obtain an estimate for the randomization threshold $E_{th}$. In the case of $SF_6$, we have $E_{th} \approx 3900 \pm 500$ cm$^{-1}$, and for $CF_3I$, $E_{th} \approx 6000 \pm 500$ cm$^{-1}$.

## 6. MECHANISM OF RANDOMIZATION OF VIBRATIONAL MOTION IN THE SF₆ MOLECULE

Theoretically, the effect of randomization of the vibrational energy comprises a change in the structure of the true characteristic wave functions at $E_{vib} \gtrsim E_{th}$, so that the wave functions of the states of the mode that interacts with the laser radiation become mixed with many other wave functions because of the intermode resonances. In general form, the true vibrational wave functions of the molecule, which depend on its normal coordinates, may be described as

$$\Psi_{\text{true}}^{(i)}(q_k) = \sum_j c_i^{(j)} \Psi_{\text{harm}}^{(j)}(q_k). \tag{4}$$

Then the cross sections of transitions from the supposedly "almost harmonic" state $(v-1)\nu_{IR}$ lying below $E_{th}$ into the states (4) lying above $E_{th}$ are proportional to $|c_i^{(v\nu_{IR})}|^2$. In this case, it is natural to expect that the maximum of the frequency dependence of the cross section occurs at the transition frequency $(v-1)\nu_{IR} \to v\nu_{IR}$ (taking into account the anharmonic shift), but the spectrum is broadened and possibly quasicontinuous, if the number of states to which the wave function of the state $v\nu_{IR}$ contributes substantially is sufficiently large. It is easy to estimate that the values of $|c_i^{(v\nu\mathrm{IR})}|^2$ which are able to ensure saturation of the transitions even at minimum laser pulse energy densities used in the experiment amount to about $10^{-2}$.

The value of $E_{\mathrm{th}}$ for the $CF_3I$ molecules agrees well with the estimate obtained earlier.[3] In this work, the experimental results on multiphoton IR excitation were compared with the spectroscopic model of transitions in the vibrational quasicontinuum and a constant was found which describes the width of the transition contour close to the mode frequency $\nu_1$; this constant increases with an increase in the vibrational energy. In accordance with the known energy deficit of the three-frequency Fermi resonances of the $CF_3I$ molecules, the energy randomization threshold for the vibrational motion was estimated from this constant; this gave the value $E_{\mathrm{ran}} \gtrsim 5000$ cm$^{-1}$, approximately equal to the value $E_{\mathrm{th}}$ obtained in our work.

For the $SF_6$ molecule, the intermode resonances give a pattern which is not so simply interpreted as in the $CF_3I$ molecule, since the values of $E_{\mathrm{th}}$ are substantially lower. Therefore, in order to study the possible mechanisms of randomization of vibrational motion in the $SF_6$ molecule, we performed a numerical quantum-mechanical calculation. Below we present the fundamental vibrational frequencies (in cm$^{-1}$) of the $SF_6$ molecule[19] that we used in the calculations[1)]

| $\nu_1(A_{1g})$ | $\nu_2(E_g)$ | $\nu_3(F_{1u})$ | $\nu_4(F_{1u})$ | $\nu_5(F_{2g})$ | $\nu_6(F_{2u})$, |
|---|---|---|---|---|---|
| 774 | 642 | 948 | 615 | 523 | 346 |

The state $4\nu_3$ was taken and all states were selected whose harmonic positions were separated from the $4\nu_3$ level by ±100 cm$^{-1}$. There were 181 such states. Practically all these states are strongly degenerate (taking into account the degeneracy, there are $\sim 3\cdot10^4$ of them). Since due to the anharmonicity only levels of the same symmetry may interact, only those states were selected which contained sublevels classified according to a certain representation of the $O_h$ point group to which the $SF_6$ molecule belongs. As an example, we took the representation $F_{2g}$. There were $\sim 1.7\cdot10^3 F_{2g}$ sublevels, and there were 87 states containing these sublevels.

We next included into consideration all the symmetry-allowed third- and fourth-order anharmonic terms connecting the selected states. The frequency combinations (Fermi resonances) corresponding to these terms are given below. We also give the energy deficits of all the resonances considered, and in parentheses we indicate how many times a single representation is contained in the product of representations corresponding to the normal coordinates in the resonance. This number allows us to determine how many fully symmetrical independent combinations of the products of normal coordinates occur, taking into account their degeneracy.

The three-frequency resonances and their deficits, in cm$^{-1}$, are:

(1) $\nu_2+\nu_6-\nu_3=40$, (1) $\nu_3-\nu_5-\nu_6=79$,
(1) $2\nu_6-\nu_2=50$, (1) $\nu_1-2\nu_6=82$,
(1) $2\nu_6-\nu_5=169$.

The four-frequency resonances and their deficits, in cm$^{-1}$, are:

(1) $\nu_1+\nu_5-\nu_3-\nu_6=3$, (1) $\nu_3+\nu_4-\nu_1-\nu_2=147$, (1) $\nu_1+\nu_5-2\nu_4=67$,
(1) $\nu_4+\nu_5-\nu_1-\nu_6=18$, (2) $\nu_4+\nu_5-\nu_2-\nu_6=150$, (2) $2\nu_5-\nu_4-\nu_6=85$,
(1) $\nu_3+\nu_5-\nu_1-\nu_4=82$, (1) $\nu_3+\nu_6-2\nu_2=10$, (1) $\nu_1+\nu_2-2\nu_4=186$.
(1) $\nu_1+\nu_2-\nu_3-\nu_6=122$, (1) $\nu_3+\nu_4-2\nu_1=15$. (2) $2\nu_2-2\nu_4=54$,
(2) $\nu_3+\nu_6-\nu_2-\nu_5=129$, (2) $\nu_3+\nu_6-2\nu_4=64$, (1) $3\nu_6-\nu_3=90$.
(1) $\nu_2+\nu_4-\nu_1-\nu_6=137$, (1) $2\nu_4-\nu_2-\nu_3=65$,

The calculation was carried out by perturbation theory without taking into account anharmonic shifts and anharmonic splittings. Since as a rule the anharmonic constants are unknown, we described the third-order terms and the fourth-order terms by the general constants $\alpha_3$ and $\alpha_4$; i.e., we represented the expansion of the potential energy as

$$V(q_i)={}^1/_2\sum_i \nu_i^2 q_i^2+\alpha_3\sum_{ijk}\nu_i\nu_j\nu_k q_i q_j q_k+\alpha_4\sum_{ijkl}\nu_i\nu_j\nu_k\nu_l q_i q_j q_k q_l. \tag{5}$$

In the expansion (5), the normal coordinates $q_i$ have dimension cm$^{1/2}$; thus, $[\alpha_3]=\mathrm{cm}^{1/2}$ and $[\alpha_4]=\mathrm{cm}$. In order to estimate the numerical value of $\alpha_3$, we used the known fact[20] that the intensity of the composite band $\nu_2+\nu_6$ in linear IR absorption is two orders of magnitude smaller than the intensity of the fundamental band $\nu_3$.

From the detuning $\nu_2+\nu_6-\nu_3=40$ cm$^{-1}$ and the known formula for the matrix elements of the normal coordinates, it is easy to find that

$$\alpha_3({}^1/_8\nu_2\nu_3\nu_6)^{1/2}\approx 4\ \mathrm{cm}^{-1} \quad\text{or}\quad \alpha_3\approx 6.8\cdot10^{-4}\ \mathrm{cm}^{1/2}.$$

As for the constant $\alpha_4$, its value was varied. We should also note that in the calculation, it is physically justified to neglect interference effects; i.e., we must sum the probabilities and not the amplitudes. This is due to two reasons. First of all, for different terms in each sum of (5) the signs of the anharmonic constants may differ. Secondly, the interaction of two degenerate states breaks up into pairwise interactions of all the sublevels of like symmetry. The signs and magnitudes of the interaction matrix elements for such pairs may be completely arbitrary, only the sum of their squares does not change.

A simple estimate shows that the cubic anharmonicity leads to strong mixing of the level $4\nu_3(a)$ with the level $d$ (Fig. 7) detuned from the level $4\nu_3$ by 1 cm$^{-1}$. The levels a and d are not directly coupled. However, they are connected by a chain of three successive three-frequency resonances, and the standard perturbation-theory formula

$$|c_a^{(d)}|^2=\left|\frac{\langle b|V|a\rangle\langle c|V|b\rangle\langle d|V|c\rangle}{(E_a-E_b)(E_a-E_c)(E_a-E_d)}\right|^2, \tag{6}$$

leads, when account is taken of the dependences of the matrix elements on the occupation numbers of the modes, to the estimate $|c_a^{(d)}|^2\approx 0.6$. The level a is connected, besides with the level b, only with two strongly detuned states, but the level d is still connected already with sixteen levels, the closest of which (e) is separated from the level $4\nu_3$ by only 4 cm$^{-1}$ and in turn is connected also with thirteen levels; in this

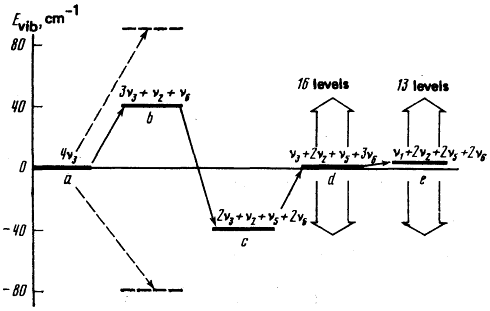

FIG. 7. Level diagram, illustrating the effect of three-step resonance in the $SF_6$ molecule.

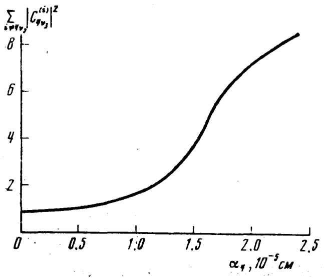

FIG. 8. The total contribution to the state $4\nu_3$ from the rest of the levels in the $SF_6$ molecule, as a function of the fourth-order anharmonicity constant $\alpha_4$.

case, more than half the nondiagonal matrix elements, in particular $\langle e|V|d\rangle$, are described by quartic anharmonic terms. Thus, the major mechanism for randomization of the vibrational motion in $SF_6$ becomes clear. Upon strong mixing of level a with level d and possibly e, the contribution from many other states is transmitted, as it were, through the levels d and e to the $4\nu_3$ state. In accordance with perturbation theory, this contribution $\propto \Delta^{-2}$, where $\Delta$ is the detuning from the level $4\nu_3$.

The mechanism discovered allows us to substantiate physically the most justified calculation scheme. To a first approximation, we must calculate the contribution to the state $4\nu_3$ from all the rest of the states, performing the summation only over the shortest paths. However, the shortest paths are not always the most effective. For example, out of the sixteen levels connected with d, only for four does the chain to the $4\nu_3$ state through the d state have of the least number of links. On the other hand, obviously, for the remaining twelve levels the path through d is the most effective. Therefore we also calculated a second approximation, in which as the initial states we also chose, in addition to the level $4\nu_3$, several other levels which are more strongly mixed with $4\nu_3$ to a first approximation. The mixing criterion was optimized using the total contribution obtained in the second approximation.

On Fig. 8 we give the total contribution as a function of $\alpha_4$. Knowing the total contribution, it is easy to renormalize the wave functions, but it is precisely the quantity $\sum|c_{4\nu_3}^{(i)}|^2$ in unnormalized form, i.e., at $c_{4\nu_3}^{(4\nu_3)}=1$ which gives the clearest idea of the degree of mixing of the levels. For $\alpha_4=0$, only strong mixing of the level $4\nu_3$ with the level d mainly occurs. However, even for $\alpha_4=10^{-5}$ cm, the total contribution to the other states also becomes significant; it is characteristic that it is distributed among many levels. For example, at $\alpha_4=0.9\cdot 10^{-5}$ cm, which corresponds to doubling the total contribution compared with $\alpha_4=0$, the relation $|c_{4\nu_3}^{(i)}|^2>10^{-2}$ holds for fifteen states. We shall use this value of $\alpha_4$ for further estimates.

If we drop down by one quantum number, i.e., consider the levels in the vicinity of the $3\nu_3$ states, then here the picture is qualitatively changed. The three-step resonance between the levels $3\nu_3$ and the level $2\nu_2+\nu_5+3\nu_6(d')$ does not occur, as before. However, Eq. (6) gives the estimate $|c_{3\nu_3}^{(d')}|\approx 0.15$. Primarily due to the fact that $|c_{3\nu_3}^{(d')}|^2 \ll 1$, the total contribution to the level $3\nu_3$ from the remaining states is substantially less than for the level $4\nu_3$, and only for four states, including $d'$, is the relation $|c_{3\nu_3}^{(i)}|^2>10^{-2}$ satisfied. Thus, the calculation quantitatively confirms the experimentally observed change of the spectroscopic characteristics at the energy $E_{\text{th}}$. Furthermore, taking into account the renormalization of the wave functions, it is easy to obtain $|c_{4\nu_3}^{(4\nu_3)}|^2\approx 0.4$. Thus, for this energy we can already speak of, if not of a complete, at least of a partial randomization of the vibrational motion. If we go up by one quantum number, then the degree of randomization increases ($|c_{5\nu_3}^{(5\nu_3)}|^2\approx 0.2$).

It is also interesting to establish the extent to which the numerical value of $\alpha_4$ corresponds to the known values of the intermode anharmonicity constants of the $SF_6$ molecule, which describe the shifts of the hot bands in the line spectra. The most accurate data[19] pertain to the anharmonicity constants $x_{26}$, $x_{36}$, and $x_{46}$. If we consider that these constants are described by only fourth-order anharmonicity, which however is not entirely accurate,[21] then it is easy to find that the constant we assumed to estimate the value of $\alpha_4$ overvalues $x_{26}$ and $x_{46}$ by about a factor of two, and $x_{36}$ by about a factor of three.

Based on the results of the calculation, we may also understand the reason for the jump in the induced-transition rate when the molecule enters the stochasticity region. The integrated cross section of transitions from the state $3\nu_3$ to the states lying close to the level $4\nu_3$, according to the sum rule, should be equal to the cross section for the transition $3\nu_3\rightarrow 4\nu_3$ in the harmonic approximation: $\sigma^{\text{int}}=\sigma_{34}^{\text{harm}}=4\sigma_{01}$. In states excited by a $CO_2$ laser close to the level $4\nu_3$, the vibrational energy is distributed over the modes in an equilibrium fashion. This means that to get the averaged cross section of the transitions one quantum number higher we must multiply $\sigma_{01}$ by $\langle E_3\rangle/\nu_3+1$, where $\langle E_3\rangle$ is the equilibrium energy in the mode $\nu_3$ at the total vibrational energy $E_{\text{vib}}=4\nu_3$. This leads to the estimate $\langle E_3\rangle/\nu_3\approx 0.2$ or $\langle\sigma^{\text{int}}(E=4\nu_3\rightarrow E=5\nu_3)\rangle\sim 1.2\sigma_{01}$, i.e., the cross section in fact drops substantially. Another reason for the decrease in the cross section is rather obvious and is connected with the broadening of the transition contour with an increase in the vibrational energy.

Thus, the calculation confirms both principal conclusions drawn from the experimental results.

1. During interaction of $SF_6$ and $CF_3I$ molecules with an IR pulse, there are excited not only vibrational modes resonant with the laser radiation, but also other vibrational modes. In this case, beginning with some vibrational energy $E_{th}$, the distribution over the modes is at equilibrium.

2. In the region of the energy $E_{th}$, a qualitative change in the transition spectrum occurs so that the rates of excitation to the energy $E_{th}$ are at least several times greater than the rates of excitation to above the energy $E_{th}$.

Of course, in the calculation we stayed away from the harmonic positions of the levels. Taking into account the anharmonic shifts apparently may lead to some change in the quantitative estimates. However, more significant is the effect of anharmonic splitting, which should improve the resonance conditions for the intermode interactions. It is possible that precisely for this reason we obtained a somewhat overestimated value for the constant which describes the fourth-order anharmonicity.

We should also point out that the model calculation performed, which does not take into account the renormalization of the wave functions, possibly overestimates the admixture contributed to the wave function of the $\nu_3$ mode by the rest of the harmonic wave functions. However, the principal effect, namely that the admixture is distributed over many states, apparently remains in force also in more accurate calculations.

## 7. DISCUSSION

As was pointed out in Sec. 1, the basic goal of our work was the study of the vibrational distribution (both intramolecular and intermolecular) produced during multiphoton excitation. Experiments with $SF_6$ and $CF_3I$ molecules showed that the vibrational energy distribution is formed by two ensembles, of hot and cold molecules. Measurements of the factor $q$—the fraction of molecules in the upper ensemble—made it possible to clarify the kinetics of excitation of the molecules by $CO_2$ laser radiation. Thus, in the case of $SF_6$, some molecules acquire an energy $\bar{\varepsilon}_q \approx 4000$ cm$^{-1}$ rather rapidly, but further excitation of these molecules with an increase in $\Phi$ is much slower. The increase of the energy absorption by the gas, which is observed in this region, is determined primarily by the increase in the factor $q$, i.e., by the number of excited molecules, and not by their energy.

The fundamental reason for the subdivision of the molecules in multiphoton excitation into two ensembles, in our opinion, is the rotational bottleneck effect. This conclusion is directly confirmed by experiments on multiphoton excitation of molecules in the presence of a buffer gas. The existence of this effect for excitation of molecules by an IR pulse was predicted earlier[22] and demonstrated experimentally.[23] Essentially, it involves the fact that due to the distribution over many rotational states, the molecules do not all interact in the same way with the field. We emphasize that all these states may interact with the field, a fact that follows even from the possibility of pure radiative excitation of all the molecules.[3] Nevertheless, there are states which interact more strongly with the field. They are rapidly depleted and the molecules excited from them to the vibration quasicontinuum from the upper ensemble. The molecules remaining below form the lower ensemble. This is a qualitative, very simplified picture. For a quantitative description of the process, we must know how the excitation of molecules from different rotational states occurs. At the moment, no such information is available. From the results of our present study of the kinetics of development of the factor $q$ we can only conclude that its magnitude is determined by the energy of the pulse passing through, and not by the intensity; therefore further investigations are necessary in this area.

The Raman diagnostics method has proven to also be suitable for the measurement of vibrational energy in modes which are not resonant with the laser IR radiation. In our work we succeeded in proving that even during interaction with the IR laser pulse the vibrational motion in the $SF_6$ and $CF_3I$ molecules is randomized, beginning with some rather low energy. The calculation performed in this work showed that this effect is primarily due to the rearrangement of the vibrational wave functions of the molecule; in other words, the randomization effect is a property of the molecule itself, and not a property of its interaction with the laser IR pulse. However, if we consider the molecule as a statistical system, then although in the region of complete randomization the most probable true wave functions (4) seem to be combinations of harmonic wave functions corresponding to the equilibrium distribution of the vibrational energy over the modes, the fluctuations are nevertheless rather significant due to the relatively small number of degrees of freedom. This means that action of weak monochromatic sources of radiation with specially selected frequencies can in principle produce a steady-state, nonequilibrium vibrational energy distribution.

Another concept which we must approach with a certain degree of caution is that of the quasicontinuum. Strictly speaking, we may regard the spectrum of transitions from an excited vibrational-rotational state as continuous if the separations between adjacent transitions from this state are smaller than the radiation width, something practically unattainable for molecules with not very many atoms even close to the dissociation energy. This condition becomes much less stringent if sources with real spectral width are used (even for cw single-mode lasers). As far as the standard pulsed $CO_2$ lasers with spectral width $\gtrsim 10^{-2}$ cm$^{-1}$ are concerned, even for the experimental values of $E_{th}$ obtained for the $SF_6$ and $CF_3I$ molecules the spectrum of the transitions may be considered as quasicontinuous. The field broadening in a rather strong IR field also leads to the fact that the discrete character of the structure of the transitions does not appear at all.[24] Thus, the quasicontinuum is a relative concept that depends on the characteristics of the radiation source used.

In conclusion, we would like to discuss the possibility of direct spectroscopic evidence for the quasicontinuum character of the spectrum of transitions from any sufficiently strongly excited vibrational-rotational state, which is usually what is had in mind when speaking of the quasicontinuum. This problem is nontrivial, since on attempting to create a significant concentration of excited molecules, inevitably we have to deal with a real distribution over many vibrational-rotational levels. One approach which somewhat eases the situation is rather obvious and presupposes intense cooling of the gas. We can propose also another approach, based on the use of coherent non-steady-state effects. Inhomogeneous broadening due to the rotational structure, does not prevent observation of these effects. However, if from any vibrational-rotational state a multitude of transitions with similar frequencies is possible, then at radiation intensities such that the field broadening exceeds the separation between the adjacent transitions but is less than the homogeneous width of the transition contour, the coherent effects should disappear. Methods suitable for such investigations, may be, for example, as photon echo or non-steady-state coherent active Raman spectroscopy.

1) To be consistent, to determine the harmonic positions of the levels we must use not the fundamental vibrational frequencies $\nu_i$ but rather the harmonic vibrational frequencies $\omega_i$. However, the latter are known with much less accuracy[19]; moreover, within the limits of known accuracy their relative deviations from the fundamental frequencies (~ 1.5%) are the same for all vibrations. Therefore, their use would lead only to an insignificant change of the energy scale.

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