Intermolecular and intramolecular distribution of vibrational energy in infrared multiphoton excitation of the CF_3Br molecule

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With the aid of Raman spectroscopy of the fundamental, overtone, and combination bands of CF_3Br, a study is made of the distribution of energy among the vibrational modes and the intermolecular distribution of vibrational energy during multiphoton excitation. The results yield a quantitative explanation of the presence of a group of highly excited molecules having an equilibrium distribution of energy over the vibrational modes. It is found that the mixing of vibrational modes begins at an energy of 7500 ± 300 cm^{-1}. The mode ν_1, in resonance with the IR radiation, is found to have an excess energy. It is shown that the excess energy belongs to molecules excited below the energy threshold for mixing.

1. INTRODUCTION

In the past few years the idea of chaos in dynamical systems is becoming a tool in the physical study of vibrations of polyatomic molecules. In part, this is due to the comprehension of the experience gained by mathematicians.[1–4] However, the main reason is apparently that the systematic experimental study of the dynamics of intramolecular motion and the spectra of transitions in the region of highly excited vibrational states is becoming increasingly practicable.

At sufficiently high energies, a general property of classical nonlinear dynamical systems with many degrees of freedom is that the motion is stochastic (see Refs. 1–4 for the various definitions). The onset of stochasticity is due to the overlap of the intermode resonances (the Chirikov criterion).[1] It is widely debated whether it is legitimate to apply the term "stochasticity" to quantum systems (see, e.g., Refs. 4 and 5), but from the standpoint of present-day experiment this is possibly not a fundamental question. The fact is that studies are being done on the *mixing* of modes of a molecule. This mixing has two main consequences: 1) It is impossible in principle to strongly excite an individual mode, in the sense that over a finite (and actually rather short) time the energy will be redistributed in an equilibrium manner over all the modes; 2) the spectrum of transitions to highly excited states (in absorption, emission, Raman scattering, etc.) gets broadened.

Of course, the dynamical and spectral characteristics mentioned can be observed only above a certain energy which is sufficient for mixing. The general mechanism of mixing discussed in the literature is the overlap of intermode resonances,[6–10] but the only active quantitative theory is that of two coupled oscillators (see, e.g., Ref. 11). Studies of real polyatomic systems, both in the classical[12] and quantum-mechanical[13] approaches are only getting started; moreover, the partial or total lack of data on the vibrational intermode anharmonicities leaves numerical experiments quantitatively indeterminate.

Physical experiments are able to give precisely that quantitative information which is of primary interest for understanding the particular mechanisms of mode mixing in a molecule: the energy thresholds for mixing, the widths of the spectra, and the mixing times. The study of the spectra of highly excited vibrational states includes the spectroscopy of the high overtones (see, e.g., Refs. 14 and 15) and the probing of the allowed IR bands for highly-excited molecules with a relatively narrow distribution over vibrational energy.[16,17]

Evidently, time-resolved measurements can actually be achieved only through the use of ultrashort laser pulses, and so far such measurements have been made only in studies of the vibrational states in the electronically excited terms (see, e.g., Ref. 18).

It should not be thought, however, that the absence of time resolution rules out the possibility of doing mixing studies. If the means of exciting the molecules is such as would lead, in the absence of mixing, to a nonequilibrium distribution of energy over the vibrational modes, then the existence of mixing can be inferred conversely from the presence of equilibrium. In this respect a convenient means of exciting a polyatomic molecule is the quasiresonant action of IR laser radiation on an isolated mode. Many polyatomic molecules are excited rather efficiently in an IR laser field (and even dissociate if the energy in the laser pulse is high enough). This process has come to be called multiphoton IR excitation, and there are many experimental and theoretical results on this subject (see reviews[19–21]). After the IR laser pulse has acted, a certain distribution of molecules over vibrational states is formed. Both the distribution of molecules over vibrational energy (often called the intermolecular distribution) and the distribution of vibrational energy over the different modes of the molecule (often called the intramolecular distribution) are of interest. Different methods have been proposed for probing the distributions that arise. In particular, the intramolecular distribution can be studied by measuring the *integrated* signal of the spontaneous anti-Stokes Raman scattering[22] and IR fluorescence[23,24] in different vibrational bands. In fact, these signals are, to good accuracy, proportional to the energies in the modes being probed.

In our studies we use spontaneous Raman scattering for diagnostics of the distributions arising during multiphoton

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excitation. A general result of our studies, which were done on the molecules SF_6 (Refs. 22 and 25–28; see also Ref. 29, by a group in the USA), CF_3I (Refs. 22, 26, and 28), and CF_2HCl (Ref. 30), is that in spite of the fact that only one mode was acted upon and in spite of the collisionless conditions of the experiment, the remaining modes give anti-Stokes Raman signals, i.e., mixing is observed above a certain energy.

Essentially, an experiment using Raman scattering to probe the anti-Stokes region gives the energies in the different modes. However, until the intermolecular distribution is known (it is known to be highly nonequilibrium under multiphoton excitation)[19–21] the values of the energies in the modes cannot themselves be used to infer which of the vibrational energies are involved in the mixing. In principle, one can attempt a crude reconstruction of the shape of the intermolecular distribution by measuring the spectrum (preferably in the Stokes region) of the Raman bands[26,27]: as a result of the anharmonic shift, the parts of a band at different frequencies correspond to different vibrational energies.

In the present study we investigate the vibrational distribution arising in the multiphoton excitation of CF_3Br. In addition to measuring the energies in the various vibrational modes, we have for the first time used another means besides measuring the spectra of the Raman bands for obtaining information on the intermolecular distribution: measuring the anti-Stokes Raman signals at the frequencies of the overtones and combination vibrations (see also Ref. 31). Previously, the method of probing distributions by IR fluorescence was also extended in an analogous direction and for an analogous purpose.[32]

In Sec. 2 we briefly consider what new information is given by probing the overtones and combination bands in addition to that obtained by probing the fundamental bands. In Sec. 3 we present the experimental results. In Sec. 4 the results are analyzed for the purpose of reconstructing the vibrational distribution. In Sec. 5 we discuss the physical consequences.

2. RAMAN SPECTROSCOPY IN THE PROBING OF VIBRATIONAL DISTRIBUTIONS

In the harmonic approximation, the integrated intensity of the fundamental band of the anti-Stokes Raman scattering is proportional to the energy in the corresponding mode:

$$I_{AS}=C_i^{(1)}\bar{n}_i. \tag{1}$$

Here $\bar{n}_i$ is the average number of vibrational quanta in mode ν_i. It is easily shown that this formula is valid for an arbitrary distribution function. Generally speaking, anharmonicity will make it approximate. The intramode anharmonicity gives small corrections as long as it can be treated as a perturbation, but even if the polyatomic molecule is highly excited this condition holds from a practical standpoint, since the average occupation numbers of the modes are small. The intermode anharmonicity can radically alter the character of the vibrational motion, but the main effect here will be a change in the shape of the bands, a broadening and a shift (as in the case of the intramode anharmonicity), but with no change in intensity.

The first overtones and combination bands are activated on account of the cubic anharmonicity (in first order of perturbation theory) and of the quadratic terms in the expansion of the dipole moment in the normal coordinates (the electrooptic anharmonicity[33]). These leading terms give the following behavior of the cross sections for anti-Stokes Raman scattering in the overtone and combination bands as functions of the vibrational quantum numbers and, accordingly, the following formulas for the integrated intensities (the derivation is simple, but in the general case it is cumbersome, and we shall not give it here; see also Ref. 34):

$$\sigma(n_i\rightarrow n_i-2)\propto n_i(n_i-1),\quad I_{AS}=C_{ii}^{(2)}\overline{n_i(n_i-1)}, \tag{2}$$

$$\sigma(n_i,n_k\rightarrow n_i-1,n_k-1)\propto n_in_k,\quad I_{AS}=C_{ik}^{(2)}\overline{n_in_k}. \tag{3}$$

Formula (2) corresponds to a transition between the initial state $|n_i,n_j\rangle$ and the final state $|n_i-2,n_j\rangle$, where n_j is the set of vibrational quantum numbers of the remaining modes, while formula (3) corresponds to a transition between the initial state $|n_i,n_k,n_j\rangle$ and the final state $|n_i-1,n_k-1,n_j\rangle$.

By measuring the integrated signals in the overtones and combination bands from molecules having some vibrational distribution, we can find the quantity n_in_k. Thus we obtain the second moments of the distribution in addition to the first moments (average energies), which are found from the integrated intensities (1) for the fundamental bands. Analogously, from the measurements in the overtone and combination bands of higher orders, one can find the higher moments of the distribution. The corresponding formulas are given in Ref. 34. In the present study, however, we measured the signals only in the first overtones and combination bands.

We shall need explicit formulas for the intensities of the overtone and combination bands in the case of a Boltzmann distribution:

$$I_{AS}=C_{ii}^{(2)}\cdot 2\bar{n}_i^2\quad([\overline{n_i(n_i-1)}]_B=2\bar{n}_i^2,\text{overtone}), \tag{4}$$

$$I_{AS}=C_{ik}^{(2)}\bar{n}_i\bar{n}_k\quad((\overline{n_in_k})_B=\bar{n}_i\bar{n}_k,\ \text{combination band}). \tag{5}$$

If the molecule is sufficiently large and the width of the vibrational energy distribution is narrower than or comparable to that of the Boltzmann distribution, then formulas (4) and (5) remain sufficiently accurate for purposes of estimation. This can be demonstrated for numerical examples, but here we shall discuss only a useful analytical result for one particular case. This is the case when all s vibrational frequencies of the molecule are the same ($\nu_i=\nu$). Then, for the microcanonical distribution with total energy $E=m\hbar\nu$ we easily obtain

$$\overline{n_i(n_i-1)}=2m(m-1)/s(s+1), \tag{6}$$

$$\overline{n_in_k}=m(m-1)/s(s+1). \tag{7}$$

Because $\bar{n}_i=m/s$, it is easy to see that for $s\gg 1$ and $m\gg 1$ the result differs little from the result for the Boltzmann distribution.

However, if the intermolecular distribution differs strongly from the Boltzmann distribution, then the signals in the overtone and combination bands will quickly indicate this. It is just such a situation that we encountered in the present study, as will be seen below.

A strong difference of the intermolecular distribution from the Boltzmann distribution can also be observed directly from the shape of the Stokes bands of the Raman scattering. In this way it has been shown[27] that the SF_6 molecules in multiphoton excitation are divided into two groups: strongly excited and weakly excited. The integrated signal in the Stokes band is

$$I_s=\tilde{C}_i^{(1)}(\bar{n}_i+1). \tag{8}$$

The strongly excited molecules (comprising a fraction q of the molecules) gave a signal $\tilde{C}_i^{(1)}q(\bar{n}_i^*+1)$ in the red-shifted part of the band, while the weakly excited molecules gave a signal of the order of $\tilde{C}_i^{(1)}(1-q)$ (for them $\bar{n}_i \ll 1$) in the unshifted part of the band. Between the two parts of the band, a dip was clearly observed. However, in order to extract information on the intermolecular distribution from the spectra, their width, which in the general case is due to both inhomogeneous and homogeneous (in the mixing region) broadening, should at least be smaller than the characteristic anharmonic shifts. In the present study we ran up against the fact that this condition does not hold in many cases, which points up even more the value of the measuring the signals in the overtone and combination bands.

3. EXPERIMENT

The experimental apparatus is described in detail in Refs. 26 and 30. The CF_3Br molecules were excited by a CO_2 laser pulse 25 nsec long. For the Raman probing we used a 10-nsec pulse of the second-harmonic of the Nd:YAG laser. To eliminate collision effects to the maximum possible extent, we tried to make the measurements with the probe pulse following immediately after the exciting pulse; the delay was actually not over 20 nsec. In a number of experiments we varied the delay between the exciting and probing pulses in order to trace the collisonal establishment of the equilibrium vibrational distribution. The Raman spectrum was detected by a multichannel television system placed behind the exit slit of a triple spectrograph; the integrated signal was measured by an FÉU-106 photomultiplier. In both cases the apparatus worked as a photon counter. All the measurements were made at room temperature.

The CF_3Br molecule, with symmetry C_{3v}, has three nondegenerate normal modes, viz., ν_1 (1084.6 cm^{-1}), ν_2 (762.0 cm^{-1}), and ν_3 (351.4 cm^{-1}), and three twofold degenerate modes, viz., ν_4 (1209.0 cm^{-1}), ν_5 (548.9 cm^{-1}), and ν_6 (302.7 cm^{-1}).[35] The strongest bands in the Raman scattering spectrum are ν_3, ν_2, and ν_1; their intensities are in the ratio 174:100:8.[35] The multiphoton excitation and dissociation of CF_3Br under the action of CO_2 laser radiation on the ν_1 mode has been studied in a number of papers (the results are reviewed in Ref. 21). In the present study the multiphoton excitation of CF_3Br was done with radiation at the 9R16 line of the CO_2 laser (1075.99 cm^{-1}).

Integrated measurements in the fundamental bands. The Raman probing of the CF_3Br molecules after their IR excitation showed that, as in the case of SF_6, CF_3I, and CF_2HCl (Refs. 22, 26, 29, 30), the resonant pumping of one of the modes (in this case ν_1) leads also to excitation of the other modes that are not directly coupled with the radiation. Detailed measurements were made for the strongest bands ν_3, ν_2, and ν_1. The absolute values of the average energy $\bar{\varepsilon}_i = \hbar\nu_i\bar{n}_i$ in these modes were determined by working from Eq. (1), with the constants calibrated by the technique described in Ref. 30. From the dependence on the gas pressure of the anti-Stokes Raman signal in the ν_2 band, it follows that $\bar{\varepsilon}_2$ is independent of pressure in the range $p = 0.1$–2.0 Torr and begins to grow only at $p \gg 3$ Torr. This permits us to conclude that for $p\tau_d < 40$ nsec·Torr the influence of collisions is unimportant.

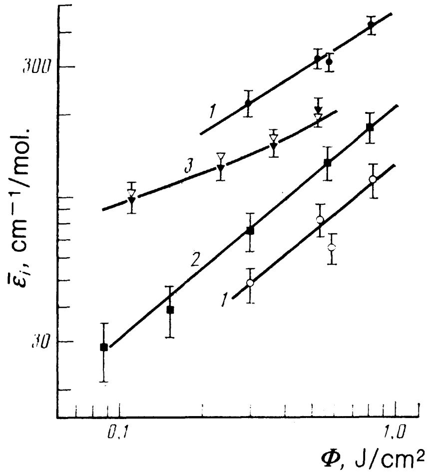

FIG. 1. Average energies $\bar{\varepsilon}_i$ in the modes ν_1 (1), ν_2 (2), and ν_3 (3) as functions of the energy density Φ in the CO_2 laser pulse (the filled-in points are for $\tau_d \leqslant 20$ nsec; the open points for $\tau_d = 4\,\mu$sec).

Figure 1 shows the average energies $\bar{\varepsilon}_i$ in the modes ν_2, ν_3, and ν_1 as functions of the energy density Φ in the CO_2 laser pulse at $p = 0.7$ Torr and for two values of the delay between the exciting and probing pulses: $\tau_d \leqslant 20$ nsec and $\tau_d = 4\,\mu$sec. An increase in Φ will lead to a growth of the energy in the modes. The slower growth of $\bar{\varepsilon}_3$ is due to the relatively large initial energy $\varepsilon_3^0 = 76\ cm^{-1}$ in the ν_3 mode at room temperature. It is noteworthy that the value of the

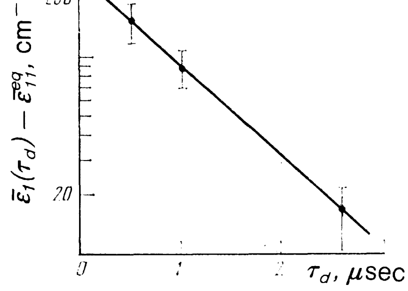

FIG. 2. Kinetics of relaxation to equilibrium in the ν_1 mode ($\Phi = 0.52$ J/cm^2, $p = 0.7$ Torr).

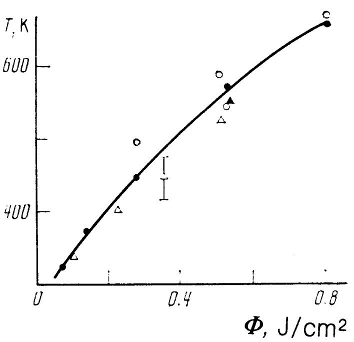

FIG. 3. Final vibrational temperature (after the establishment of vibrational equilibrium) as a function of the energy density Φ in the CO_2 laser pulse; from measurements in the modes: ○) ν_1; ●) ν_2; △) ν_3; ▲) ν_4.

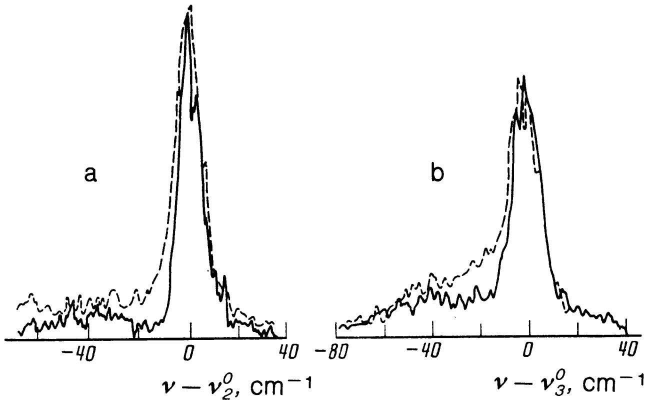

FIG. 4. Stokes spectra of the bands ν_2 (a) and ν_3 (b). The dashed lines are for $\Phi = 0.5$ J/cm^2; the solid lines for $\Phi = 0$ ($p = 1.4$ Torr, $\tau_d < 20$ nsec).

energy in the pumped resonant mode ν_1 is larger than the energies in the nonresonant modes ν_2 and ν_3. In addition, it is seen that when vibrational equilibrium is established as a result of collisions ($\tau_d = 4\,\mu$sec), the greatest change in energy also occurs in mode ν_1. Both these facts indicate a substantially nonequilibrium character of the vibrational distribution formed directly during the exciting IR pulse.

The kinetics of relations to equilibrium in the ν_1 mode is illustrated in Fig. 2, which shows a plot of the difference between $\bar{\varepsilon}_1(\tau_d)$ and the equilibrium value $\bar{\varepsilon}_1^{eq}$ for $\tau_d = 4\,\mu$sec as a function of τ_d. We see that the curve is well described by an exponential dependence with a time constant corresponding to $p\tau_d = 1.4 \pm 0.2\ \mu$sec·Torr. Thus it can be assumed that in any case the distribution of the energy over the modes at $\tau_d = 4\ \mu$sec is an equilibrium distribution. This conclusion is confirmed by Fig. 3, which shows the dependence on Φ of the corresponding temperatures in the various modes. The temperatures were calculated from the measured values of $\bar{\varepsilon}_i$ for $\tau_d = 4\,\mu$sec or for $p\tau_d = 2.8\ \mu$sec·Torr. It is seen that within the error of the measurements the temperature is the same for all the modes. We note that at this value of τ_d there is sufficient time for the absorbed energy to be redistributed only within the vibrational degrees of freedom, and the "heating" of the translational and rotational degrees of freedom can still be neglected, as follows from Ref. 30. Consequently, the values of the temperature given in Fig. 3 can be used to determine the total vibrational energy $\bar{\varepsilon}$ that the molecules have immediately after the end of the IR pulse. In particular, for $\Phi = 0.45$ J/cm^2 we have $\bar{\varepsilon} = 1280 \pm 60$ cm^{-1}.

Spectral measurements in the fundamental bands. Figure 4 shows the Raman scattering spectra in the Stokes region in the bands ν_2 and ν_3, as measured in the absence of IR excitation and immediately after an exciting pulse with $\Phi = 0.5$ J/cm^2. In the analogous spectra in the case of SF_6 and CF_2HCl (Refs. 26, 27, 30) a two-humped structure was clearly observed, which, as we pointed out above, permitted the conclusion that the molecules were divided into two groups, "hot" and "cold." In CF_3Br, the deformation of the spectra in the bands ν_2 and ν_3 (Fig. 4) during excitation turned out to be substantially smaller. Only an insignificant (about 2 cm^{-1} at half-height) broadening of the ν_2 band toward the red side and a somewhat larger shift of the ν_3 band are observed.

The main reason for the small deformation of the bands ν_2 and ν_3 is possibly the small value of the anharmonic shift. The anharmonic shift $\Delta\nu_i$ of the transition frequency from a state with energy E distributed equally over the modes can be expressed[19] in terms of the "average" anharmonicity constant $\bar{x}_i$

$$\Delta\nu_i=\bar{x}_i\frac{E}{\hbar\nu_i},\qquad \bar{x}_i=\frac{1}{s}\sum_{k=1}^{s}x_{ik}\frac{\nu_i}{\nu_k}(1+\delta_{ik}), \tag{9}$$

where s is the number of vibrational degrees of freedom. Using the values of x_{ik} from Ref. 35, we find that $\bar{x}_2 = -0.04$ cm^{-1} and $\bar{x}_3 = -0.3$ cm^{-1}, i.e., that the anharmonic shifts are actually expected to be small.

A different situation obtains for the mode ν_1. For this mode the intramode anharmonicity is $x_{11} = -3.4$ cm^{-1} and the average anharmonicity is $\bar{x}_1 = -5.6$ cm^{-1} (Ref. 35). Figure 5 shows the anti-Stokes spectrum of the band ν_1 for $\Phi = 0.45$ J/cm^2. We see that it is strongly broadened

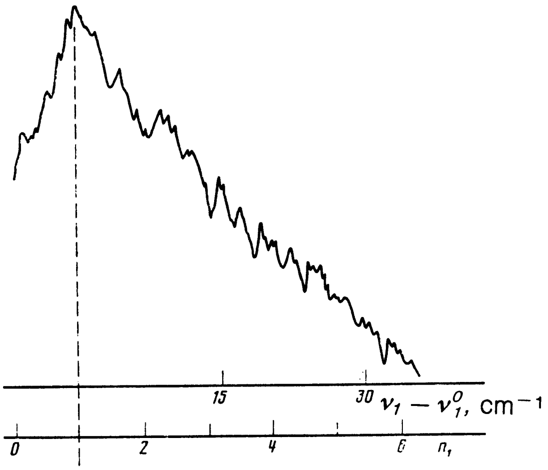

FIG. 5. Anti-Stokes spectrum of the ν_1 band during multiphoton excitation of CF_3Br. The positions of the vibrational transitions $|n_1\rangle \rightarrow |n_1 - 1\rangle$ are noted below ($p = 1.5$ Torr, $\tau_d < 20$ nsec, $\Phi = 0.45$ J/cm^2).

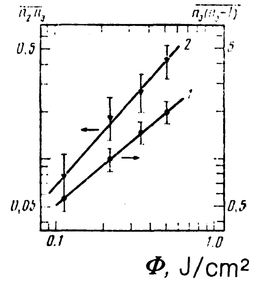

FIG. 6. Dependence of $\overline{n_3(n_3-1)}$ (1) and $\overline{n_2n_3}$ (2) on the energy density Φ in the CO_2 laser pulse ($p = 1.5$ Torr, $\tau_d \leqslant 20$ nsec).

toward the red. The spectrum in Fig. 5 will be used below in the interpretation of the experimental results.

Integrated measurements in the overtone and combination bands. The strongest of the overtone and combination bands in the Raman spectrum of the molecule CF_3Br are $2\nu_3$ and $\nu_2+\nu_3$; the latter is approximately one-eightieth as strong as the ν_2 band.[36] Preliminary experiments[31] on CF_3Br at various gas temperatures have demonstrated the legitimacy of using relations (2)–(5) for analysis of the Raman scattering signal from excited molecules. The calibration of the constants in these relations was done at room temperature.

In the experiment the integrated Raman signals were measured in the $2\nu_3$ and $\nu_2+\nu_3$ bands in the anti-Stokes region immediately after the exciting pulse of the CO_2 laser. From the measured signals we found the values of $\overline{n_3(n_3-1)}$ and $\overline{n_2n_3}$ corresponding to the vibrational distributions that had been created. These values are plotted in Fig. 6 as a function of Φ.

A joint analysis of the results shown in Figs. 1 and 6 immediately indicates that the vibrational distribution differs substantially from the Boltzmann distribution. In fact, if we assume a Boltzmann distribution, then, knowing the values of $\bar{n}_i$ from experiment (Fig. 1), we can easily calculate $\overline{[n_3(n_3-1)]_B}$ and $\overline{(n_2n_3)_B}$ from (4) and (5). For example, at $\Phi = 0.36$ J/cm² we have $\overline{[n_3(n_3-1)]_B} = 0.36$, whereas the experimental value (Fig. 6) is $\overline{n_3(n_3-1)} = 1.44$. Similarly, $\overline{(n_2n_3)_B} = 0.05$, whereas the experimental value for the combination band $\nu_2+\nu_3$ is $\overline{n_2n_3} = 0.27$

4. RECONSTRUCTION OF THE VIBRATIONAL DISTRIBUTION FROM EXPERIMENTAL DATA

As we have seen, the experimental data definitely show that the vibrational distribution arising during IR multiphoton excitation of CF_3Br is, on the whole, substantially nonequilibrium. The presence of excitation of the ν_2 and ν_3 modes, which are not in resonance with the IR radiation, makes it natural to assume that part of the CF_3Br molecules are located in the mixing region, where the energy is distributed over the modes in an equilibrium manner. Let us denote the fraction of the molecules that fall in this category by q and their average vibrational energy by $\bar{\varepsilon}_q$. We note that the presence of an equilibrium distribution over the modes in the upper group of molecules in each relatively narrow energy interval generally does not mean that these molecules have a Boltzmann energy distribution. However, if the distribution is sufficiently narrow, then (see the diffusion in Sec. 2) we can for simplicity use the Boltzmann formulas (4) and (5) for the second moments of the distribution, where we replace $\bar{n}_2$ and $\bar{n}_3$ by $\bar{n}_i^* = [\exp(\hbar\nu_i/kT_q)-1]^{-1}$, with a temperature T_q that is found from the energy $\bar{\varepsilon}_q$. We further assume that the distribution in the ν_2 and ν_3 modes for the remaining molecules corresponds to the initial room temperature.

Under the assumptions made, the quantities q and $\bar{\varepsilon}_q$ should satisfy the following equations:

$$\bar{n}_2=(1-q)\bar{n}_2{}^0+q\bar{n}_2{}^*, \tag{10}$$

$$\bar{n}_3=(1-q)\bar{n}_3{}^0+q\bar{n}_3{}^*, \tag{11}$$

$$\overline{n_3(n_3-1)}=(1-q)\cdot 2(\bar{n}_3{}^0)^2+q\cdot 2(\bar{n}_3{}^*)^2, \tag{12}$$

$$\overline{n_2n_3}=(1-q)\bar{n}_2{}^0\bar{n}_3{}^0+q\bar{n}_2{}^*\bar{n}_3{}^*, \tag{13}$$

in which all the quantities of the left-hand sides are known from experiment. The quantities $\bar{n}_i^0$ correspond to room temperature and are also known. The quantities q and $\bar{\varepsilon}_q$ can be determined from measurements in the ν_3 band and the $2\nu_3$ overtone band, i.e., from the pair of equations (11) and (12), and also independently from measurements in the bands ν_2, ν_3, and $\nu_2+\nu_3$, i.e., from equations (10), (11), and (13). The dependence of q and $\bar{\varepsilon}_q$ on Φ is shown in Fig. 7. We see that both versions of the calculation of q and $\bar{\varepsilon}_q$ give the same results to within the experimental errors. The first version of the calculation is expected to be more reliable, since the experimental error in the measurements of the signals in the $2\nu_3$ band is smaller than for measurements in the $\nu_2+\nu_3$ band (see Fig. 6). Therefore, in what follows we use the values obtained from the data for $2\nu_3$. In particular, for $\Phi = 0.45$ J/cm² we have $q \approx 0.09$ and $\bar{\varepsilon}_q \approx 8300$ cm^{-1}.

Up till now we have used the results of measurements relating only to the nonresonant modes ν_2 and ν_3. Let us now consider the distribution of energy in the IR-pumped mode ν_1. It follows from the experimental results that the energy $\bar{\varepsilon}_1$ in the ν_1 mode is substantially higher than the energy in the ν_2 and ν_3 modes. Assuming as before that the upper group of

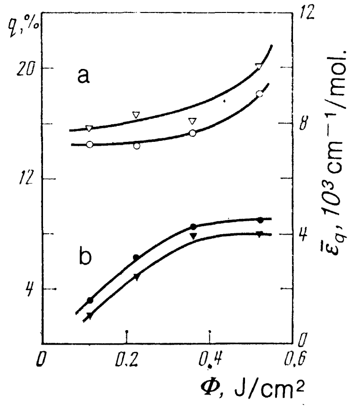

FIG. 7. Fraction q of the molecules in the upper ensemble (a) and their average energy $\bar{\varepsilon}_q$ (b) versus the energy density Φ in the CO_2 laser pulse. The results of two different versions of determining q and $\bar{\varepsilon}_q$ from the experimental data are shown: the circles are obtained from the data on ν_3 and $2\nu_3$; the triangles from the data on ν_2,ν_3, and $\nu_2+\nu_3$.

molecules, whose total average energy $\bar{\varepsilon}_q$ we have just determined, has an equilibrium distribution over the modes, we can find the "equilibrium" component $\bar{\varepsilon}_1^*$ of the energy in the ν_1 mode. In particular, for $\Phi = 0.45$ J/cm^2 we find $\bar{\varepsilon}_1 = 290$ cm^{-1} and $q\bar{\varepsilon}_1^* = 68$ cm^{-1}; consequently, there is an excess energy $\delta\bar{\varepsilon}_1 = \bar{\varepsilon}_1 - q\bar{\varepsilon}_1^* = 222$ cm^{-1}. It is natural to assume that this energy belongs to molecules which have not reached the mixing region. This assumption finds confirmation in the spectrum of the anti-Stokes ν_1 band (see Fig. 5) for $\Phi = 0.45$ J/cm^2. The average anharmonicity (defined in Sec. 3) of the ν_1 mode is $\bar{x}_1 = -5.6$ cm^{-1} (Ref. 35). This means that the upper group of molecules, with an average of 8300 cm^{-1}, should give a signal at frequencies shifted with respect to the frequency of the 1–0 transition by 35–40 cm^{-1}. We see, however, that a significant part of the band occurs at smaller shifts. One can attempt to process the spectrum shown in Fig. 5 in order to determine the form of the distribution at the lower levels of the ν_1 mode. The intramode anharmonicity of ν_1 is $x_{11} = -3.4$ cm^{-1} (Ref. 35). Writing the intensities I_{n_1} at the frequencies $\nu_1 + 2(n_1 - 1)x_{11}$ in the form

$$I_{n_1} \infty \sigma_{n_1, n_1-1} C_{n_1} = n_1 \sigma_{10} C_{n_1}, \qquad (14)$$

where the C_{n_1} are the populations of the levels of the ν_1 mode, one can obtain a rough estimate of the distribution. The result is conveniently represented in the form of a plot of $\ln(n_1 I_1/I_{n_1})$ versus n_1 (see Fig. 8), since for the Boltzmann distributions this should be a straight line. We see that to good accuracy for $1 \leqslant n_1 \leqslant 5$, the dependence is actually linear, i.e., the population falls off exponentially with the number of the level, and therefore, to within the experimental error, we can assume a Boltzmann distribution over the lower levels of the ν_1 mode. From the slope of the line in Fig. 8 we can find the corresponding temperature at $\Phi = 0.45$ J/cm^2: 1945 ± 70 K. In an analogous way, the processed Stokes spectrum of the ν_1 band also gives an exponential decay of the populations of the states with $1 \leqslant n_1 \leqslant 5$. The corresponding temperature, $T_1 = 1900 \pm 90$ K, agrees with the temperature determined from the anti-Stokes spectrum to within the experimental errors.

It turns out, however, that the temperature T_1 thus found cannot be associated with the entire fraction $1 - q$ of the molecules in the lower group. In fact, denoting by r the fraction of the molecules having temperature T_1, we obtain the relation

$$\delta\bar{\varepsilon}_1 = r\hbar\nu_1[\exp(\hbar\nu_1/kT_1) - 1]^{-1},$$

whence for $\Phi = 0.45$ J/cm^2 we obtain $r = 0.26$. An appreciable fraction at molecules, $1 - q - r = 0.65$, belongs neither to the upper ensemble nor to that part of the distribution over the lower levels which is described by the temperature T_1. This fraction of the molecules is found in the ground state with respect to the ν_1 mode. Altogether, the fraction of all the molecules that is in the ground state with respect to the ν_1 mode is $r[1 - \exp(-\hbar\nu_1/kT_1)] + 0.65 = 0.8$

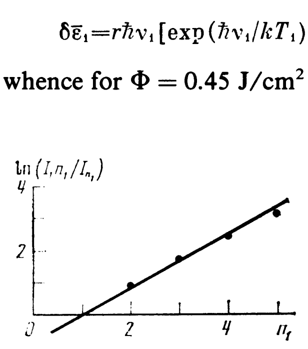

FIG. 8. Relative populations of the levels of the ν_1 mode as determined from the anti-Stokes spectrum shown in Fig. 5.

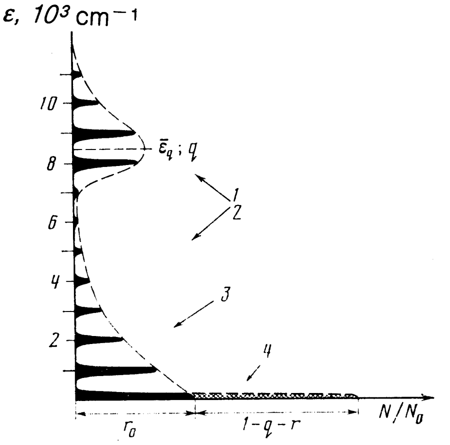

FIG. 9. Qualitative picture of the vibrational distribution in CF_3Br as a result of multiphoton excitation: 1) "hot" molecules; 2) "cold" molecules; 3) ν_1-excited ensemble; 4) unexcited molecules; $r_0 = r[1 - \exp(-\hbar\nu_1/kT_1)]$; the other notation is given in the text.

In the experiment, the energies in the three modes ν_4, ν_5, and ν_6 of CF_3Br were not measured to sufficient accuracy, since the intensities of the corresponding Raman-scattering bands are small. We can make a simple check by calculating these energies using formulas of type (10) and (11), viz., $\bar{n}_i = (1 - q)\bar{n}_i^0 + q\bar{n}_i^*$, and then comparing the total energy with that measured under conditions such that the vibrational degrees of freedom are known to be in equilibrium, i.e., with a relatively long delay of the probe pulse with respect to the exciting pulse (see Sec. 3). As a result, we obtain $\bar{\varepsilon} = 1298$ cm^{-1} for $\Phi = 0.45$ J/cm^2, in agreement with the value measured in Sec. 3 for the same energy density in the IR pulse.

The reconstructed vibrational distribution is illustrated in Fig. 9. The distribution over vibrational energy in the upper, "hot" ensemble remains incompletely determined. According to the existing ideas about multiphoton excitation in the mode-mixing region (in the so-called vibrational quasicontinuum),[19,21] it should, as a rule, be narrower than the Boltzmann distribution with the same value of the average energy $\bar{\varepsilon}_q$. In calculating q and $\bar{\varepsilon}_q$ we have for convenience used the formulas for the Boltzmann distribution. By a simple exhaustion of the levels, we also carried out numerical calculations in which we assumed the distribution in the upper ensemble to be very narrow, with a width of the order of 100 cm^{-1}. Within the experimental error, these calculations gave the same values of q and $\bar{\varepsilon}_q$.

In the lower, "cold" ensemble, the temperature of the nonresonant modes remained equal to room temperature. The temperature of the resonant mode for a certain fraction r of the molecules can be substantially higher (around 1900 K for $\Phi = 0.45$ J/cm^2).

5. DISCUSSION

The main physical results of this study are:

1) As in the case of the molecules SF_6, CF_3I, and CF_2HCl (Refs. 22, 26, 29, 30), it is found that when IR laser radiation acts on one of the vibrational modes of the CF_3Br molecule (in this case the ν_1 mode), the other modes are also excited. The results of the experiment can be explained quantitatively by assuming the presence of a group of molecules with an equilibrium distribution of energy over all the vibrational modes.

2) The data shown in Fig. 7 imply the presence of a vibrational energy threshold below which mixing is simply not observed in the experiment ($\bar{\varepsilon}_q$ approaches a stationary value as Φ decreases). This energy, which we shall call the mixing threshold, amounts to $\varepsilon_q^{\min} = 7500 \pm 300\ \mathrm{cm}^{-1}$.

3) The experiment has shown the presence of an excess energy in the IR-pumped ν_1 mode of CF_3Br. This excess energy is distributed among molecules excited below the mixing threshold. These molecules have nearly a Boltzmann distribution over the excited levels of the ν_1 mode.

Point 1 apparently needs no additional commentary. As to point 2, it must first be noted that the approach of $\bar{\varepsilon}_q(\Phi)$ to a stationary value on decrease of Φ was also observed previously[26] for the molecules SF_6 and CF_3I. Such behavior in and of itself is of great interest for understanding the process of multiphoton excitation. It is natural to assume (see also Ref. 26) that upon the transition through the mixing threshold the cross section for multiphoton excitation falls off because of the decrease in the amount of energy in the pumped mode due to its the redistribution among the other modes. However, until the excitation channels of CF_3Br at the lower transitions are identified, this assumption cannot be quantitatively confirmed.

It is natural to identify the threshold $\varepsilon_q^{\min}$ found in this study as the energy above which the modes in the molecule itself are mixed by the anharmonic interaction, or, in analogy with classical systems, the energy above which a stochastic vibrational motion occurs. The values $\varepsilon_q^{\min} = 3900 \pm 600\ \mathrm{cm}^{-1}$ and $6000 \pm 500\ \mathrm{cm}^{-1}$ found previously[26] for SF_6 and CF_3I, respectively, have been given a satisfactory quantitative explanation of the basis of the pattern of intermode resonances for these molecules.[26,8] The closest three-frequency resonances for the CF_3Br molecule are the following:

$$2\nu_5-\nu_1\approx 10\,\mathrm{cm}^{-1};\quad \nu_2+\nu_3-\nu_1\approx 28\,\mathrm{cm}^{-1};\quad \nu_2-2\nu_3\approx 60\ \mathrm{cm}^{-1}.$$

Chirikov's empirical criterion of stochasticity[1] requires that the intermode anharmonic interaction be rather large for overlap of the intermode resonances. In our experiment the intensity of the $2\nu_3$ band at the energies $\varepsilon_q^{\min}$ was negligible compared to the intensity of the ν_2 band, while the intensity of the $\nu_2+\nu_3$ band was comparable to that part of the intensity of the ν_1 band which corresponds to the upper ensemble. From these data it is difficult to judge unambiguously whether the three-frequency resonances provide the mixing (this can be shown only by detailed calculations, which are complicated because of insufficient information on the intermode anharmonicity constants). However, the small mixing of ν_2 and $2\nu_3$ and the absence of good three-frequency resonances for the ν_4 and ν_6 modes make it realistic to assume that the higher-order resonances play an important role in the mixing.

Also deserving of discussion is the question of whether we have actually observed the effect of a mixing of the modes in the molecules itself or whether the cause of the excitation of all the modes is that the IR laser radiation induces resonance transitions to the many high-order difference bands. The mechanisms of activation of the difference bands are essentially the same as those that lead to mixing. In principle, a situation is possible in which the intermode anharmonicity is still too small for mixing but is large enough that the strengths of the high-order difference bands are sufficient for saturation in a strong IR laser field, and that this occurs at the energy $\varepsilon_q^{\min}$. There is one objection, however. In this case the transitions in the resonant mode remain energywise highly favored, and therefore, if they occur up to the energy $\varepsilon_q^{\min}$ it is hard to assume that they will not continue to occur after. Favored transitions in the resonant mode are absent only in the case when the true vibrational states of the molecule are a random mixture of many harmonic states,[7,8,21] and this corresponds precisely to mixing. It seems to us that this argument is rather convincing evidence that the experiment detected mixing as a property of the molecule itself.

Point 3 requires two comments. The presence of excess energy resonant mode has been observed previously[37] in an experiment on the CARS probing of the distribution during multiphoton excitation of SF_6. In that study, as in this, a Boltzmann distribution over the levels of the resonant mode was found for part of the molecules. We note that the Boltzmann distribution is a well-known result of a model problem, viz., the incoherent radiative excitation of the harmonic oscillator.[38] Just how much bearing this simple model has on the extremely complex process (including cascade and multiphoton transitions[21]) of molecular excitation in an IR field in the region of the lower levels is the subject of further theoretical studies and generalizations. We also call attention to a curious fact: Figure 9 shows the vibrational distribution for one of the energy densities, $\Phi = 0.45\ \mathrm{J/cm}^2$. If the energy of the upper ensemble is used to find its effective temperature, it turns out that it agrees, within the experimental error, with the temperature of the molecules found at the lower levels of the ν_1 mode. Whether this coincidence is accidental or whether it has some physical significance will be shown by further studies.

In conclusion, let us summarize the results from the standpoint of the dynamical development of the process of multiphoton excitation. Molecules are gradually drawn into the process from their initial states, absorb about 7 quanta at transitions in the resonant mode, in the last step exchanging energy among all the modes, and then their excitation slows down. With increasing energy density of the laser pulse, there is an increase in both the fraction of the molecules involved in the process and their energy in the upper ensemble. This qualitative picture is in good agreement with experiment.

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