

Infrared photodissociation spectroscopy of vibrationally overexcited molecules

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A new universal method is proposed for observing the infrared spectra of molecules that are vibrationally overexcited to states above the dissociation limit. The method is based on the measurement of the small increments in dissociation yield that occur when vibrationally excited molecules are exposed to a measuring infrared laser pulse, and has been used to investigate $(\text{CF}_3)_3\text{CI}$ molecules. The dissociation yield of these molecules was measured by resonant multiphoton ionization of the atoms by a UV dye-laser pulse. The Lorentz shape of the spectrum of vibrational transitions in highly excited molecules (half-width $\gamma = 9 \text{ cm}^{-1}$) was obtained experimentally for the first time. Analysis of the infrared spectrum shows that its broadening is largely due to intramolecular energy relaxation from the excited mode with a time constant $\tau_{\text{IVR}} = 0.3 \times 10^{-12} \text{ s}$.

1. INTRODUCTION

The infrared spectroscopy of polyatomic molecules with vibrational energies on the order of the dissociation energy is of considerable fundamental and practical interest.¹ There are only a few published experiments^{2–7} in which the infrared absorption spectrum of vibrationally highly excited polyatomic molecules was measured. The interpretation of most of them is complicated by considerable inhomogeneous broadening. Methods capable of solving the problem of vibrational inhomogeneous broadening of the infrared spectra of highly excited molecules are proposed in Refs. 6–7. The most direct method⁶ involves the preparation of vibrationally highly excited molecules, using internal molecular conversion, but is restricted to a narrow class of molecules in which radiationless $S_1 \rightarrow S_0$ transitions can take place.

In our previous letter,⁸ we showed that large molecules such as $(\text{CF}_3)_3\text{CI}$ could be highly overexcited ($E \gtrsim 2D$) above the dissociation limit during multiphoton infrared excitation because the lifetimes of such overexcited molecules ($\sim 10^{-3} \text{ s}$; Refs. 8, 10, and 11) could be significantly longer than the duration of the laser pump pulse ($\sim 10^{-7} \text{ s}$). In this paper, we report measurements of the infrared absorption spectrum of $(\text{CF}_3)_3\text{CI}$ molecules with twofold overexcitation above the dissociation limit. The measurements were carried out by a new universal photodissociation method of recording infrared spectra of highly excited molecules. This method is capable of suppressing almost completely the contribution of inhomogeneous broadening to the measured infrared spectrum. It has enabled us, for the first time, to measure the homogeneous Lorentzian infrared spectrum of $(\text{CF}_3)_3\text{CI}$. It was found to have a half-width $\gamma = 9 \pm 1 \text{ cm}^{-1}$, which corresponds to an intramolecular vibrational relaxation time constant $\tau_{\text{IVR}} \approx 3 \times 10^{-3} \text{ s}$.

2. PHOTODISSOCIATION METHOD OF MEASURING THE INFRARED SPECTRA OF HIGHLY EXCITED POLYATOMIC MOLECULES

The method we have employed consists of measuring the spectral dependence of the small increments $\delta\beta$ in dissociation yield when a weak infrared probe pulse is applied to

molecules that have first been vibrationally excited. Let us demonstrate the advantages of this experimental procedure as compared with conventional measurements of absorption δE (i.e., as compared with experiments such as infrared-infrared resonance^{3,4}).

Let us suppose that an ensemble of vibrationally highly excited molecules has been prepared by some method (e.g., by multiphoton infrared absorption). A proportion β of the molecules that have become overexcited above the dissociation limit will decay in a time t_0 :

$$\beta = \sum_n f_n [1 - \exp(-k_n t_0)], \quad (1)$$

where f_n and k_n are, respectively, the number and rate of decay of molecules with energy $n\hbar\omega_L$, and ω_L is the frequency of the laser radiation used to produce the preliminary excitation of the molecules. We now apply a short ($\tau_{\text{IR}} \ll t_0$) infrared probe pulse to the distribution f_n , and again determine the dissociation yield at time t_0 . The increase in the dissociation yield results from the change in the distribution f_n due to the absorption of probe radiation by the molecules:

$$\delta\beta = \sum_n \delta f_n [1 - \exp(-k_n t_0)]. \quad (2)$$

The quantity δf_n can readily be found to first order in the energy density $\delta\Phi$ of the probe radiation from the kinetic equations⁹ describing the excitation of molecules in the quasicontinuum. Neglecting the decay of the molecules during the infrared probe pulse, we find that

$$\delta f_n = \frac{\delta\Phi}{\hbar\omega_L} [-f_n(\sigma_n^+ + \sigma_n^-) + f_{n-1}\sigma_{n-1}^+ + f_{n+1}\sigma_{n+1}^-], \quad (3)$$

where σ_n^\pm is the cross section for the absorption and stimulated emission by molecules of energy $n\hbar\omega_L$. Since it follows from the principle of detailed balance that

$$\sigma_n^+ \rho_n = \sigma_{n+1}^- \rho_{n+1},$$

where ρ_n is the density of the vibrational states, we obtain

$$\begin{aligned} \hbar\omega_L \frac{\delta\beta}{\delta\Phi} &= \sum_n \sigma_n^+ F_n^{\text{sp}} \\ &= \sum_n \sigma_n^+ \left(f_n - f_{n+1} \frac{\rho_n}{\rho_{n+1}} \right) [\exp(-k_n t_0) - \exp(-k_{n+1} t_0)]. \end{aligned} \quad (4)$$

For comparison, we reproduce the expression for the absorbed energy:

$$\frac{\delta E}{\delta \Phi} = \sum_n \sigma_n^+ F_n^{\delta E} = \sum_n \sigma_n^+ \left(f_n - f_{n+1} \frac{\rho_n}{\rho_{n+1}} \right). \quad (5)$$

The functions $F_n^{\delta \beta}$ and $F_n^{\delta E}$ indicate the contribution of molecules of energy $n \hbar \omega_L$ to the measured quantity, i.e., $\delta \beta$ or δE . It follows from (5) that all the molecules in the ensemble that participate in the radiation absorption process contribute to the energy absorbed from the infrared probe field.

The question is: what is the characteristic width of the vibrational distributions of highly excited molecules? It is shown in Ref. 8 that the half-width of the distribution of $(CF_3)_3CI$ molecules that are doubly overexcited above the dissociation limit ($D = 18\,000\text{ cm}^{-1}$) by multiphoton infrared absorption is comparable with the half-width of the Boltzmann distribution at the same average energy, and amounts to about $10\,000\text{ cm}^{-1}$. Since the spectra of molecules having different energy are shifted relative to one another by the anharmonicity of the oscillations, measurements of absorption energy as a function of wavelength yield a spectrum that is subject to considerable inhomogeneous broadening. Actually, when the anharmonic shift is typically $\sim 1\text{ cm}^{-1}$, we find that the inhomogeneous broadening is about $\pm 10\text{ cm}$ per 1000 cm^{-1} of vibrational energy.

The expression for $\delta \beta / \delta \Phi$, given by (4), shows that, in contrast to the average absorbed energy δE , not all the molecules in the ensemble contribute to the increase in the dissociation yield. The function $F_n^{\delta \beta}$ differs from $F_n^{\delta E}$ by the presence of the additional factor $\exp(-k_n t_0) - \exp(-k_{n+1} t_0)$, describing the increase in the decay probability of a molecule at time t_0 as a result of the absorption of an infrared photon. This factor differs from zero only in a certain energy interval in which $k_n t_0 \sim 1$ holds. This result is of clear qualitative significance. Molecules for which $k_n t_0 \ll 1$ and $k_{n+1} t_0 \ll 1$ hold do not decay even on absorption of an infrared photon. Molecules for which $k_n t_0 \gg 1$ and $k_{n+1} t_0 \gg 1$ hold decay even in the absence of the infrared radiation. Consequently, the presence of the probe field leads to an increase in the decay probability, but only for those molecules for which we have $k_n t_0 \sim 1$. Because the growth rate k_n is high, the energy interval in which $\exp(-k_n t_0) - \exp(-k_{n+1} t_0)$ and, consequently, $F_n^{\delta \beta}$, as well, are different from zero is quite narrow. For example, for the $(CF_3)_3CI$ molecules, the condition $k_n t_0 \sim 1$ is satisfied for $t_0 = 10^{-5}$ when $n \hbar \omega_L = 39\,000 \pm 2500\text{ cm}^{-1}$ holds (Ref. 8), which is narrower by a factor of four than the Boltzmann distribution with mean energy $n \hbar \omega_L$. The inhomogeneous broadening during photodissociation measurements of the infrared spectra is smaller by a similar factor. The photodissociation method is thus seen to have significant advantages in infrared spectroscopy of highly excited molecules as compared with conventional measurements of absorbed energy.

Recalling that $F_n^{\delta \beta}$ as a function of n has a well-defined resonance, and assuming that σ_n^+ does not change significantly in the neighborhood of n^* , we find that

$$\hbar \omega_L \delta \beta / \delta \Phi = \sigma_{n^*}^+ (\omega_L) A(n^*), \quad (6)$$

$$A(n^*) = \sum_{n \sim n^*} F_n^{\delta \beta}. \quad (7)$$

3. EXPERIMENTAL SETUP

The experimental setup consisted of the following principal components: (1) a vacuum chamber with the source of the pulsed molecular beam, (2) two pulsed CO_2 lasers working at atmospheric pressure, (3) a dye laser pumped by an XeCl excimer laser, (4) the laser locking system and measuring equipment, and (5) the photoion collection and measurement system.

The vacuum chamber was equipped with BaF_2 and quartz windows for infrared and ultraviolet radiation, and was pumped down to 10^{-6} torr. The mixture $(CF_3)_3CI:Ar:He = 3:1:10$ at a total pressure of 300 torr was then introduced into the pulsed nozzle that served as a molecular beam source. The molecular beam pulses were produced by a skimmer with an aperture of 0.7 mm, located at 5 cm from the nozzle.

Two infrared beams generated by the pulsed CO_2 lasers propagated practically collinearly with the molecular beam, but in the opposite direction (Fig. 1). The lateral size of the two beams ($0.8 \times 0.8\text{ cm}$) was greater than the size of the molecular beam. The frequency of the first infrared field was $\omega_1 = 952.9\text{ cm}^{-1}$ ($10P\,10$ line), the energy density was $\Phi_1 = 0.9\text{ J/cm}^2$, and the pulse length was $\tau_{IR} \lesssim 1.5\text{ }\mu\text{s}$. This laser field produced the preliminary vibrational excitation of the $(CF_3)_3CI$ molecules by multiphoton infrared absorption.

The frequency of the second infrared field was varied in the range $866.1\text{--}966.3\text{ cm}^{-1}$ (the $10P\,112\text{--}10P\,32$ lines of the $C^{13}O_2^{16}$ laser and the $10P\,44\text{--}10R\,6$ lines of the $C^{12}O_2^{16}$ laser). The energy density could be up to 1 J/cm^2 , and the pulse length was $\lesssim 1.5\text{ }\mu\text{s}$. The energy of the second infrared field was varied by CaF_2 attenuators. The lateral energy density distribution in this radiation was measured for each CO_2 laser line. This laser beam served as the infrared probe field in measurements of the spectrum of vibrationally highly excited $(CF_3)_3CI$ molecules.

At a distance of 10 cm from the skimmer (Fig. 1), the molecular beam crossed a third laser beam in the form of the second harmonic of a dye laser (rhodamine 6G) pumped by an XeCl laser. The energy carried by the frequency-tunable ultraviolet pulse was $120\text{ }\mu\text{J}$. The pulse length is 8 ns and its spectral width was 1 cm^{-1} . It was focused at the center of the molecular beam by a quartz lens ($f = 7\text{ cm}$). The second harmonic of the dye laser was used in photoionization mea-

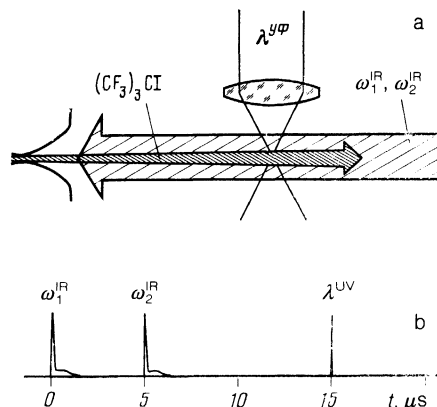


FIG. 1. Disposition in space (a) and the time sequence (b) of laser pulses used in the experiment.

measurements of either the concentration of the decay products of the original molecules, i.e., iodine atoms in the ground state ($5p^2P_{3/2}$), or the concentration of undecayed molecules. In the former case, the ultraviolet radiation was tuned to the two-photon resonance $5p^2P_{3/2}-6p^4P_{3/2}$ ($\lambda = 2982.3 \text{ \AA}$) of three-photon ionization of unexcited atoms of iodine. In the latter case, it was tuned to the two-photon resonance $5p^2P_{1/2}-7p^2D_{5/2}$ ($\lambda = 2959.0 \text{ \AA}$) of metastable iodine atoms produced by ultraviolet photolysis of the undecayed molecules by the same ultraviolet radiation. Photoionization diagnostics of the decaying iodides was described in detail in Refs. 8 and 11.

Ions produced during the photoionization process were accelerated by a constant electric field ($E = 60 \text{ V/cm}$, $l = 1 \text{ cm}$) perpendicular to the molecular and ultraviolet beams and, after crossing a 5-cm field-free region, were admitted to the VEV-4 detector. The signal from the latter was first amplified and then received by the V9-5 stroboscopic voltmeter, adjusted to respond to I^+ ions with $me = 127$.

4. EXPERIMENTAL RESULTS

Figure 2 shows the measured dissociation yield β of $(CF_3)_3CI$ as a function of the energy density Φ_2 of the infrared probe field for three different frequencies: $\omega_2 = 902.4$, 925.0 , and 933.0 cm^{-1} . The parameters of the first infrared beam ($\Phi_1 = 0.9 \text{ J/cm}^2$, $\omega_1 = 952.9 \text{ cm}^{-1}$), used to produce the preliminary vibrational excitation of the molecules, and the parameters of the ultraviolet pulse ($\lambda = 2982.3 \text{ \AA}$, $\Phi_{UV} = 10\hbar\omega_{UV}/\sigma_{UV}$), used in photoionization measurements of the dissociation yield, are held constant. For small Φ_2 , the experimental points shown in the figure can be fitted satisfactorily with a straight line whose slope is related to the absorption cross section of the highly excited molecules by (4).

Figure 3 shows the frequency dependence of $\hbar\omega_2\partial\beta/\partial\Phi_2$, deduced from the experimental function $\beta(\Phi_1, \Phi_2)$ obtained for different frequencies of the infrared probe field. Curve 1 in Fig. 3 is the Lorentzian $\text{const}/[\gamma^2 + (\omega_2 - \omega_0)^2]$ with $\gamma = 9 \text{ cm}^{-1}$ and $\omega_0 = 942 \text{ cm}^{-1}$. It is clear from this figure that, in the wide spectral range $-5.3\gamma < \omega_2 - \omega_0 < 3.6\gamma$, the experimental points can be described by a Lorentzian.

To obtain a more complete interpretation of the spectrum obtained in this way, we carried out auxiliary measurements of the concentration $N(t)$ of undecayed molecules as a function of the delay between the infrared pulse producing the preliminary vibrational excitation and the infrared pulse used in the photoionization measurements (infrared probe pulse absent). These measurements are shown in Fig. 4 and suggest that the data obtained by detecting the decay products ($\lambda_{UV} = 298.3 \text{ \AA}$) and the undecayed molecules ($\lambda_{UV} = 2959.0 \text{ \AA}$) are in good agreement.

5. ANALYSIS OF THE INFRARED PHOTODISSOCIATION SPECTRUM

Analysis of the spectrum shown in Fig. 3 can be reduced to three mutually related questions. First, what is the energy corresponding to the photodissociation spectrum, i.e., what is the value of n^* for which the resonance function $F_n^{\alpha\beta}$ reaches its maximum value? Second, what is the value of the proportionality constant between $\partial\beta/\partial\Phi_2$ and σ_n^+ [see (6)

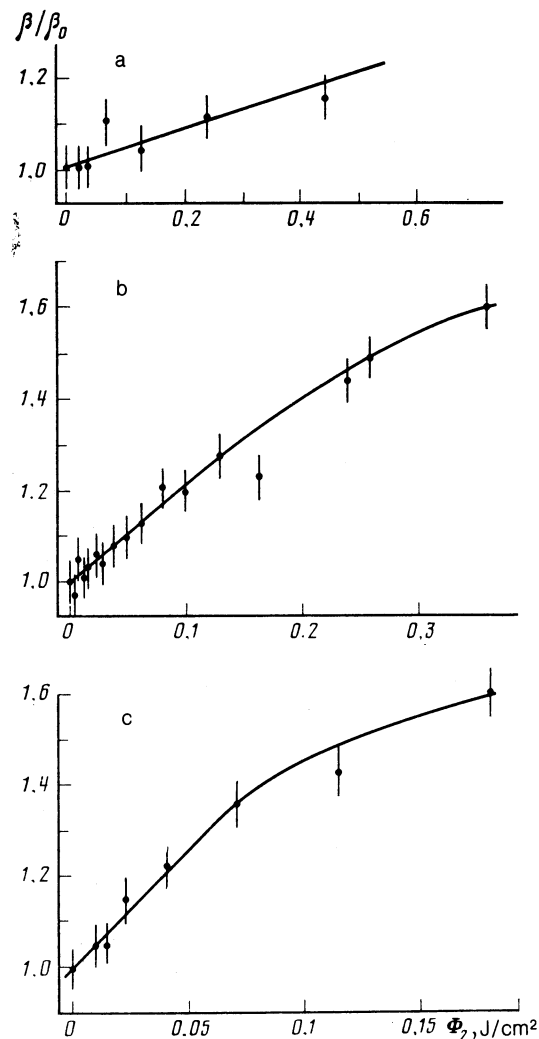


FIG. 2. Typical dissociation yields of $(CF_3)_3CI$ as functions of the energy density of infrared probe radiation at frequencies $\omega_2 = 900.4$ (a), 925.0 (b), and 933.0 (c) cm^{-1} .

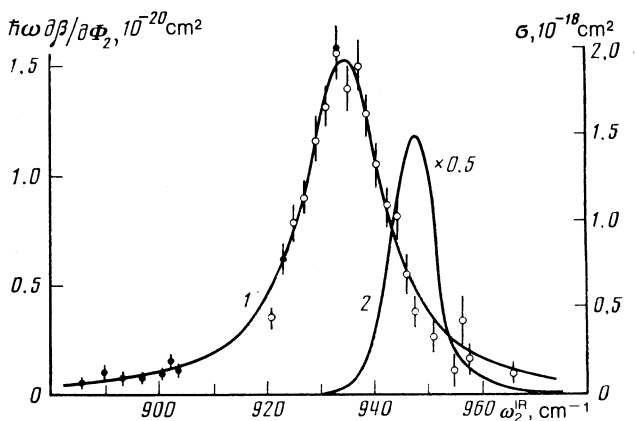


FIG. 3. The infrared spectrum of $(CF_3)_3CI$ molecules with $E = 35\,000 \pm 2500 \text{ cm}^{-1}$ ($D = 18\,000 \text{ cm}^{-1}$); \circ —probe CO_2 laser using $C^{12}O_2$; \bullet —probe CO_2 laser using $C^{13}O_2$. 1— $\text{const}/[\gamma^2 + (\omega - \omega_0)^2]$, where $\omega_0 = 932 \text{ cm}^{-1}$, $\gamma = 9 \text{ cm}^{-1}$; 2—infrared absorption spectrum at room temperature. The spectrum is normalized (right-hand scale) as described in Sec. 5.

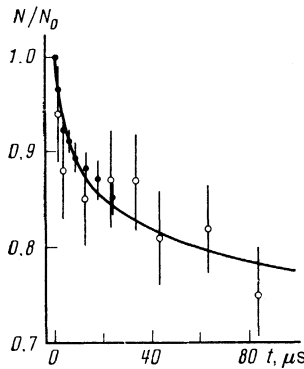


FIG. 4. Fraction of undecayed molecules as a function of the delay between the infrared pulse producing the preliminary vibrational excitation and the ultraviolet pulse producing the diagnostic photoionization (infrared probe radiation absent); ●— $\lambda_{UV} = 2982.3 \text{ \AA}$ (detection of decay products, i.e., iodine atoms in the ground state); ○— $\lambda_{UV} = 2959.0 \text{ \AA}$ (detection of undecayed molecules); solid curve shows calculated results.

and (7)]? Third, what is the contribution of inhomogeneous broadening. (This question is related to the width of the resonance function $F_n^{\alpha\beta}$.) To answer all three questions, we must find $F_n^{\alpha\nu}$.

Calculations of $F_n^{\alpha\beta}$ based on (4) demand a knowledge of the decay rate k_n and of the distribution function f_n in the region of the maximum of $\exp(-k_n t_0) - \exp(-k_{n+1} t_0)$ ($t_0 = 10 \mu\text{s}$). The former quantity was calculated and confirmed experimentally in Ref. 8 for $(\text{CF}_3)_3\text{CI}$; f_n can be estimated from the data on decay kinetics, shown in Fig. 4. Actually, $N(t)$ is related to the distribution $f_n^{(0)}$ produced by the infrared pump pulse:

$$N(t) = \sum_i f_n^{(0)} \exp(-k_n t). \quad (8)$$

The distribution $f_n^{(0)}$ is, in turn, related to the required distribution f_n as follows:

$$f_n = f_n^{(0)} \exp(-k_n t_1),$$

where $t_1 = 5 \mu\text{s}$ is the delay between the infrared pulses.

Before we proceed to the direct determination of $N(t)$, let us find the energy range of molecules that contribute to the dissociation yield during the time of observation. It is clear that molecules for which $k_n \lesssim 10^3 \text{ s}^{-1}$ remain practically intact during the time of observation ($80 \mu\text{s}$). On the other hand, the experimental function shows that the highest decay rates among the ensemble as a whole do not exceed 10^5 s^{-1} . We may therefore conclude that a negligible fraction of molecule in the ensemble has decay rates $k_n \gtrsim 10^6 \text{ s}^{-1}$. Decay constants in the range $10^3 < k_n < 10^6 \text{ s}^{-1}$ correspond to energies in the range $31\,000 \text{ cm}^{-1} < n\hbar\omega_L < 43\,000 \text{ cm}^{-1}$ (Ref. 8). It is precisely in this range that we shall take $f_n^{(0)}$.

The function $N(t)$ was determined as follows. We assumed that the populations of levels with $n = 31-36$, $36-39$, and $40-43$ were, respectively, n_1 , n_2 , and n_3 . The chosen energy ranges correspond to monomolecular decay rates of $(\text{CF}_3)_3\text{CI}$, differing by approximately an order of magnitude. The characteristic decay times of molecules in the first, second, and third groups are, respectively, 200, 20, and $2 \mu\text{s}$.

The formula given by (8) was then used for the populations n_1 , n_2 , n_3 to calculate the function $N(t)$, and the results were compared with experiment. Figure 4 shows the calculated $N(t)$ for $n_1 = 0.025$, $n_2 = 0.025$, and $n_3 = 0.015$.

Figure 5 shows the calculated $F_n^{\delta\beta}$, obtained from the above distribution $f_n^{(0)}$. Similar calculations were performed with other model distributions $f_n^{(0)}$ that were in satisfactory agreement with the experimental decay kinetics. They show that $F_n^{\delta\beta}$ is not very sensitive to the details of $f_n^{(0)}$. It is clear from the calculations shown in Fig. 5 that the measured infrared spectrum of the $(\text{CF}_3)_3\text{CI}$ molecules corresponds to $n^* = 35 \pm 2.5$ ($E = 35\,000 \pm 2500 \text{ cm}^{-1}$), which is greater by a factor of about two than the dissociation limit ($D = 18\,000 \text{ cm}^{-1}$).

The normalization factor $A(n^*)$, calculated from $F_n^{\delta\beta}$ [see (6) and (7)], is $A(N^*) = 0.008 \pm 0.003$. To check this value of A , we found the integrated intensity of the band of upward infrared transitions in the $(\text{CF}_3)_3\text{CI}$ molecules. The result was in good agreement with independent measurements of the integrated intensity of the infrared absorption band of the molecules at room temperature.

We must now estimate the contribution of vibrational inhomogeneous broadening to the infrared spectrum of $(\text{CF}_3)_3\text{CI}$, shown in Fig. 3. This broadening occurs because the spectra of molecules with different vibrational energy are shifted relative to one another by anharmonicity. First, note that the position of the maximum of the measured $(\text{CF}_3)_3\text{CI}$ spectrum of molecules with energy $E = 35\,000 + 25\,000 \text{ cm}^{-1}$ is red-shifted by 24 cm^{-1} from the corresponding harmonic frequency $\nu_{21} = 968 \text{ cm}^{-1}$ (Ref. 12). Consequently, as the vibrational energy is varied within the width of $F_n^{\delta\beta}$, the infrared spectrum of $(\text{CF}_3)_3\text{CI}$ shifts by $\pm 1.7 \text{ cm}^{-1}$. The vibrational inhomogeneous broadening $2\gamma_{\text{inh}} = 3.5 \text{ cm}^{-1}$, obtained in this way, is significantly smaller than the width $2\gamma \approx 18 \text{ cm}^{-1}$ of the experimental spectrum.

Rotational inhomogeneous broadening is also negligible under the conditions of our experiment. Actually, the rotational half-width of the absorption spectrum of $(\text{CF}_3)_3\text{CI}$ is less than 5 cm^{-1} even at room temperature (see Fig. 3). Expansion of the $(\text{CF}_3)_3\text{CI}$ gas into vacuum results in considerable cooling of the rotational degree of freedom of the molecules ($T_{\text{rot}} \approx 20 \text{ K}$; cf. Ref. 13). As a result, the rotational width of the molecular band under molecular beam conditions is significantly smaller than at room temperature. We may therefore conclude that we have obtained experimentally the homogeneous infrared spectrum of the $(\text{CF}_3)_3\text{CI}$ molecules with energy $E \approx 35\,000 \text{ cm}^{-1}$.

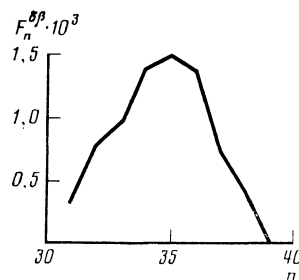


FIG. 5. Calculated $F_n^{\delta\beta}$ ($\hbar\omega_L \approx 1000 \text{ cm}^{-1}$) for $t_0 = 10 \mu\text{s}$.

6. DISCUSSION OF THE HOMOGENEOUS INFRARED SPECTRUM OF $(CF_3)_3CI$

The Lorentzian shape of the infrared absorption spectrum of highly excited molecules was predicted by a number of theoretical calculations,¹⁴⁻¹⁸ but had not been seen experimentally. The necessary condition for this shape to appear is a high density of component vibrations coupled anharmonically to the infrared-mode. If we take into account only the lowest-order anharmonic interaction, we find that the condition for the density of Fermi resonances can be written in the form¹⁷

$$\rho^{res} \gg (2\gamma)^{-1}. \quad (9)$$

Figure 6 shows the nearest three-frequency Fermi resonances with the above mode ν_{21} of $(CF_3)_3CI$ that are allowed for by selection rules. It is clear from the figure that condition (9) is satisfied in our case ($2\gamma \approx 18 \text{ cm}^{-1}$; $1/\rho^{res} \approx 3 \text{ cm}^{-1}$). The high density of Fermi resonances is typical for large molecules and ensures that the $(CF_3)_3CI$ spectrum consists of a structureless absorption band [i.e., the spectrum does not contain the side maxima observed for the relatively small C_2F_5Cl molecules in Ref. 5 and the CF_3I molecules in Ref. 7, for which condition (9) is not satisfied].

Let us now consider the connection between the measured infrared spectrum and intramolecular vibrational relaxation in $(CF_3)_3CI$. Homogeneous broadening of the absorption bands of highly excited molecules is due to two types of process. First, the anharmonic interaction which is linear in the coordinate of the excited mode and which, in the classical limit, corresponds to linear friction, leads to intramolecular relaxation of energy from the excited mode to the equilibrium value $\bar{\epsilon}$ (Ref. 19):

$$d\epsilon/dt = -\gamma_1(\epsilon - \bar{\epsilon}), \quad (10)$$

where γ_1 is the relaxation rate. Second, anharmonic terms in the Hamiltonian that are proportional to the mode occupation number a^+a produce linear dephasing of the oscillations, and do not give rise to energy relaxation.^{20,21,18} This process determines the decay of induced polarization in the mode:

$$d\langle q \rangle / dt = -\gamma_2 \langle q \rangle. \quad (11)$$

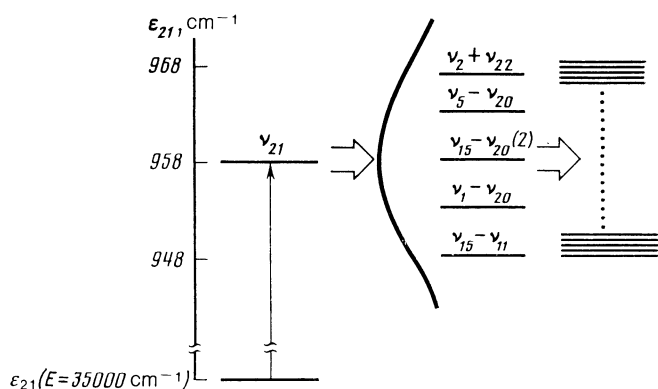


FIG. 6. Nearest three-particle Fermi resonances of the mode ν_{21} that are allowed by selection rules. The thick solid curve is a schematic representation of the $(CF_3)_3CI$ absorption band. The Fermi resonance $\nu_{15}-\nu_{20}$ is doubly degenerate.

where q is the coordinate of the excited mode and γ_2 the dephasing rate. The shape of the absorption band in the case of linear relaxation and dephasing processes is Lorentzian with half-width $\gamma = \gamma_1 + \gamma_2$. This resultant broadening was, in fact, measured in our experiment. The rate γ_1 that determines the kinetics of energy redistribution in the isolated molecule is of the greatest interest.

Let us estimate the relative contributions of γ_1 and γ_2 to the spectrum of the $(CF_3)_3CI$ molecules. In the lowest-order anharmonic interaction, dephasing is due to terms of the form $x_4 a^+ a q_i q_j$, where a^+ and a are, respectively, the photon creation and annihilation operators in the excited mode, q_i are coordinates in the reservoir consisting of the remaining modes of the molecule, and X_4 represents the fourth-order anharmonic constants. The contribution of these terms to γ is^{20,22}

$$\gamma_2 = \frac{X_4^2}{2\bar{\gamma}} \sum_{i=1}^{S_a} g_i \bar{\nu}_i (\bar{\nu}_i + 1), \quad (12)$$

where g_i and $\bar{\nu}_i$ are, respectively, the degeneracy and occupation number of mode i , S_a is the number of active modes in the reservoir that are directly coupled by the anharmonic interaction to the excited mode, and $\bar{\gamma}$ is the characteristic mode width. We shall assume, for the purposes of estimates, that we have $S_a \sim S$, i.e., S_a is of the order of the total number of modes in the reservoir and $\bar{\gamma} \sim \gamma$, where $\gamma = 9 \text{ cm}^{-1}$ is the measured half-width of the spectrum of the mode ν_{21} . We then have $\gamma_2 \approx 3X_4$. The characteristic magnitude of the anharmonic constants X_4 can be estimated from the shift of the spectrum $\Delta = 24 \text{ cm}^{-1}$ ($\Delta \approx X_4 \bar{\nu} S$). Hence, we find that $X_4 \approx 0.7 \text{ cm}^{-1}$, so that $\gamma_2 \approx 1.5 \text{ cm}^{-1} \ll \gamma$ holds. The rate of intramolecular dephasing thus turns out to be of the order of the inhomogeneous broadening of the measured spectrum (see Sec. 5).

In the lowest (third) anharmonic order, the width γ_1 is given by the expression^{17,18}

$$\gamma_1 = \pi X_3^2 \bar{\nu} \rho^{res} \quad (13)$$

where it is assumed that, for the mode ν_{21} , most of the resonances have the form $\nu_{21} \approx \nu_i - \nu_j$ (see Fig. 6), X_3 is the characteristic third-order anharmonic constant, and $\rho^{res} \approx 0.3 \text{ cm}^{-1}$ is the density of resonances of the form $\nu_{21} \approx \nu_i - \nu_j$. Hence, $\gamma_1 \sim X_3^2$. Since $\gamma_1 \approx \gamma$, we find that $X_3 \approx 3 \text{ cm}^{-1}$. This value of X_3 enables us to verify the validity of the above assumption that the homogeneous broadening of the $(CF_3)_3CI$ absorption band is largely due to the lowest-order anharmonic interaction (third order for energy relaxation and fourth order for dephasing).

The anharmonic order m^* that provides the main contribution to homogeneous broadening of the absorption band of a highly excited molecule is determined by the rate at which the anharmonic interaction decreases with increasing m : $X_{m+1} \sim \lambda X_m$, where $\lambda > 1$. It is shown in Ref. 18 that m^* can be estimated from the formula

$$m^* \sim S_a \lambda^2 [\bar{\nu}(\bar{\nu} + 1)]^{1/2}. \quad (14)$$

Since $\lambda^2 \sim (X_4/X_3)^2 \sim 0.05$, we find that $m^* \sim 2$. Since (14) was obtained on the assumption that $m^* \gg 1$, this estimate shows that higher order anharmonicity does not provide a dominant contribution to the broadening of the $(CF_3)_3CI$ absorption band.

The broadening of the $(\text{CF}_3)_3\text{CI}$ absorption band at $E \approx 35\,000\text{ cm}^{-1}$ is thus largely due to processes such as linear friction. The rate of relaxation of the energy of the mode ν_{21} to its equilibrium value can therefore be found from the experimental width of the infrared band: $\tau_{\text{IVR}} = (2\gamma \cdot 2\pi c)^{-1} \approx 0.3\text{ ps}$.

7. CONCLUSION

In conclusion, our results may be summarized as follows.

1. A universal photodissociation method has been proposed for measuring the infrared spectra of vibrationally highly excited polyatomic molecules. The method is capable of suppressing almost completely the vibrational inhomogeneous broadening.

2. The homogeneous Lorentzian infrared absorption spectrum of $(\text{CF}_3)_3\text{CI}$ molecules with twofold overexcitation above the dissociation limit has been obtained experimentally.

Analysis of the result shows that the homogeneous broadening of the $(\text{CF}_3)_3\text{CI}$ absorption band at $E \approx 35\,000\text{ cm}^{-1}$ is largely due to energy relaxation from the excited modes. This enables us to estimate the intramolecular vibrational relaxation time constant as $\tau_{\text{IVR}} \approx 0.3\text{ ps}$.

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