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# Evolution of the Homogeneous IR Spectrum of a Highly Vibrationally Excited Molecule as a Result of a Change in Its Vibrational Energy

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**Abstract.** Using a photodissociation technique, we have measured the IR spectrum of the $\nu_{21}$ mode of the $(CF_3)_3CI$ molecule with a vibrational energy of $E_2 = 42500 \pm 3500\ \mathrm{cm}^{-1}$ which is more than two times the dissociation energy. The experimental spectrum of a Lorentzian shape with a halfwidth of $\gamma_2 = 10.8 \pm 1.5\ \mathrm{cm}^{-1}$ has been analyzed simultaneously with the results of the preceding work ($\gamma_1 = 8.6 \pm 0.6\ \mathrm{cm}^{-1}$) that were obtained at a lower vibrational energy ($E_1 = 36500 \pm 2500\ \mathrm{cm}^{-1}$).

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It is now a well-established fact that as the vibrational energy of a polyatomic molecule grows higher, there comes into play the intramolecular vibrational relaxation (IVR) process, and the linear IR absorption spectrum changes its line character to a quasi-continuous one. These new properties of the microscopic object molecule that are, generally speaking, typical of macroscopic objects, have attracted close attention of a number of investigators [1–6]. The homogeneous IR absorption spectrum of the $\nu_{21}$ mode of $(CF_3)_3CI$ excited above the dissociation limit has recently been measured experimentally in [5, 7]. The spectrum has been found to have a Lorentzian shape, which was predicted in various theoretical works [8–12]. To gain an understanding of the nature of highly vibrationally excited molecules requires that experimental investigations should be launched into the energy dependence of the homogeneous band width, $\gamma(E)$. To study the evolution of homogeneous IR spectra is of practical importance as well, particularly as regards laser isotope separation by way of IR MP dissociation, IR laser-radical synthesis, and so on [2]. In the present paper, we report on the first attempt to advance in this direction. Using the photodissociation technique of [13, 14], we have measured the IR absorption spectrum of $(CF_3)_3CI$ at a higher vibrational energy and analyzed the obtained results simultaneously with the results of the preceding work [5, 7].

## 1. Experimental

The experimental setup is shown in Fig. 1. It has been described in detail in [5, 7]. For this reason, we will only touch upon this question. A beam of the $(CF_3)_3CI$ molecules was successively irradiated with two IR and an UV laser pulses. The IR pulses were produced by two TEA-$CO_2$ lasers. The first IR pulse ($\Phi_1 = 0.85\ \mathrm{J/cm}^2$, $\omega_1 = 949.5\ \mathrm{cm}^{-1}$) effected the preliminary excitation of the molecules by way of multiple-photon absorption, and the second IR pulse ($\omega_2 = 880$–$980\ \mathrm{cm}^{-1}$) served the purpose of a probe. The pulses were 100 ns in width at half-maximum and 300 ns at the base, which was achieved by using a nitrogen-free laser mixture. The UV pulse (second-harmonic output from a dye laser pumped by a XeCl

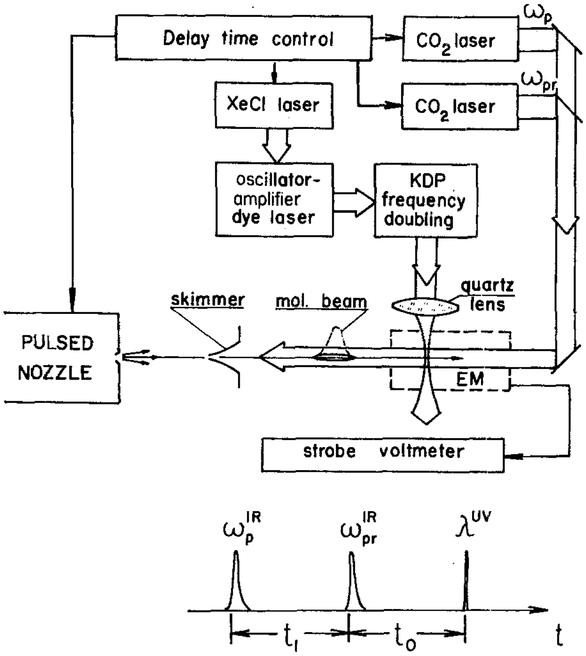

Fig. 1. Block diagram of the experimental setup. Time sequence of operation of the exciting IR, probe IR, and probe UV laser pulses

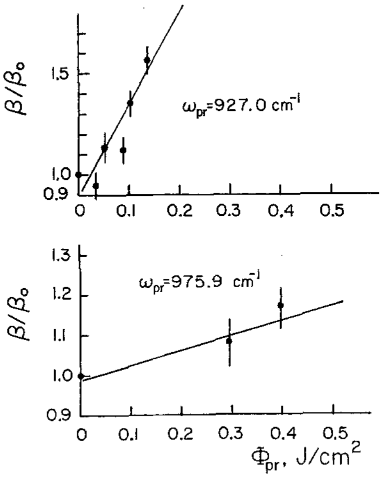

Fig. 2. Dissociation yield of highly vibrationally excited $(CF_3)_3CI$ molecules as a function of the probe IR radiation energy density at frequencies of 927 and 975.9 $cm^{-1}$. The exciting IR field parameters are: $\Phi_1=0.85$ J/cm$^2$, $\omega_1=949.5$ cm$^{-1}$

excimer laser) carried out the photodissociation detection of the I atoms resulting from the decomposition of the starting molecules. For this purpose, the UV radiation was tuned to the two-photon resonance $5p^2P_{3/2}\rightarrow 6p^4P_{3/2}$ ($\lambda=2982.3$ Å) of the three-photon atomic ionization process. The photoionization detection technique has been described in detail in [15]. The delay time between the IR pulses and also between the probe IR pulse and the UV pulse was $t_1=t_0=0.5$ µs.

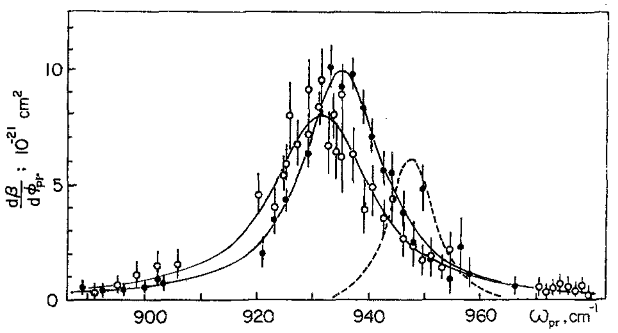

Fig. 3. IR photodissociation spectra of $(CF_3)_3CI$ molecules at vibrational energies of $E_1=36500\pm2500$ cm$^{-1}$ (●) [5] and $E_2=42500+3500$ cm$^{-1}$ (○) (dissociation energy $D=18000$ cm$^{-1}$). Solid lines – model calculation spectra. Dashed line – linear IR absorption spectrum of $(CF_3)_3CI$ at room temperature (in arbitrary units)

In the experiment, we measured the dissociation yield $\beta(\Phi_{pr})$ as a function of the energy fluence of the probe IR field for various frequencies of this field. Figure 2 shows typical results. As can be seen, at low $\Phi_{pr}$ the experimental data points fall well enough on straight lines. As demonstrated in [14], the slope $d\beta/d\Phi_{pr}$ of these lines is proportional to the IR absorption cross section $\sigma_{E^*}(\omega)$ of the molecules whose vibrational energy can be found from the relation $k(E^*)t_0=1$, where $k$ is the unimolecular decay rate and $t_0$ the delay time between the probe IR pulse and the UV pulse. Such staging of the experiment allowed us practically completely to suppress the inhomogeneous vibrational broadening [5, 7, 13].

Figure 3 shows the photodissociation spectrum $d\beta(\omega)/d\Phi_{pr}$ obtained from the experimental relationships $\beta(\Phi_{pr})$ similar to those illustrated in Fig. 2. Figure 3 also shows the results of the previous measurements [5, 7] obtained for a lower vibrational molecular energy. If plotted in in the $(\omega-\omega_0)^2-(d\beta/d\Phi_{pr})^{-1}$ coordinate system (where $\omega_0^1=934.5$ cm$^{-1}$ and $\omega^2=931$ cm$^{-1}$ are the positions of the maxima of the spectra), the photodissociation spectra will be approximated by straight lines sufficiently well, i.e., the experimental spectra are Lorentzian. The slopes of the lines correspond to $\gamma_1=8.6\pm0.6$ cm$^{-1}$ and $\gamma_2=10.8\pm1.5$ cm$^{-1}$.

## 2. Analysis of IR Photodissociation Spectra

The broadening of the measured spectra may have the following causes.

(1) The distribution of the highly vibrationally excited molecules among various rotational states leads to an inhomogeneous rotational broadening of the spectra.

(2) The increase in the dissociation yield under the effect of the weak probe IR pulse is caused by molecules differing in vibrational energy. This results in an inhomogeneous vibrational broadening of the spectra.

(3) The homogeneous broadening of the absorption band of the highly excited molecule contributes to the total photodissociation spectrum width.

Let us estimate the contribution of the inhomogeneous broadenings to the measured spectra in order to find the homogeneous component of the greatest interest. Note at once that the rotational broadening is in our case negligible. Indeed, the halfwidth of the $\nu_{21}$ band of the $(CF_3)_3CI$ molecules is $\delta\nu \simeq 5\ \text{cm}^{-1}$ at room temperature. This value includes not only rotational, but also vibrational inhomogeneous broadening. Now bear in mind that our experiments have been conducted with a beam of cooled molecules the rotational temperature of which is $T_r \leqq 20$ K [16]. Therefore, the rotational bandwidth of the molecule under study can be estimated as $\delta\nu_r \leqq \delta[20\ \text{K})/(300\ \text{K})]^{1/2} \simeq 1.3\ \text{cm}^{-1}$. This is practically an order of magnitude smaller than the width of our experimental bands, and so we will give no consideration to this broadening mechanism.

To take account of the inhomogeneous vibrational broadening, we use the following relationship between the measured quantity $d\beta/d\Phi_{pr}$ and the desired absorption cross section of the highly vibrationally excited molecules [14]:

$$h\omega(d\beta/d\Phi_{pr}) = \sum_n \sigma_{n,n+1}[f_n - f_{n+1}(\varrho_n/\varrho_{n+1})] \times (e^{-k_n t_0} - e^{-k_{n+1} t_0}). \qquad (1)$$

Here $\sigma_{n,n+1}$ is the cross section of the upward IR transitions for molecules with an energy of $nh\omega$, $f_n$ is the proportion of such molecules at the moment the probe IR pulse fires, $\varrho_n$ and $k_n$ are the unimolecular density of states and decay rate, respectively, and $t_0$ is the time interval between the moment the probe IR pulse fires and the moment the dissociation yield is measured. In model calculations, we have taken the distribution $f_n^0$ produced by the IR pumping to be a constant in the vicinity of the maximum of $[\exp(-k_n t_0) - \exp(-k_{n+1} t_0)]$. The results obtained in this approximation agree well with the more exact calculations presented in [5, 7]. Thus, $f_n^0 = f_n \exp(-k_n t_1)$, where $t_1$ is the delay time between the IR pumping and probe pulses. Using the results of calculations for $k(E)$ presented in [15], we find that $E_1 = 36500 \pm 2500\ \text{cm}^{-1}$ for the first spectrum [5, 7] ($t_1 = 5\ \mu$s, $t_0 = 10\ \mu$s) and $E_2 = 42500 \pm 3500\ \text{cm}^{-1} \simeq 1.15E$ for the second spectrum ($t_1 = t_0 = 0.5\ \mu$s).

In model calculations of the spectrum of $d\beta(\omega)/d\Phi_{pr}$, the desired frequency dependence of $\sigma_{n,n+1}$ has been considered to be a Lorentzian with a maximum whose position depends on the molecular energy: $\omega_0 = \omega_L - 0.67n$, where $\omega_L = 958\ \text{cm}^{-1}$ is the harmonic frequency [17]. The halfwidth $\gamma^L$ has been the variable. The calculated spectrum has been compared with its experimental counterpart by the least standard deviation criterion. The best fit has been obtained at $\gamma_1^L = 8.3\ \text{cm}^{-1}$ for $E_1 \simeq 36500\ \text{cm}^{-1}$ and $\gamma_2^L = 10.5\ \text{cm}^{-1}$ for $E_2 \simeq 42500\ \text{cm}^{-1}$. These values practically do not differ from the total spectral widths $\gamma_1 = 8.6 \pm 0.6\ \text{cm}^{-1}$ and $\gamma_2 = 10.8 \pm 1.5\ \text{cm}^{-1}$ obtained above without allowing for the inhomogeneous vibrational broadening. Thus, we have obtained practically homogeneous IR absorption spectra of highly excited molecules.

## 3. Discussion

As already noted in the introduction, the relationship between the width of the Lorentzian absorption band of a molecule and its energy is of great interest. This relationship may, in principle, help clarify the most interesting questions concerning the Lorentzian spectrum, namely, the relative contribution of purely phase relaxation and energy relaxation to the absorption band broadening and the possible role of the higher-order anharmonic interactions. These questions have recently been discussed in the literature [11, 12, 18–20].

In our preceding work [7] concerning the $(CF_3)_3CI$ molecule, we have made an estimate which has shown that at molecular energies of $E \simeq 40 \times 10^3\ \text{cm}^{-1}$ the main contribution to the absorption band broadening of the $\nu_{21}$ mode are made by the processes of energy transfer along this mode to the other molecular modes on account of the third-order Fermi resonances of the type $\nu_{21} \simeq \nu_i - \nu_j$. The density of such lower-order resonances is the highest. For processes of this type, the theory [12] predicts the following expression for the linewidth:

$$\gamma = \pi\Phi^2_{(3)}(\bar{n}_j - \bar{n}_i)\varrho_3^{\text{res}}(\nu_{21}, l=1), \qquad (2)$$

where $\Phi_{(3)}$ is the characteristic anharmonicity constant in the Hamiltonian for the terms of the type $(1/3!)\Phi_{ijk}q_i q_j q_k$; $\bar{n}_i$ and $\bar{n}_j$ are the characteristic occupation numbers for the vibrational modes entering into the resonances $\nu_{21} \simeq \nu_i - \nu_j$; for various $i$'s and $j$'s. $\varrho_3^{\text{res}}(\nu_{21}, l=1)$ is the density of resonances of this type (see [11, 12] for the notation). The energy dependence of the linewidth is related to that of the occupation numbers by the standard relations with the total molecular energy $E$ being converted to the vibrational temperature $T(E)$, and so for the ratio of two values of $\gamma$ at the different energies $E_1$ and $E_2$, we have

$$\gamma_1/\gamma_2 = \{\bar{n}_j[T(E_1) - \bar{n}_i[T(E_1)]\}/\{\bar{n}_j[T(E_2)] - \bar{n}_i[T(E_2)]\}. \qquad (3)$$

Theoretical calculations by the above formulas yield $(\gamma_1/\gamma_2)_{\text{theor}} = 8.9 \times 10^{-1}$, while the experimental ratio is $(8.1 \pm 1.6) \times 10^{-1}$.

Unfortunately, the high experimental error and the narrow range within which it proves possible to measure the variation of $\gamma(E)$ make the agreement between theory and experiment not very convincing. Indeed, within this energy range, the theory predicts an almost linear relationship between the linewidth and energy, because the occupation numbers for the lower frequency entering into the resonance condition $\nu_{21} \simeq \nu_i - \nu_j$ are greater than unity, $n_j > 1$, and therefore, $n_j \propto T \propto E$, and even so crude an estimate yields $\gamma_1/\gamma_2 = E_1/E_2 = 8.7 \times 10^{-1}$. The slight deviations from the linear law $\alpha E + \beta E^2$ may be due to the influence of Fermi resonances of order four or higher, whose density rises rapidly with increasing order [12], but we cannot as yet say what is the contribution of such processes to the linewidth for lack of experimental material.

## 4. Conclusion

The main results of the present work may be summarized as follows.

1. Homogeneous IR absorption spectra of a highly vibrationally excited polyatomic molecule have been experimentally obtained for various values of its vibrational energy.
2. The anharmonic shift of the IR absorption band of the highly excited $(CF_3)_3CI$ molecule is linear in energy.
3. The energy dependence $\gamma(E)$ does not contradict the theory based on the assumption of the dominant contribution of three-quantum IVR processes to the homogeneous broadening of the IR absorption band of the molecule.

A more detailed comparison between theory and experiment requires measuring the dependence $\gamma(E)$ over a wider energy range.

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