

# Uniform spectrum of vibrational transitions and the intramolecular vibrational-relaxation time of a highly excited polyatomic molecule

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A uniformly broadened Lorentz spectrum of IR absorption of a polyatomic molecule vibrationally overexcited above the dissociation boundary has been measured experimentally for the first time. The half-width of the spectrum of a  $(\text{CF}_3)_3\text{CI}$  molecule ( $\gamma = 9 \pm 1 \text{ cm}^{-1}$ ) corresponds to the time of the intramolecular vibrational relaxation from the excitable mode  $\tau_{\text{IVR}} \approx 0.3 \times 10^{-12} \text{ s}$ .

The stochastic properties of vibrationally excited polyatomic molecules has recently attracted considerable interest.<sup>1-4</sup> One of the manifestations of the stochastic aspect of the vibrational motion of highly excited molecules is the fast intramolecular vibrational relaxation from the excited mode to the other vibrational degrees of freedom of the molecule. The dynamics of such a relaxation is associated with the shape of the absorption spectrum of the excited mode of a molecule. In the simple case of experimental damping of the energy excess in the mode  $(\epsilon - \bar{\epsilon}) \sim \exp(-t/\tau)$ , the absorption spectrum should have a Lorentzian shape with a width  $1/\tau$  if the purely phase-relaxation processes contribute only negligibly.

Using the new photodissociation method proposed by us for measuring infrared spectra of polyatomic molecules which are overexcited above the dissociation boundary, we found the spectrum for the absorption of  $(\text{CF}_3)_3\text{CI}$  molecules with an energy  $E = 35\,000 \text{ cm}^{-1}$  well above the dissociation energy  $D = 19\,000 \text{ cm}^{-1}$ . On the basis of the measurements of the spectrum shape we have estimated the intramolecular vibrational relaxation time of such molecules to be  $\tau_{\text{IVR}} = 0.3 \times 10^{-12} \text{ s}$ .

The measurement method used by us is shown in Fig. 1. Let us assume that some method is used to rapidly distribute vibrationally highly excited molecules,  $f(E)$ . The molecules above the dissociation boundary  $D$  are subjected to a monomolecular decomposition at the rate  $k(E)$  which depends very strongly on the margin of the vibrational energy  $E$  stored by the molecule. Over an interval of time  $t_0$  after the excitation, only the molecules with  $E \gtrsim E^*$  decompose. Here the energy  $E^*$  is determined by the condition  $t_0 k(E^*) \approx 1$ . We denote by  $\beta$  the relative fraction of these decomposed molecules. Let us now subject the vibrational excited molecules to a short ( $\tau_{\text{pulse}} \ll t_0$ ), low energy IR laser test pulse which can deform only slightly the vibrational distribution  $f(E)$  due to the linear absorption. As a result of such a slight increase of the vibrational energy, the fraction of molecules that break up over the same interval of

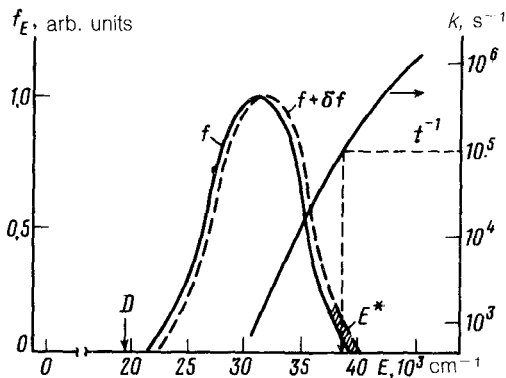


FIG. 1.  $f_E$ —The initial vibrational distribution of highly excited molecules;  $f_E + \delta f_E$ —distribution after the molecule is subjected to an IR test pulse;  $k$ —the rate of monomolecular decomposition of  $(CF_3)_3CI$  (from data of Ref. 5). The hatching shows the region in which the molecules contribute the augmentation of the dissociation yield  $\Delta\beta(t_0)$  as a result of application of an IR test pulse.

time increases to  $\beta + \Delta\beta$ . In a linear approximation with respect to the test pulse flux, the increment  $\Delta\beta$  results from the absorption of radiation by molecules with energies  $E$ , for which the condition  $t_0 k(E) \approx 1$  is satisfied. Since the decomposition rate  $k(E)$  increases rapidly with the energy of the molecule, the energy interval  $\Delta E$  around  $E^*$  is very narrow (the hatched area in Fig. 1). In the narrow energy interval there is accordingly a relationship between the dissociation increment  $\Delta\beta$  and the absorption cross section  $\sigma_E$  of highly excited molecules. By measuring the absorption spectrum  $\sigma_E(\omega_2)$  in this manner we can suppress substantially the inhomogeneous broadening due to the small energy interval  $\Delta E$ .

The distinctive feature of our experiment is the highly sensitive photoionization diagnostic analysis of the dissociation of iodine-containing molecules based on their disintegration product (the iodine atom) in the ground state ( $^2P_{3/2}$ ) or the excited state ( $^2P_{1/2}$ ). This dissociation process was studied in detail in Ref. 5 for  $(CF_3)_3CI$ . We will mention here only certain modifications of this method. We assume that at the time  $t$  some of the vibrationally overexcited molecules,  $\beta$ , are broken up:  $(CF_3)_3CI \xrightarrow{\beta} (CF_3)_3C + I(^2P_{3/2})$ . We now subject the nondecomposed molecules (the number of these molecules is  $1 - \beta$ ) to an ultraviolet pulse (Fig. 2). After absorbing a single UV photon, the molecule moves from a bonding orbital to an antibonding orbital and breaks up rapidly, producing  $I^*(^2P_{1/2})$  with a 95% yield and  $I(^2P_{3/2})$  with a 5% yield. In our experiment, the energy density of a UV pulse corresponds to a greater than tenfold saturation of the molecule photodissociation band, which leads to a nearly total UV photodissociation of the vibrationally overexcited, nondecomposed molecules. Under these conditions the concentration of the excited atoms,  $I^*(^2P_{1/2})$ , is proportional to the concentration of the nondecomposed molecules:  $N(I^*) = 0.95(1 - \beta)n_0$ , while the concentration of the ground-state atoms,  $I(^2P_{3/2})$ , is associated with the IR dissociation yield of the vibrationally overexcited molecules:  $n(I) = [\beta + 0.05(1 - \beta)]n_0$ , where  $n_0$  is the initial concentration of molecules.

The concentration of the ground-state atoms, which is associated with the dissociation yield of the vibrationally overexcited molecules, was measured by a resonant multiphoton ionization method (Fig. 2). We used in this case the same second har-



monic of the dye laser that was used for the photolysis of molecules. The UV light was tuned to the two-photon resonance,  $5p(^2P_{3/2}) - 6p(^4P_{3/2})$  ( $\lambda_1 = 2982.3 \text{ \AA}$ ), of the three-photon ionization of the I atom.

The experimental apparatus had the following components: 1) A vacuum chamber with a pulse nozzle used as a source of molecules; 2) two pulsed atmospheric-pressure  $\text{CO}_2$  lasers for producing vibrationally overexcited molecules and for probing their IR absorption spectrum; 3) a dye laser pumped by an excimer XeCl laser; 4) a system for synchronizing the lasers and measurements; 5) a system for collecting and detecting photoions.

Figure 3 is a plot of  $h\omega\partial\beta/\partial\phi_2$  as a function of the IR test pulse frequency found from the experimental curves for  $\beta(\phi_1, \phi_2)$ , where  $\beta$  is a fraction of vibrationally overexcited molecules which break up in the electronic ground state, and  $\phi_1$  and  $\phi_2$  are the energy fluxes of the first exciting pulse and the second IR test pulse, respectively. The time delay between the IR pumping ( $\phi_1$ ) and the test ( $\phi_2$ ) IR field is  $5 \mu\text{s}$  and the time delay between the IR test pulse and the UV pulse, which measured the dissociation yield, is  $t_0 = 10 \mu\text{s}$ . The quantity  $\partial\beta/\partial\phi_2$ , which was measured within a constant, is equal to  $\sigma_E$ , the cross section for the IR transitions of molecules, whose energy,  $E \simeq E^*$ , is represented by the hatching in Fig. 1. The solid curve (1) is a Lorentzian function with a half-width  $\gamma = 9 \text{ cm}^{-1}$ . Let us estimate  $E^*$  and the width of the energy interval  $\Delta E$  from the condition  $t_0 k(E) \simeq 1$ . Using the decomposition rate  $k(E)$  obtained in Ref. 5 (see also Fig. 1), we find that the energy interval  $\Delta E$  which we are seeking includes the molecules with  $E \simeq 38\,000 \pm 2600 \text{ cm}^{-1}$ . The result of an exact calculation, which will be reported in a more detailed paper, gives  $E = 35\,000 \pm 2500 \text{ cm}^{-1}$ , a value slightly lower than the estimate given here.

From the magnitude of the anharmonic red shift, from the spectrum measured by us, and from the half-width of the energy interval,  $\Delta E = 2500 \text{ cm}^{-1}$ , which we have determined, we find the nonuniform vibrational broadening of the spectrum (Fig. 3) to be  $\delta = 2 \text{ cm}^{-1}$ , a value appreciably smaller than  $\gamma$ . The contribution from the nonuniform vibrational broadening is also negligible, since  $T_{\text{vib}} \simeq 20 \text{ K}$  upon cooling the molecules down to a vacuum. We have thus obtained a uniform spectrum of vibrational transitions of highly excited  $(\text{CF}_3)_3\text{CI}$  molecules. The time for the relaxation of the energy from the excitable active IR mode ( $\nu_{21}$ ) is  $\tau_{\text{IVR}} \simeq 0.3 \times 10^{-12} \text{ s}$  if it is assumed that the intramolecular phase relaxation<sup>6</sup> does not contribute to the spectral broadening.

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