Direct measurements of the lifetimes of polyatomic molecules vibrationally excited above the dissociation threshold in intersecting laser and molecule beams

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A method is proposed for measuring the lifetime of $(CF_3)_3$ CBr molecules which are "overexcited," i.e., excited above the dissociation threshold, by the pulse from a CO_2 laser. The molecules are in a beam intersected by the laser beam. The first results on the use of this method are reported. Information has been obtained on the dynamics of the excitation of levels above the dissociation threshold.

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1. The intramolecular redistribution of vibrational excitation energy and the dynamics of monomolecular decay are questions of importance in connection with the many-photon infrared excitation and dissociation of polyatomic molecules.[1] The most direct way to experimentally study the intramolecular redistribution of energy during monomolecular decay is to measure the distribution of lifetimes, $P(\tau)$, of a system of monoenergetically excited molecules.[2] Although the molecules pumped by an IR laser beam are not excited in a monoenergetic fashion, and the actual vibrational distribution has some nonzero width, a study of the distribution $P(\tau)$ can still yield information on the intramolecular redistribution of energy and on the distribution of the total internal energy of the excited molecules. Such a study can also yield information on the dynamics of the excitation of levels above the dissociation threshold. von Hellfeld *et al.*[3] have studied the distribution $P(\tau)$ of SF_5^+ molecular ions during their dissociation into $SF_4^+ + F$ after infrared many-photon excitation. Under the assumption that the behavior of the molecules was statistical, they determined the distribution of the internal energy of the over-excited SF_5^+ ions from the measured distribution $P(\tau)$ and showed that this internal-energy distribution is not the equilibrium distribution.

In this letter we describe a method, and report the first results of the use of this method, for measuring the lifetimes of neutral polyatomic molecules which have been vibrationally excited above the dissociation threshold. The present experiments were carried out with the molecule $(CF_3)_3CBr$. According to the statistical theory,[4] this molecule has a respectable lifetime[5] ($\cong 10^{-5}$–10^{-2} s) even when excited well above the dissociation threshold. A lifetime of this magnitude can be measured in a molecular beam by a time-of-flight method. This molecule has a strong absorption band in the spectral region corresponding to the output of a CO_2 laser,[6] and it has a low C–Br binding energy ($\lesssim 24\,000$ cm^{-1}; Ref. 5), so that it effectively undergoes dissociation at a moderate excitation energy density.

2. The experimental apparatus is described in detail in Ref. 7. Let us outline the experimental method. The molecules in a beam at the point (x_1) of intersection with the laser beam are excited by the laser pulse. The vibrationally overexcited molecules undergo a dissociation in accordance with $P(\tau)$, so that the total vibrational energy of the beam molecules, E_v, falls off over time, t, or over distance $x - x_1 [t = (x - x_1)/v$, where v is the velocity of the molecules]. By measuring E_v at various distances $(x - x_1)$ from the excitation zone we can determine the lifetime of the overexcited molecules.

In the present experiments a pulsed $(CF_3)_3CBr$ molecular beam, in a 1:1:10 mixture with Ar and He, respectively, was excited by the pulse from a CO_2 laser [$E \lesssim 1.5$ J; the $P(10)$ line; the 10.6-μm band; spot dimensions of 6×7 mm in the region where the beams intersect]. The total pressure of the mixture at the nozzle was 2.5 atm; the beams intersected at a distance $x_1 = 6$ cm from the nozzle. We measured the energy of the beam molecules at various distances from the point x_1, with and without excitation of these molecules by the laser pulse. As the detector we used a fast-response pyroelectric detector (4×4 mm; response time $\cong 3$–5 μs). This detector could be moved along the beam axis.

The output signal from the pyroelectric detector corresponding to the vibrationally excited molecules is proportional to the quantity[7] $S^* \sim n^*(x)vE_b$, where $n^*(x)$ is the number density of vibrationally excited molecules at the surface of the detector, and E_b is the energy absorbed from the laser pulse by a molecule ($E_b = E_v$). At low excitation energy densities Φ, at which the molecules do not dissociate ($E_v < E_d$, where E_d is the dissociation energy), the signal S^* (and also the signal corresponding to unexcited molecules) falls off with distance at $x \gg d_0$ ($d_0 = 0.75$ mm is the diameter of the nozzle aperture) because of the beam divergence [a decrease in $n(x)$] in proportion to $1/x^2$; at $x > x_1$ we have $n^*(x) = n^*(x_1)(x_1/x)^2 = n^*(x_1,x)$. With increasing Φ, as the molecules are excited above the dissociation threshold ($E_v > E_d$) and begin to dissociate, the value of $n^*(x)$ at each point $x > x_1$ also depends on the lifetime of the vibrationally overexcited molecules; i.e.,

$$n^*(x) = n^*(x_1, x) \left[1 - \int_{E_d}^{\infty} \rho(E)\,dE + f(\tau) \int_{E_d}^{\infty} \rho(E)\,dE \right],$$

where $\int_{E_d}^{\infty} \rho(E)\,dE$ is the relative number of molecules which are excited above the dissociation threshold, and $f(\tau)$ is a function which describes the monomolecular decay
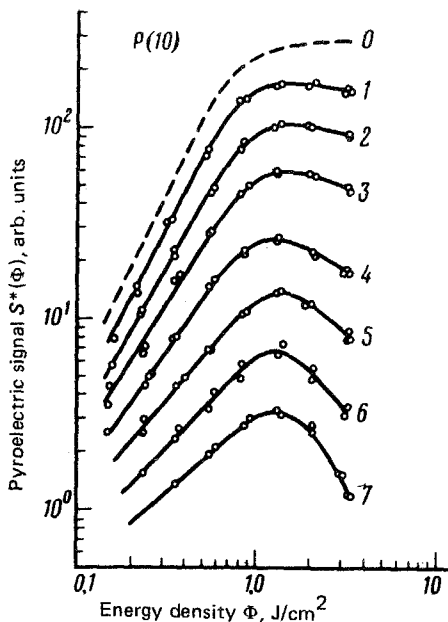
FIG. 1. $S*(\Phi)$ at various distances from the point where the laser and molecular beams intersect. 0—$x - x_1 = 0$; 1—1.4; 2—2.5; 3—3.7; 4—5.7; 5—7.7; 6—9.7; 7—11.7.

of the over-excited molecules. The change in E_v along the beam axis $[E_v \sim n*(x)]$ is thus described by the function $f(\tau)$.

Since part of the vibrational energy of the molecules is carried off by the fragments after the dissociation,[8] these fragments will also induce a signal if they reach the detector. This signal may influence the results of the measurements. However, since the angular divergence of the fragments is much greater than that of the molecular beam, the probability for these fragments to reach the detector can be substantially reduced by using skimmers immediately in front of the detector as a diaphragm for the molecular beam.

3. Figure 1 shows the signal $S*$, which is the signal induced by the vibrationally excited $(CF_3)_3CBr$ molecules, vs the energy density Φ at various distances $(x - x_1)$ from the excitation zone. With increasing distance, the nature of the dependence $S*(\Phi)$ changes substantially: The slope of the curves decreases, and the extent of the decay at $\Phi > 1$ J/cm² increases. These effects result from the dissociation of a progressively greater fraction of the vibrationally excited molecules during the transit to the detector as the distance $(x - x_1)$ is increased. The dashed curve in Fig. 1 shows the function $S*(\Phi)$ found by approximating the $S*(x - x_1)$ curves found from the experimental results for various fixed values of Φ up to the point $x = x_1$. If there is no other pathway for the decay of the excited molecules (through an excited electronic state, for example[9]), this curve is the Φ dependence of the absorbed energy E_b.
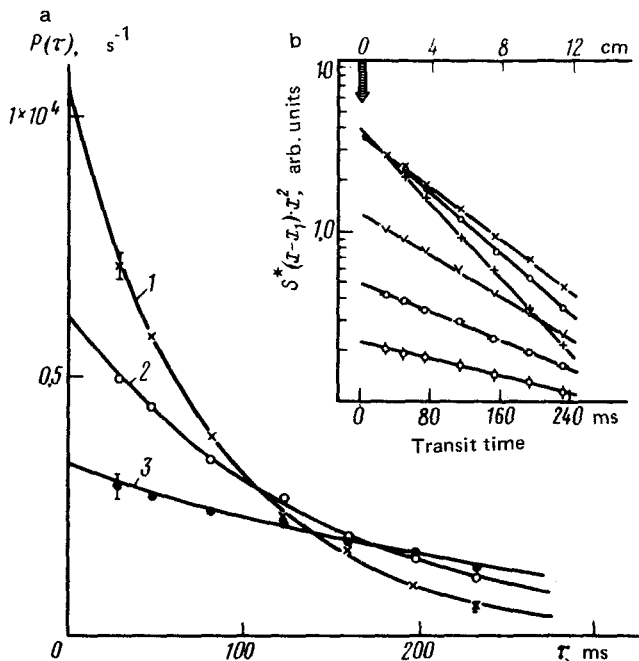
FIG. 2. a: $S^*(x - x_1)x^2$ for various values of Φ. $\circ$—0.2; -o—0.3; v—0.5; x—1.0; $\bullet$—2.0; $+$—3.0 J/cm². b: Lifetime distributions $P(\tau) = k_a \exp(-k_a\tau)$ with $k_a = 1.05 \times 10^4$ s^{-1} (a), $k_a = 6.4 \times 10^3$ s^{-1} (2), and $k_a = 3.4 \times 10^3$ s^{-1} (3) and curves of $S^*(x - x_1)x^2$ normalized to the corresponding rate constants with $\Phi = 3.0$ (1), 0.5 (2), and 0.2 (3) J/cm².

From the results in Fig. 1 we can find the behavior of $S^*(x - x_1)x^2$, i.e., the function $f(\tau)$, for various values of Φ, after normalizing the $S^*(\Phi, x - x_1)$ signals to the value of $1/x^2$. Some corresponding curves are shown in Fig. 2a. These are exponential curves. Figure 2b shows the experimental results for $\Phi = 3.0$ (1), 0.5 (2), and 0.2 (3) J/ cm², normalized to the corresponding rate constants. Also shown here are the lifetime distributions $P(\tau) = k_a \exp(-k_a\tau)$ [$P(\tau)$ is the probability for a molecule to have a lifetime τ, and k_a is the rate constant of the monomolecular decay] for three values of the rate constant: $k_a = 1.05 \times 10^4$ s^{-1} (1), $k_a = 6.2 \times 10^3$ s^{-1} (2), and $k_a = 3.4 \times 10^3$ s^{-1} (3). We see that the experimental points conform well to these $P(\tau)$ curves. At the values $\Phi = 2.0$ and 1.4 J/cm² the experimental results can be approximated well by the $P(\tau)$ curves with $k_a = 8.2 \times 10^3$ s^{-1} and 7.2×10^3 s^{-1}, respectively. In the case of pumping in the $P(10)$ line of the 10.6-μm band of the laser, the $(CF_3)_3CBr$ molecules are effectively dissociated at a value of only $\Phi \cong 0.2$ J/cm².

Figure 3 shows k_a vs the excitation energy density. Only at $\Phi < 1.0$ J/cm² does k_a increase rapidly with increasing Φ; at large values of Φ, k_a changes only slightly. The apparent reason is that with increasing Φ in the region $\gtrsim 1.0$ J/cm² the average level of the vibrational excitation of molecules above the dissociation threshold increases
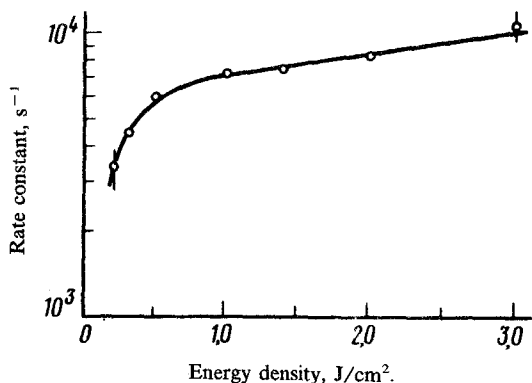
FIG. 3. Rate constant of the monomolecular decay of $(CF_3)_3CBr$ vs the excitation energy density.

slightly. This interpretation agrees well with the result in Fig. 1: The absorbed energy [the signal $S^*(\Phi)$ at the point $x = x_1$] also essentially reaches saturation $\Phi > 1.0$ J/cm^2. We have observed similar curves of $E_b(\Phi)$ in the excitation of $(CF_3)_3CBr$ in a cell at room temperature. The slow increase (or saturation) of E_b at $\Phi > 1.0$ J/cm^2 is attributed to a decrease in the absorption cross section of the excited molecules at the pump frequency due to a red shift of their absorption spectrum caused by anharmonicity.

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