

stable polynutron systems with  $x \geq 6$  are not formed in  $\sim 700$ -MeV proton interactions with uranium. The results of this experiment are, therefore, in rather direct disagreement with those of Detraz<sup>4</sup> who reports evidence for the formation of polyneutrons with  $x = 4, 6, 8,$  or  $10,$  with cross sections of  $2800, 85, 70,$  or  $300 \mu\text{b},$  respectively. That experiment involved  $24$ -GeV protons on tungsten and used a  $^{70}\text{Zn} \rightarrow ^{72}\text{Zn}$  detector. Thus Detraz's polyneutrons either have  $x = 4,$  to which the present experiment is insensitive, or their production has an exceedingly steep energy dependence.

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## Collisionless Multiphoton Dissociation of SF<sub>6</sub>: A Statistical Thermodynamic Process\*

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A calorimetric experiment, which combines picosecond CO<sub>2</sub>-laser pulses with acoustic detection techniques, proves that the collisionless multiphoton dissociation of SF<sub>6</sub> is a statistical thermodynamic process. The standard Rice-Ramsberger-Kassel-Marcus theory of unimolecular reactions provides a *quantitative* explanation of the dissociation effect. The reaction rate is primarily limited by transitions in the quasicontinuum rather than by the anharmonicity of the first few discrete levels.

The interest in laser dissociation of molecules<sup>1</sup> became widespread when it was first shown<sup>2</sup> to be isotopically selective. It was quickly established<sup>3-5</sup> that the process is essentially collisionless, involving only the interaction of an isolated molecule with the intense radiation field. A schematic quantum level structure<sup>5</sup> of SF<sub>6</sub>, used to explain the absorption of about thirty infrared quanta necessary for the dissociation of an isolated molecule, is shown in Fig. 1. The detailed structure<sup>6</sup> is omitted, both for simplicity and also because much of it is not yet known. The energy levels in Fig. 1 are divided<sup>7</sup> into three groups, as indicated by the large Roman numerals. The salient properties of each region are as follows. Region I is characterized by *coherent interaction*, discrete

energy levels, "anharmonicity bottleneck," Bloch equations, rotating-wave approximation, isotopic selectivity, and resonantly enhanced multiphoton absorption.<sup>5</sup> In region I, the peak power, which determines the Rabi precession frequency, is much more important than the laser energy.

With increasing vibrational excitation, the density of states  $\rho(E)$  rises and the oscillator strength of the  $\nu_3$  mode is spread over a quasicontinuum of states. In this regime II, Fermi's Golden Rule may be applied when the condition

$$\rho(E) \gg \Delta E / (\mu \mathcal{E})^2 \quad (1)$$

is satisfied,<sup>8</sup> where  $\Delta E$  is the energy width of the band into which the oscillator strength is smeared and  $\mu \mathcal{E}$  is the dipole matrix element from the

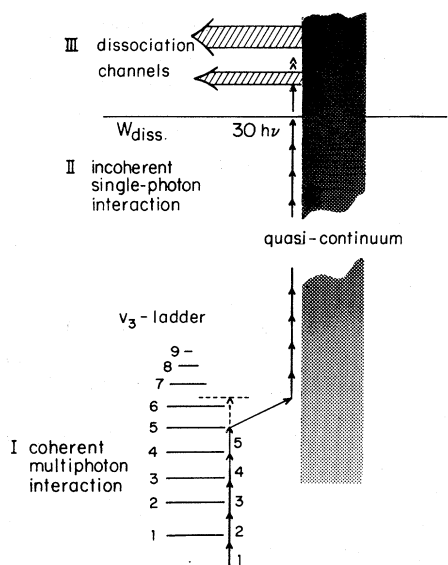


FIG. 1. A schematic energy-level diagram for the multiphoton dissociation of  $\text{SF}_6$ .

ground state. Region II is characterized by *incoherent interaction*, quasicontinuum of levels, Fermi's Golden Rule, rate equations, and the oscillator-strength sum rule. In this regime, successive absorption and re-emission of single photons takes place, described by rate equations

$$dW_i/dt = \sum_j (K_{ij}IW_j - K_{ji}IW_i), \quad (2)$$

where  $W_i$  is the probability of occupation of the  $i$ th stationary state, and  $K_{ij}I$  is the transition rate between  $i$  and  $j$ , which is proportional to the laser intensity  $I$ . The laser intensity  $I$  can be divided from the right-hand side of Eq. (2) to show explicitly that the molecular evolution in regime II depends only on the product of intensity and pulse duration, i.e., on energy fluence.

Region III is the true continuum of levels above the dissociation limit  $W_{\text{diss}}$ . Dissociation may occur during and after the picosecond pulse, before de-excitation by collisions takes place.

By comparing the dissociation yield for varying pulse duration, we can determine experimentally whether pulse energy or peak power is more important. The Harvard University short-pulse  $\text{CO}_2$ -laser facility<sup>9</sup> generates 500-psec pulses by optical free induction decay,<sup>10</sup> and amplifies them to the 0.15-J level. For a given energy, these ultrashort pulses have 200 times higher peak power than the typical 100-nsec  $\text{CO}_2$ -laser pulse. As shown by Kolodner, Winterfeld, and Yablonovich<sup>11</sup> the dissociation yield increases only 30% as the

pulse duration is reduced by a factor of 200. Therefore, the important dissociation-rate-limiting physics is occurring in region II where pulse energy plays a dominant rule, rather than in region I where the peak power is critical. The "anharmonicity bottleneck" of the first few discrete levels<sup>5</sup> is not important<sup>12</sup> for the ultrashort pulses, where the Rabi precession frequency at the 1.4-J/cm<sup>2</sup> dissociation threshold is about 10 cm<sup>-1</sup>.

The transitions in the quasicontinuum are those of an *incoherently* driven harmonic oscillator, which assumes a Planck distribution function<sup>13</sup> at a well-defined temperature determined by the total energy absorption from the laser pulse. If intramolecular  $VV$  relaxation is much faster<sup>14</sup> than the rate of photon absorption, all fifteen vibrational degrees of freedom of  $\text{SF}_6$  are at the same temperature. Our results are consistent with an ergodic behavior of the isolated molecule in the quasicontinuum.

The Rice-Ramsberger-Kassel-Marcus (RRKM) theory is the accepted statistical model for unimolecular reactions.<sup>15</sup> The simple Kassel form for the dissociation rate of a molecule which has absorbed  $n$  photons is

$$\text{Rate} = \omega \frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!}, \quad (3)$$

where  $m$  is the minimum number of photons needed for dissociation,  $s$  is the number of vibrational degrees of freedom (which is 15 for  $\text{SF}_6$ ) and  $\omega$  is the vibrational (or laser) frequency. Equation (3) predicts that  $n$  must exceed  $m$  by 6–10 photons in order to produce dissociation during a typical transverse-excitation-atmosphere laser pulse. This is in good agreement with the molecular-beam measurements of Lee *et al.*<sup>16</sup> For very short pulses,  $n-m$  may be larger, but if it is not, most of the dissociation will occur after the light pulse is gone, but still before the molecule collides.

Formula (3), when averaged over a full statistical distribution, gives<sup>15</sup> a mean dissociation rate:

$$\text{Rate} = \omega \exp\left\{-\frac{ms}{\langle n \rangle}\right\} \equiv \omega \exp\left\{-\frac{W_d}{kT}\right\}, \quad (4)$$

where  $kT \equiv \langle n \rangle \hbar \omega / s$ ,  $\langle n \rangle$  is the mean number of photons/molecule, and  $W_d$  is the dissociation energy. Formula (4) is the familiar Arrhenius equation which is valid for many kinetic processes.

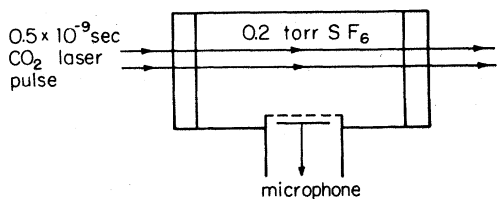


FIG. 2. The opto-acoustic experiment for measuring the vibrational temperature in the quasicontinuum. The ultrashort CO<sub>2</sub>-laser pulse ensures that all molecules reach the quasicontinuum shown in Fig. 1.

We have made direct opto-acoustic<sup>17</sup> measurements of the vibrational temperature, which in combination with the dissociation data<sup>11</sup> confirm Eq. (4) quantitatively. The apparatus is shown in Fig. 2. The system must be carefully calibrated, since a major portion of the deposited energy is conducted to the walls without contributing to the acoustic impulse. A valid temperature measurement demands an ultrashort CO<sub>2</sub>-laser pulse. The peak power must be high enough to ensure that all molecules in the rotational manifold overcome the "anharmonicity barrier" and reach the quasicontinuum where the behavior is statistical.<sup>18</sup>

Figure 3 plots a comparison between  $\langle n \rangle$  and  $\langle n' \rangle$ , the number of photons/molecule deposited by the ultrashort and conventional CO<sub>2</sub>-laser

pulse, respectively. The difference between  $\langle n \rangle$  and  $\langle n' \rangle$  is attributed to the fraction  $f$  of molecules which cannot reach the quasicontinuum from their initial vibrational-rotational state in the longer pulse with lower peak intensity,

$$f \sim (\langle n \rangle - \langle n' \rangle) / (\langle n \rangle - 3), \tag{5}$$

under the assumption that 3 is the average excitation of the molecules which remain bottlenecked among the discrete levels. The fraction,  $f$ , is about  $\frac{2}{3}$  at dissociation threshold,<sup>11</sup> 1.4 J/cm<sup>2</sup>, and eventually goes to zero as the energy fluence rises to 10 J/cm<sup>2</sup>.

From Fig. 3,  $\langle n \rangle = 20$  photons-molecule are deposited by the ultrashort pulse at dissociation threshold, implying a vibrational temperature for the isolated molecule of  $T = 1800^\circ\text{K}$ . This absolute measurement is in good agreement with the Arrhenius estimate,  $\sim 1500^\circ\text{K}$ , of the threshold temperature required for dissociation under our experimental conditions. It is also in good agreement with shock-tube measurements<sup>19</sup> of the threshold temperature required for thermal dissociation of SF<sub>6</sub>. The slow temperature increase above threshold implies, through Eq. (4), a rapid increase in dissociation yield per pulse, again consistent with observations<sup>3,11</sup> which show that this yield rises from 10<sup>-4</sup> at observable threshold to near 1 for an energy fluence one or-

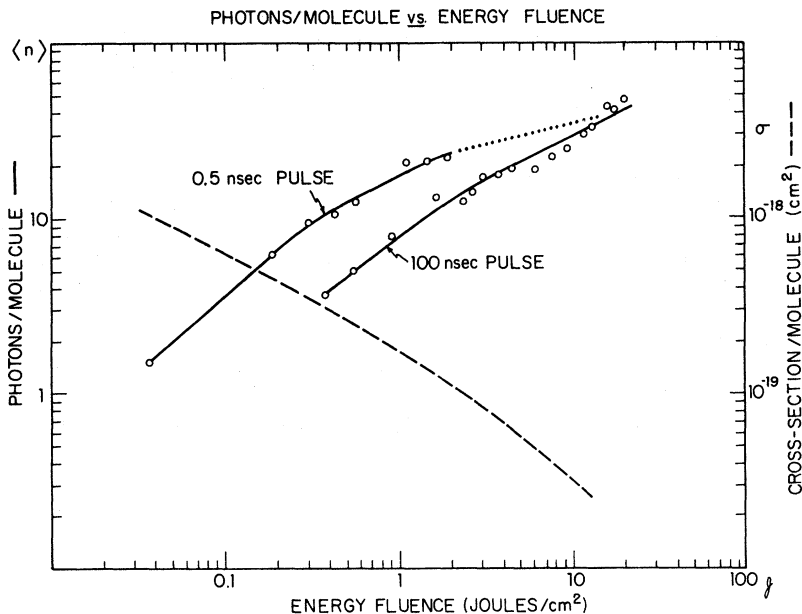


FIG. 3. The vibrational excitation per molecule as a function of laser energy fluence for two pulse duration. "Bottlenecking" in the lower discrete rungs of the vibrational ladder occurs for the longer laser pulse. The dashed line (right-hand scale) indicates the absorption cross section defined by the slope of the short-pulse data.

der of magnitude higher than threshold.<sup>20</sup> Therefore, the statistical theory (RRKM) provides good quantitative agreement between our measurements of quasicontinuum temperature and the dissociation yield.

The measurement of  $\langle n \rangle$  may also be interpreted in terms of the absorption cross section  $\sigma$  of the SF<sub>6</sub> molecule,

$$\sigma = d(\langle n \rangle \hbar \omega) / d g, \quad (6)$$

where  $g$  is the energy fluence in Joules per square centimeter. The trend of this continuum absorption cross section with vibrational excitation is also sketched in Fig. 3. The absorption cross section falls rapidly to less than  $10^{-19}$  cm<sup>2</sup> as the molecule is heated in the quasicontinuum. The drop in cross section is due to a shift and broadening in absorption spectrum as the molecule is heated.<sup>21</sup> In fact, the absorption cross section which we measure at  $\langle n \rangle \hbar \omega / sk = 1700^\circ\text{K}$  is in good agreement with the observed<sup>21</sup> cross section in shock-tube-heated SF<sub>6</sub>. Clearly, more work is needed on the spectral properties<sup>22</sup> in the quasicontinuum of polyatomic molecules.

The data on energy absorption and dissociation of SF<sub>6</sub> are consistent with the statistical thermodynamical behavior of the molecule in the quasicontinuum of vibrational states.

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