

COLLISIONLESS MULTIPHOTON DISSOCIATION OF SF₆:
A STATISTICAL THERMODYNAMIC PROCESS

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ABSTRACT

An experiment, which combines picosecond CO₂ laser pulses with opto-acoustic techniques, proves that the collisionless multiphoton dissociation SF₆ is a statistical thermodynamic process. The RRKM theory of unimolecular reactions, familiar to most physical chemists, 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.

I. INTRODUCTION

The interest in laser dissociation of molecules¹ became widespread when it was first shown² to be isotopically selective. Figure 1, the early work^{3,4} of Letokhov and Ambartsumyan, shows that the isotopic selectivity is simply due to the mass shift in the infra-red spectrum of SF₆.

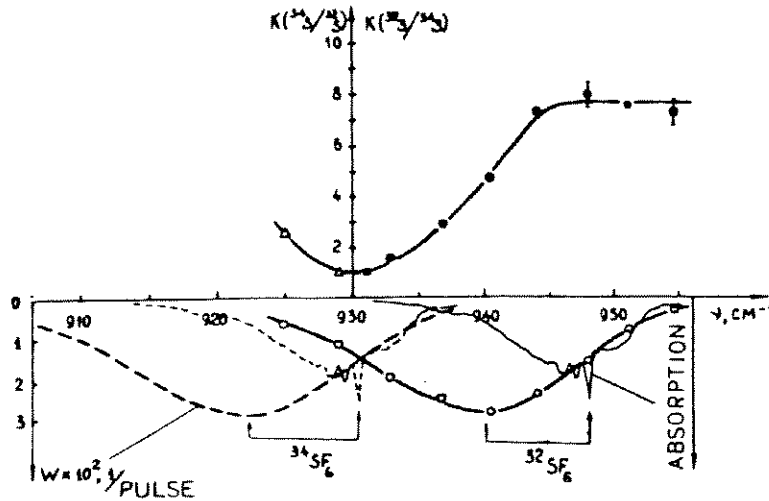


Fig. 1. This is early data by Ambartsumyan et al., (ref.4). The upper part of the graph shows the isotopic selectivity, while the lower part compares the dissociation yield spectrum with the linear absorption spectrum for the two isotopes ^{34}S and ^{32}S . Notice the red shift in the dissociation spectrum.

It was quickly established⁵ that the process is essentially collisionless, involving only the interaction of an isolated molecule with the intense radiation field. As such, it presents an interesting and novel physical problem: How can an isolated molecule absorb the 40 or more infrared quanta needed for dissociation?

This paper will stress the physics of the multiphoton dissociation mechanism. We will find that statistical thermodynamics plays a major role in the effect. The paper will be divided into four sections:

The first section will describe the quantum levels of the SF_6 molecule, from the ground state, through the quasicontinuum, up to dissociation. The changing spectral properties of each region will be emphasized.

The second section of the paper will describe measurements of the dissociation yield as a function of laser energy and pulse duration down to 500 picoseconds. We will show why the pulse duration measurements are able to distinguish between the "anharmonicity bottleneck" and other dissociation inhibiting mechanisms.

In the third section of the paper we will show that a statistical thermodynamic approach is appropriate for the quasicontinuum. Therefore we will introduce the RRKM theory of unimolecular reactions.

The fourth section of the paper will describe direct opto-acoustic measurements of the vibrational temperature induced by ultrashort CO₂ laser pulses. These measurements are in good agreement with the statistical thermodynamic theory of dissociation yield. They permit a direct estimate of the fraction of molecules stuck in the "anharmonicity bottleneck." The measurements also show a rapidly falling absorption cross-section as the molecule ascends the quasicontinuum.

II. QUANTUM LEVEL STRUCTURE OF SF₆

A physical understanding has to be based on a knowledge of the energy spectrum of the SF₆ molecule. As a result of the upsurge of interest in the past year⁶ we now have rough idea of the SF₆ molecular energy levels, as shown in Figure 2. The detailed structure⁷ is omitted both for simplicity and also because much of it is not yet known. Nevertheless, the important overall features are present in Fig. 2. In particular the energy levels are divided into three regions,⁸ as indicated by the large Roman numerals.

Region I, the lowest excited states, consists of

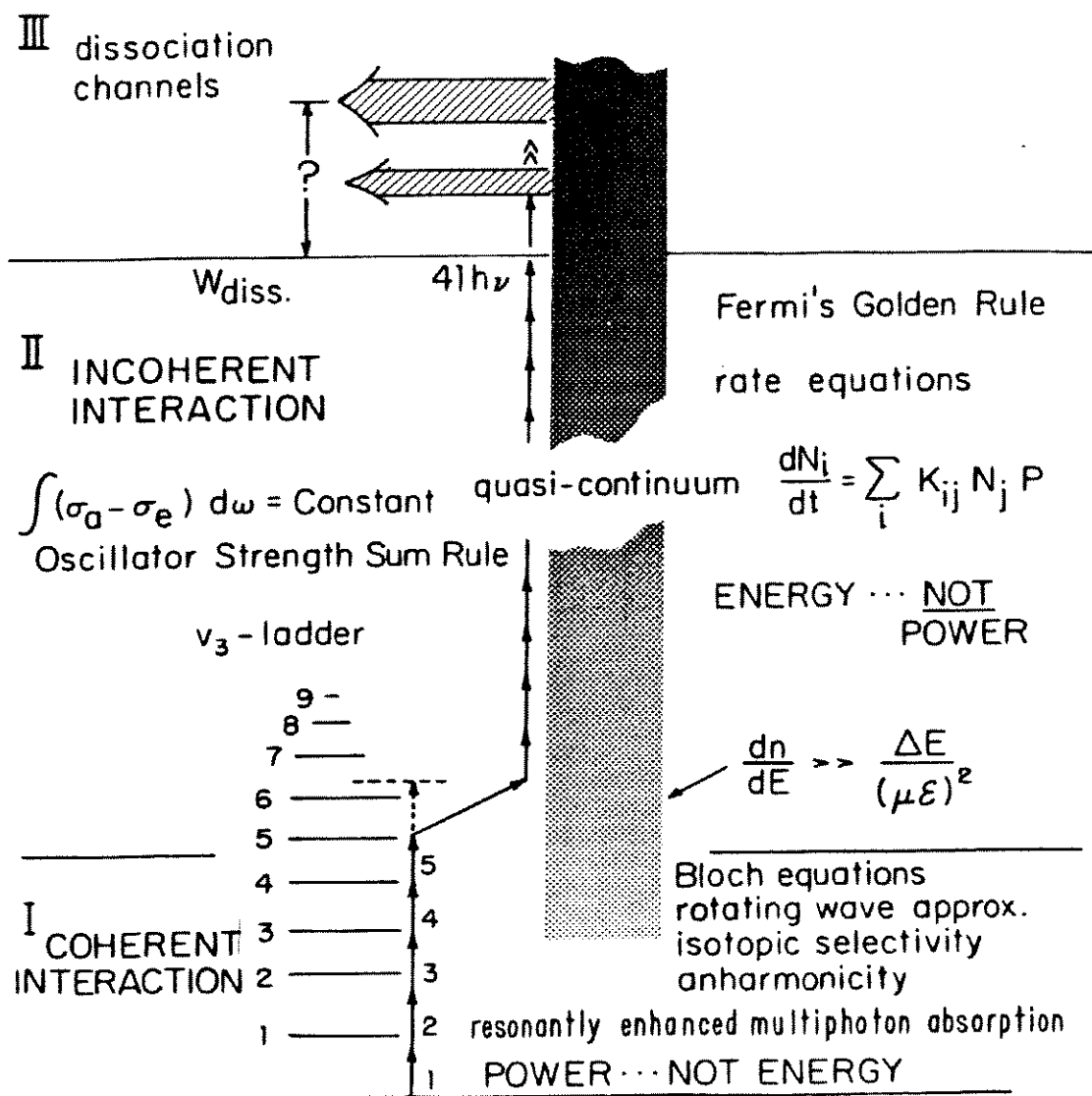


Fig. 2. The quantum level structure of the SF₆ molecule (simplified!). The energy levels are divided into three regions; Region I, the discrete levels in which the interaction is coherent, Region II the quasicontinuum of levels where incoherent interaction predominates and Region III, the true continuum where dissociation actually occurs. The quasicontinuum sets in when Eq. (1) becomes valid. Transitions in region I are primarily peak power dependent, while those in region II are energy fluence dependent.

discrete energy levels. It is symbolized by the ladder of anharmonic oscillator levels of the ν_3 vibrational mode. Of course, the other vibrational modes are not shown. With increasing energy, the phase space volume of a polyatomic molecule rises very rapidly, resulting in a high density of quantum levels. In SF₆ this quasicontinuum already sets in at a level of excitation corresponding to only 5 or 6 CO₂ laser photons (10.6 μ wavelength). This we will call region II. Finally there is the true continuum of energy levels lying beyond the dissociation energy, W_{diss} , about 40 laser photons. This is region III.

There is much to be learned by following a laser excited molecule up through Fig. 2, from the ground state to dissociation. In region I, containing discrete levels, the molecular evolution is best described in terms of Bloch equations.⁹ This is the region of coherent interaction. The rotating-wave approximation is appropriate. Anharmonicity of the vibrational ladder tends to limit the sequential absorption of photons. This is called the "anharmonicity bottleneck". Resonantly enhanced multiphoton absorption⁶ tends to overcome the "anharmonicity bottleneck." But the peak absorption is then red-shifted a few wave numbers from the linear absorption peak, as shown in Fig. 1. Due to the multiphoton character⁶ of the absorption it is the peak power of the laser pulse rather than its energy which is important in driving the molecule through region I. Finally, the most important property of region I is the isotopic shift of the discrete levels, which permits the selectivity. The other isotopic species is not excited and remains near the bottom of region I.

At a level of excitation corresponding to about 5 laser photons, the density of states rises and the oscillator strength of the ν_3 mode becomes spread over a number of vibrational levels. When the density of states is large enough and the matrix elements are small enough, Fermi's Golden Rule takes over as the correct description of the molecular evolution. From the conditions of validity⁹ of Fermi's Golden Rule, region II begins when the density of states is:

$$\frac{dn}{dE} \gg \frac{\Delta E}{(\mu E)^2}, \quad (1)$$

where ΔE is the energy width of the band into which the oscillator strength is smeared and μE is the dipole matrix element from the ground state. Equation (1) becomes valid at a level of excitation of 5 or 6 photons, marking the onset of region II.

Fermi's Golden Rule implies that Rate equations rather than Bloch equations are appropriate for the temporal evolution of the molecule in the quasicontinuum. Therefore incoherent interaction describes region II. A typical rate equation is

$$\frac{dN_i}{dt} = \sum_j K_{ij} N_j P - K_{ji} N_i P, \quad (2)$$

where N_i is the probability of occupation of the i -th stationary state and $K_{ij} P$ is the transition rate between i and j which is explicitly proportional to the laser power P . The important property of Eq. (2) is that the right hand side is explicitly proportional to the laser power P which can therefore be divided out. Equation (2) becomes:

$$\frac{dN_i}{d(Pt)} = \sum_j K_{ij} N_j - K_{ji} N_i \quad (3)$$

Equation (3) depends only on (Power) × (time) or in other words laser energy. Only the laser energy, rather than the peak power, is important for transitions in the quasicontinuum.

Another important property, the oscillator strength sum rule,¹⁰ is valid for any state in region II:

$$\int (\sigma_a - \sigma_e) d\omega = \text{Constant} \quad (4)$$

The net absorption cross section ($\sigma_a - \sigma_e$) is the difference between the absorption and stimulated emission cross-sections. We may anticipate that further smearing of the oscillator strength in the quasicontinuum will reduce the net absorption cross-section, hindering dissociation.

Finally we come to region III of figure 2. Here the important question is how much excess energy, above W_{diss} , would be required to produce dissociation in a finite time.

III. PICOSECOND MEASUREMENTS OF DISSOCIATION YIELD

A typical measurement¹¹ of dissociation yield is shown in Fig. 3. The absolute dissociation probability rises rapidly from a threshold at 1.4 Joules/cm². At a laser fluence of 10 J/cm² the probability is already near unity. There are two possible "bottlenecks" which would tend to limit the dissociation:

(i) Anharmonicity of the first few discrete levels.¹² This may prevent excitation of the molecule while it is in region I.

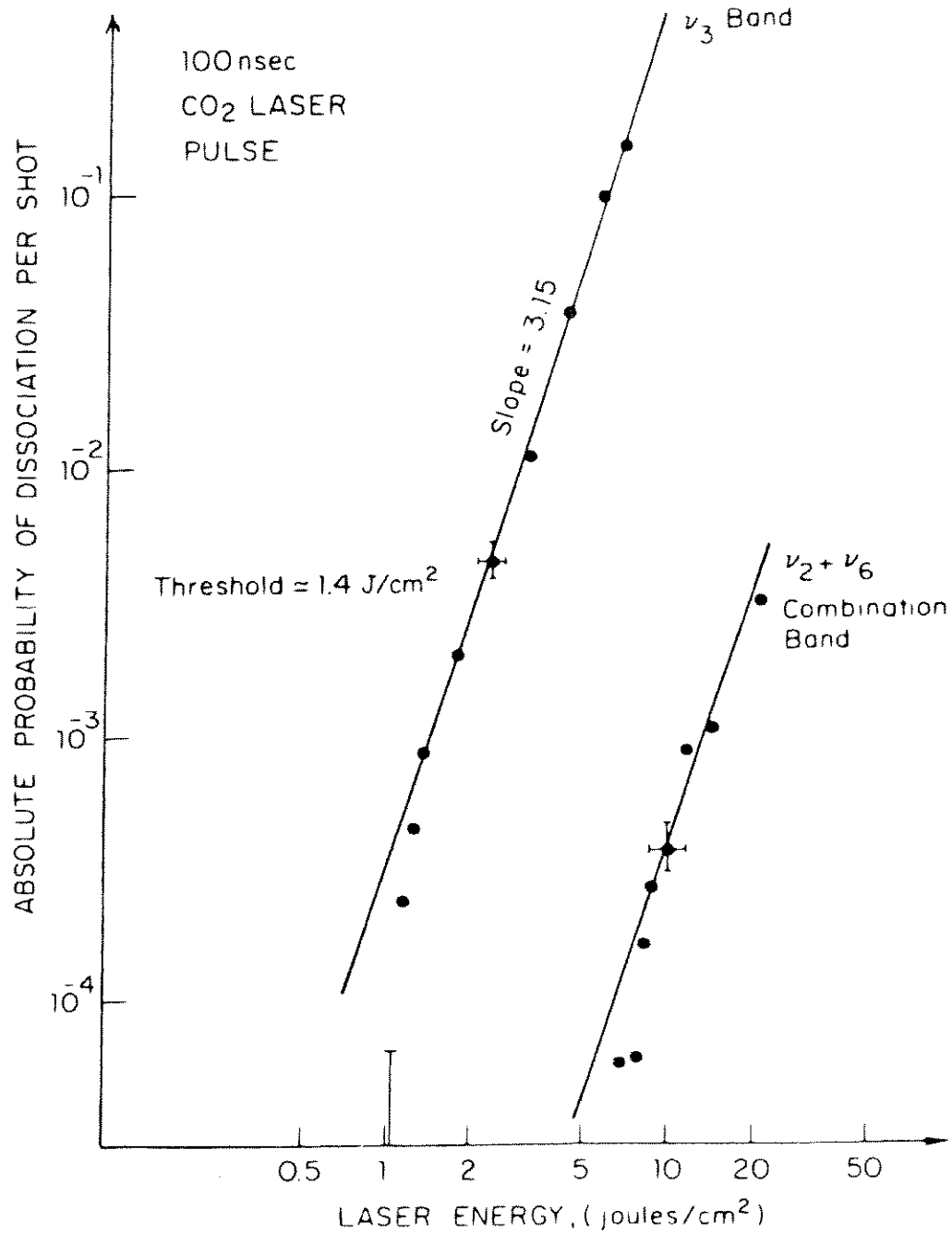


Fig. 3. The absolute dissociation yield vs. energy fluence for irradiation in the ν_3 band. There is a sharp threshold at $J = 1.4 \text{ J/cm}^2$ followed by a rapid rise to near unity probability. Also shown is the yield for irradiation in the $\nu_2 + \nu_6$ combination band.

(ii) Smearing of the oscillator strength in the quasicontinuum. This would lead to a reduced absorption cross-section and less efficient heating of the molecule in region II.

Pulse duration dependence of the dissociation yield is able to discriminate between these two possible bottlenecks. Overcoming the "anharmonicity barrier" is quite sensitive to the peak power of the laser beam. Multiphoton absorption in region I is rather dependent on the magnitude of the Rabi-precession frequency $\mu E/\hbar$. On the other hand, only the laser energy, not the peak power, is important for transitions in the quasicontinuum, region II.

Harvard's short pulse CO₂ laser facility¹³ was available for these measurements. It generates 500 psec pulses by the optical free induction decay technique¹⁴ and amplifies them up to the 0.15 J level. For a given energy, these ultrashort pulses have 200 times higher peak power than the typical 100 nsec TEA CO₂ laser pulses. Therefore, if mechanism (i) is at all important, the reduction of pulse duration, for fixed energy, should have a powerful effect on the dissociation yield. Figure 4 shows the experimental result. While the peak power is changing 2 orders of magnitude, the dissociation increases only 30 per cent!

Therefore mechanism (i) plays only a minor role and it is mechanism (ii), transition in the quasicontinuum, which acts to limit the dissociation yield. Region II, of the quantum level structure (Fig. 2), is where the important rate-limiting physics is taking place.

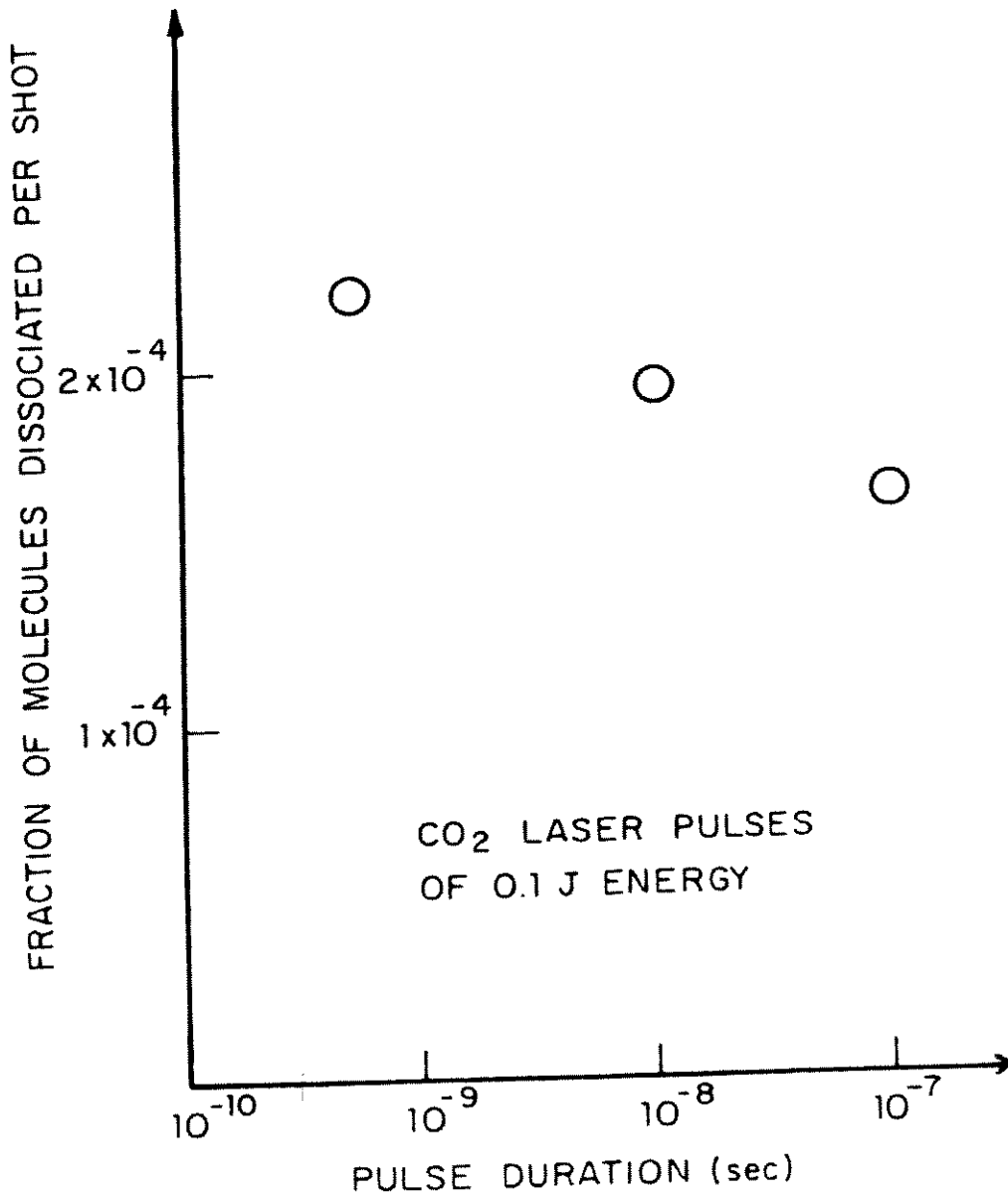


Fig. 4. A comparison of the dissociation yield for pulses of widely varying duration, but fixed energy. For a 200-fold increase in peak power the fraction of molecules dissociated increased only 30%. This proves that interactions in the quasicontinuum are more important than the "anharmonicity bottleneck" in the discrete levels.

IV. STATISTICAL DESCRIPTION OF THE QUASI-CONTINUUM

We have already mentioned that transitions in the quasicontinuum are of an incoherent nature. That is, the molecular evolution is best described in terms of kinetic rate equations (2), rather than the coherent Bloch-type⁹ equations. Two conclusions follow directly from this:

(a) In spectral region II only the energy fluence (Joules/cm²) is important. This was proved earlier in this paper.

(b) It is known in quantum electronics that an incoherently driven oscillator assumes¹⁵ a "Planck" distribution at a well-defined temperature. This is shown in Reference 15 or may be proven directly from the rate equations for an oscillator.

Conclusions (a) and (b) follow from the kinetic rate equations (2). They rely on the assumption of ergodicity, which is justified if the rate of intramolecular VV relaxation is faster than the rate of absorption of photons. A large body of experimental evidence¹⁶ shows that intramolecular VV times are in the one picosecond range for polyatomics. Absorption cross-section measurements, to be described later in this paper, indicate that the rate of photon absorption is indeed slower than this.

Conclusion (b) is very important. Together with ergodicity it implies that all the oscillators in the SF₆ molecule have a "Planck" distribution at a well defined temperature. Therefore statistical thermodynamics may be employed in the description of the molecular evolution. A statistical approach is well known to physical chemists and is described, for example, in the text-book¹⁷ by Robinson and Holbrook,

entitled "Uni-Molecular Reactions."

In the RRKM theory, the accepted statistical model¹⁷ for molecular dissociation, the molecular energy must exceed the dissociation energy by a finite amount in order to get reasonable dissociation rates. Physically, this is because the phase space of a highly excited polyatomic is so huge. The fraction of phase space which leads directly to dissociation is relatively small unless the dissociation energy is significantly exceeded. A typical formula¹⁷ for the rate of dissociation is:

$$\text{Rate} = \omega \frac{n! (n-m+s-1)!}{(n-m)! (n+s-1)!} \quad (5)$$

Here ω is an average vibrational frequency, s is the no. of vibrational degrees of freedom (15 for SF_6), m is the minimum no. of absorbed photons needed for dissociation and n is the number actually absorbed. Formula (5) predicts that n must exceed m by 10 to 15 photons in order to produce dissociation during a typical laser pulse. This is in rough agreement with the molecular beam measurements of Lee¹⁸ et al.

When formula (5) is averaged over a statistical distribution of SF_6 states, the result for the average rate of dissociation is:

$$\text{Average Rate} = \omega \exp \left\{ -\frac{ms}{\langle n \rangle} \right\} \equiv \omega \exp \left\{ -\frac{W_d}{kT} \right\}, \quad (6)$$

where $\langle n \rangle$ is the average number of photons absorbed per molecule. The temperature of the molecule is:

$$kT \equiv \frac{\langle n \rangle \hbar \omega}{s} \quad (7)$$

Formula (6) is the familiar Arrhenius equation, which is valid for many kinetic processes.

The theoretical arguments given in this section, imply that a statistical thermodynamic approach is appropriate to describe the multiphoton dissociation of SF₆. An experimental confirmation of this approach demands a direct measurement of the molecular temperature, as well as good agreement with the Arrhenius equation (6). These measurements are described in the next section.

V. PICOSECOND, OPTO-ACOUSTIC, TEMPERATURE MEASUREMENT

As discussed in Section III of this paper, ultrashort CO₂ laser pulses are particularly suited for measuring the quasicontinuum properties of SF₆. The high peak power of an ultrashort pulse, implies a high Rabi precession frequency, which implies that all molecules in the rotational manifold overcome the anharmonicity barrier and interact in the quasicontinuum. Figure 5 shows a simple opto-acoustic¹⁹ apparatus used for measuring the quasicontinuum temperature of SF₆.

The microphone responds to the pressure rise induced in the gas. The system must be carefully calibrated since a major portion of the energy is conducted to the walls without contributing to the acoustic impulse. A laser power meter determined the energy deposited per molecule at 5 torr pressure. Leaving the illumination conditions unchanged, the pressure was reduced to 0.2 torr and the acoustic signal was determined for the given energy deposition. (This technique is similar to that employed by Letokhov¹⁹ except that the ultrashort pulses obviated the need for a long optically thick cell).

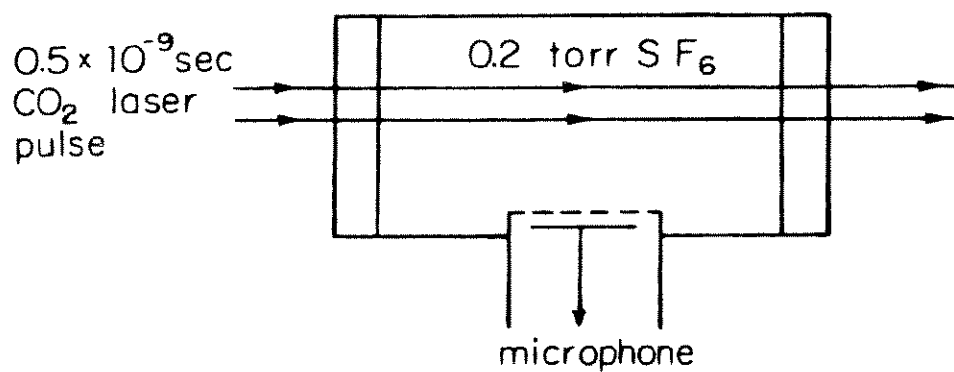


Fig. 5. The opto-acoustic experiment for the measurement of the energy deposited per molecule. This directly determines the vibrational temperature to be used in the Arrhenius Eq. (6). The ultra-short CO₂ laser pulse ensures that there is no bottlenecking in the discrete levels.

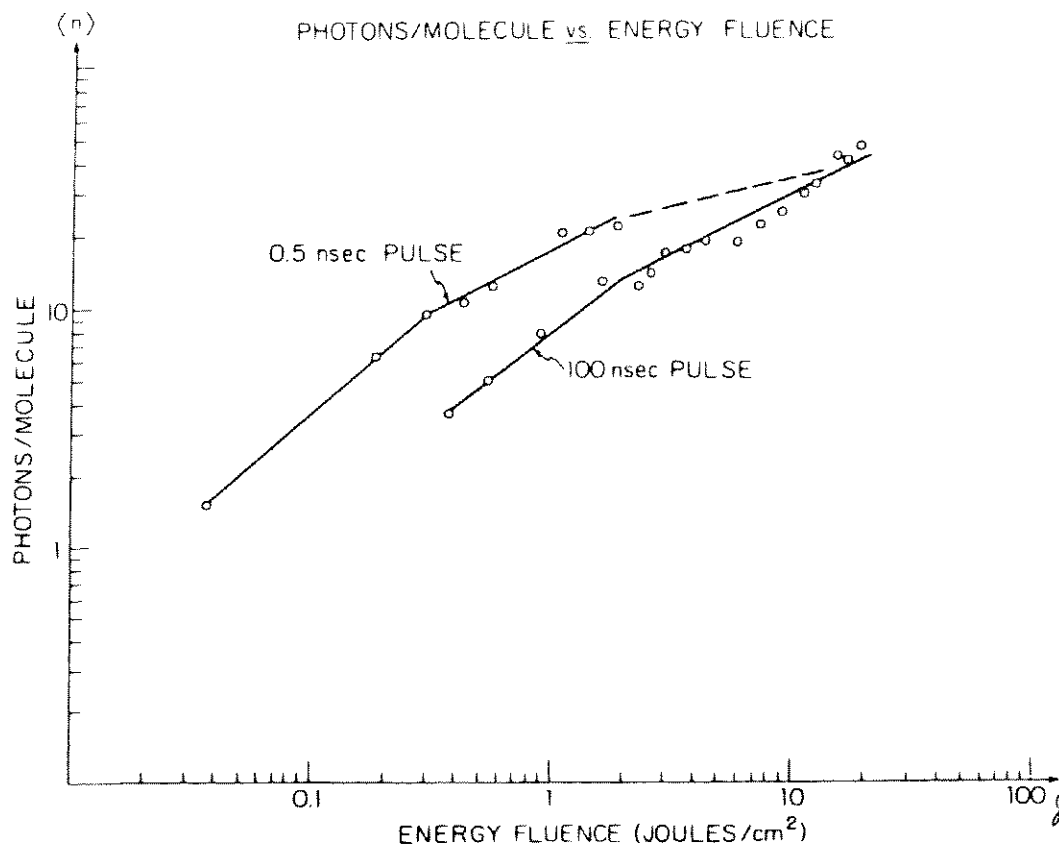


Fig. 6. The number of photons per molecule vs. the energy fluence (J/cm^2). The difference between the two curves permits an estimate of the fraction, f , of molecules stuck in the discrete energy levels. The vibrational temperature as measured by the 0.5 nsec pulses, is in good quantitative agreement with the Arrhenius eq. (6), confirming the statistical thermodynamic approach.

A comparison of the number of photons/molecule deposited by an ultrashort pulse and a conventional TEA laser pulse is shown in Figure 6. At dissociation threshold, 1.4 J/cm^2 , the 100 nsec pulse deposits $\langle n' \rangle = 10$ photons/molecule while the ultrashort pulse deposits $\langle n \rangle = 20$ photons/molecule. The difference²⁰ between $\langle n \rangle$ and $\langle n' \rangle$ must be attributed to anharmonicity bottlenecks in the long TEA laser pulse. Therefore the fraction, f , of bottleneck molecules may be readily estimated;

$$f \sim \frac{\langle n \rangle - \langle n' \rangle}{\langle n \rangle - 3}, \quad (8)$$

assuming 3 is the average excitation of the molecules which remain bottlenecked in the discrete levels. The fraction, f , which is about $2/3$ at the dissociation threshold, 1.4 J/cm^2 , eventually goes to zero as the energy fluence rises to 10 J/cm^2 .

The number $\langle n \rangle = 20$ photons/molecule implies a vibrational temperature of the isolated molecule, $T = 1800^\circ\text{K}$ at threshold. This absolute measurement is in good quantitative agreement with the Arrhenius equation (6) estimate, $\approx 2000^\circ\text{K}$, of the threshold temperature required for dissociation under the experimental conditions. The dissociation yield rises rapidly above threshold (see Fig. 3) even for the small observed vibrational temperature increase (see Fig. 6), again consistent with the Arrhenius equation. Therefore the statistical theory (RRKM) provides good quantitative agreement between measurements of dissociation yield and vibrational temperature.

The measurement of $\langle n \rangle$, the number of photons absorbed per molecule, may also be interpreted in terms

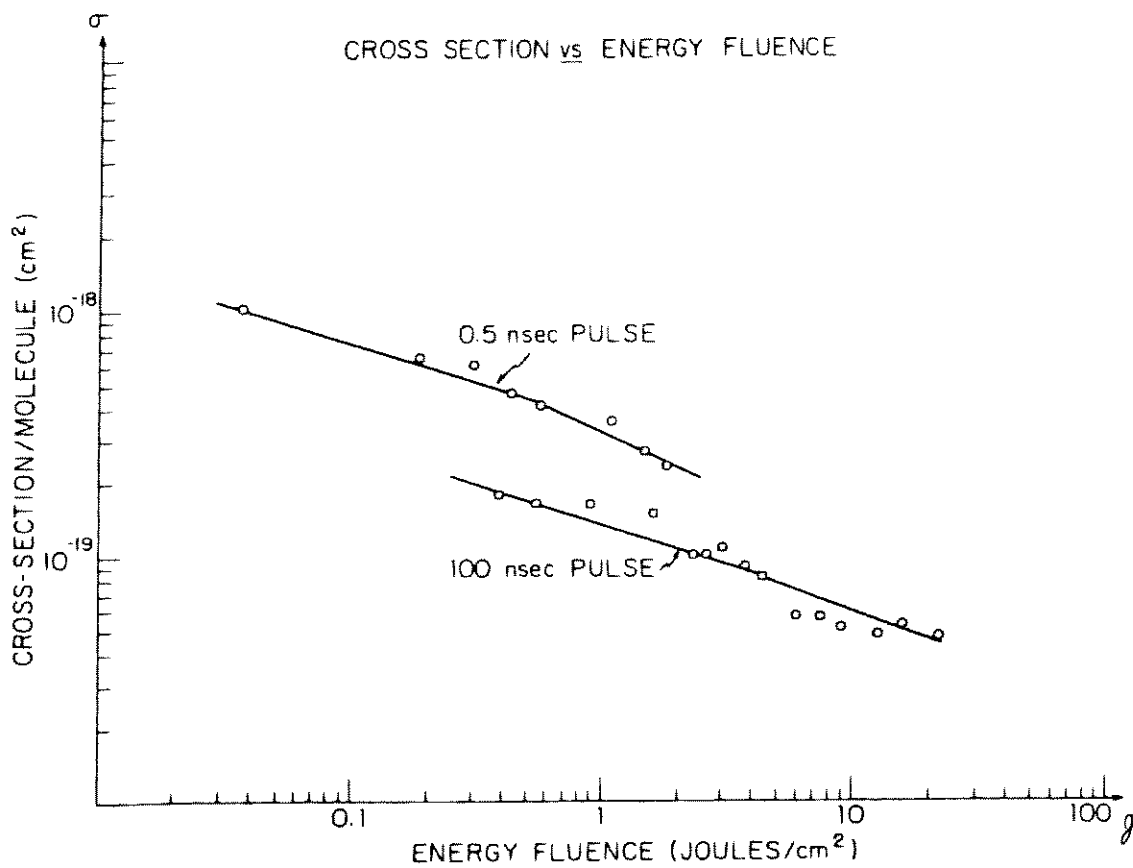


Fig. 7. The cross section falls rapidly as the molecule is heated. This is the major dissociation limiting mechanism.

of the absorption cross section, σ , of the SF₆ molecule.

$$\sigma = \frac{\langle n \rangle \hbar \omega}{J} \quad , \quad (9)$$

where $\hbar \omega$ is the photon energy and J is the energy fluence in Joules/cm². This data is plotted in Figure 7. Of perhaps greater interest is the absorption cross section σ' of the excited molecule in the quasicontinuum, which is given by the differential version of formula (9):

$$\sigma' = \frac{d}{dJ} (\langle n \rangle \hbar \omega) \quad . \quad (10)$$

Obviously, σ and σ' differ only by a factor α , which is the logarithmic slope of the curve in Figure 6.

Figure 7 shows that the absorption cross-section falls rapidly to less than 10^{-19} cm², as the molecule is heated in the quasicontinuum. This is consistent with the oscillator-strength sum rule¹⁰, Eq. (4), provided that the oscillator strength is smeared over 1000 cm⁻¹. Alternatively, the drop in cross-section may be due to a shift in the absorption spectrum as the molecule is heated. Clearly, more work is needed on the spectral properties²¹ in the quasicontinuum of polyatomic molecules.

REFERENCES

1. N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. 18, 225 (1971).
2. R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov and N. V. Chekalin, JETP Lett. 20, 273 (1974).
J. L. Lyman, R. J. Jensen, J. Rink, C. P. Robinson and S. D. Rockwood, Appl. Phys. Lett. 27, 87 (1975).
3. Proceedings of the Nordfjord Conference on Tunable Lasers and Applications, ed. by A. M. Mooradian (Springer-Verlag, 1976).
4. See the article by R. V. Ambartsumyan in Ref. 3.
5. See the article by Kompa in Ref. 3.
6. See the article by N. Bloembergen, C. D. Cantrell and D. M. Larsen in Ref. 3.
7. C. D. Cantrell and H. W. Galbraith, Opt. Comm. 18, 513 (1976).
8. S. Mukamel and J. Jortner, Chem. Phys. Lett. 40, 150 (1976).
9. R. H. Pantell and H. E. Puthoff, Fundamentals of Quantum Electronics, (Wiley, New York, 1969).
10. E. Merzbacher, Quantum Mechanics, (Wiley, New York, 1961).
11. P. Kolodner, C. Winterfeld and E. Yablonovitch, Opt. Comm. to be published.
12. N. Bloembergen, Opt. Comm. 15, 416 (1975).
13. H. S. Kwok and E. Yablonovitch, Rev. Sci. Instrum. 46, 814(1975).
14. E. Yablonovitch and J. Goldhar, Appl. Phys. Lett. 25, 580 (1974).
15. W. H. Louisell, Quantum Statistical Properties of Radiation, (Wiley, New York, 1973).
16. J. D. Rynbrandt and B. S. Rabinovitch, J. Phys. Chem. 75, 2164 (1971).

17. P. J. Robinson and K. A. Holbrook, Uni-Molecular Reactions (Wiley, New York, 1972).
18. M. J. Coggiola, P. A. Schulz, Y. T. Lee and Y. R. Shen, Phys. Rev. Lett. 38, 17 (1977).
19. V. N. Bagratashvili, I. N. Knyazev, V. S. Letokhov and V. V. Lobko, Opt. Comm. 18, 525 (1976).
20. The departure from RRKM theory observed by D. F. Dever and E. Grumwald, J. Am. Chem. Soc. 98, 5055 (1976) was probably due to the fraction, f , of molecules which were unable to overcome the "anharmonicity barrier". A similar departure would be observed here if $\langle n' \rangle$ rather than $\langle n \rangle$ were used to determine the vibrational temperature.
21. R. V. Ambartsumyan, N. P. Fuzikov, Yu. A. Gorokhov, V. S. Letokhov, G. N. Marakhov and A. A. Puretzky, Optics Comm. 18, 517 (1976).