

A statistical theory for collisionless multiphoton dissociation of SF₆

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A statistical thermodynamic theory is used to calculate the dissociation efficiency of SF₆ by CO₂ laser photons. The dissociation efficiency calculated with the model presented is compared to that calculated with two other statistical models, one a more sophisticated model (RRKM) and the other a very crude model. We find that the calculated dissociation efficiency is insensitive to the particular statistical model used.

I. INTRODUCTION

Since its discovery in the early 1970's,¹ laser induced dissociation of polyatomic molecules has been the subject of many investigations.² Interest in this dissociation became widespread when it was shown to be isotopically selective.³ Soon after, it was established that the process is collisionless, involving only the interaction of an isolated molecule with the intense radiation field. As such, it presents an interesting and novel question: How can an isolated molecule absorb the 30 or more infrared photons required for dissociation?

Efforts to elucidate the answer to the above question have resulted in the following general picture of dissociation.^{4,5} The molecular energy levels are divided into three regions; the first is characterized by discrete energy levels and coherent excitation, the second is the quasicontinuum where the level density is very high, and the last is the true continuum.

In a recent publication, Kolodner, Winterfeld, and Yablonovitch⁶ have studied the dissociation efficiency as a function of laser intensity and pulse duration, and were able to show that the efficiency is a function of the product of intensity times pulse duration. This result suggested that, provided the laser intensity is high enough that the molecule is able to absorb the three to six photons necessary to climb through region one, the dissociation efficiency is controlled by the properties of region two. A subsequent calorimetric experiment⁷ showed that absorption and dissociation in the second region is consistent with statistical thermodynamics.

In this paper we present a quantitative calculation which assumes not only the energy is randomized over the vibrational modes of the molecule, but also that the molecular distribution function is well characterized by a vibrational temperature, and that this distribution is not significantly perturbed by dissociation. Since experimental evidence¹² indicates that intramolecular VV relaxation times are on the order of 1 psec for highly excited polyatomics, the randomization assumption seems to be on a fairly firm ground. As mentioned above, a recent experiment by Black *et al.*⁷ was consistent with a thermal distribution model. Indeed, part of the purpose of this calculation was to perform a calculation based on the thermal distribution assumption but employing quantum statistics and eliminating the classical equipartition assumption used in the earlier work to further test the consistency of the thermal distribution

model with experimental results. Preliminary results indicate that although perhaps a bit narrow, a thermal distribution accounts well for experimental measurements. This comparison will be explored further in a subsequent publication. The final assumption of this work, i. e., that the thermal distribution is not greatly altered by dissociation, should be fairly good in the low yield limit.

Throughout this paper we shall primarily discuss a simple statistical model for calculating the total fraction of molecules which dissociate in a given laser pulse. This model incorporates the above three assumptions and further assumes that all molecular vibrations are degenerate. This last assumption leads to a conceptually simple model with a direct physical interpretation for all parameters. In addition, this final assumption simplifies the calculations so that one can quickly test the effect of a given molecular distribution function on the dissociation yield. However, since the degenerate vibration assumption is admittedly crude, we compared results of this calculation both to results of the more accurate and widely used RRKM model and to a much simpler model. We find that our results are insensitive to the particular statistical model used. In fact, the differences between our simple model and the RRKM model are smaller than the present experimental uncertainty. In addition, the differences between the two models are smaller than the uncertainty in the molecular distribution function.

In this publication we will primarily discuss unimolecular theory.⁸ The next section describes the quantities involved in the theory, the third section presents the results, and the final section discusses the conclusions to be drawn.

II. THE THEORY

A basic assumption of this theory is that in order for a molecule to undergo unimolecular dissociation, that molecule must contain a minimum amount of energy. That is, there is a critical energy below which no reaction occurs. For laser induced dissociation, the critical energy is acquired via absorption of infrared photons. Thus, there are a minimum number of photons which must be absorbed before the molecule can dissociate. For the present discussion, we will call this unspecified number m .

If all the molecules possessing the minimum energy

reacted instantaneously, it would only be necessary to know the distribution of molecules over the energy levels to calculate the total fraction of molecules that dissociate. Realistically, the molecules react at only a finite rate. Therefore, we will first calculate the rate of reaction for molecules with a given amount of energy, then we will calculate the fraction of molecules with that energy which dissociate, and finally we will calculate the distribution of the molecules over the energy levels. Given the above quantities, we will then calculate the total fraction of molecules which dissociate given a particular laser pulse.

A. The reaction rate

The finite dissociation rate arises as follows. For example, for bond breaking, consider the molecule as a collection of s oscillators. Then the oscillator representing the bond to be broken (the reactive coordinate) must be able to stretch to infinity, i. e., that bond must contain at least a critical energy. If the distribution of energy in the molecule is such that less than this critical energy is in the reactive coordinate, then the bond will not break, and the molecule will not dissociate. However, the energy in the molecule will be constantly redistributing over the molecule, and after a sufficient time the bond of interest will have enough energy to break, provided, of course, that the isolated molecule contained sufficient energy to start with. Thus, the reaction rate is the inverse of the time that it takes the required m excitations to have unit probability to be in the desired oscillator.

We shall discuss a simple statistical model for calculating the reaction rate and compare the results to a calculation⁹ using the more sophisticated RRKM theory. We have chosen to use the less sophisticated model for the present discussion because it offers a simple yet realistic picture for the dissociation while giving a dissociation rate which is in qualitative agreement with RRKM results. In addition, we shall show that it makes little difference which model is used, since our final calculation is not very sensitive to the particular model used.

The theory we shall use is a slight modification of the *quantum* version of Kassel theory. We shall refer to it as the QRRK theory—the *Q* being added to emphasize that this is the quantum version and not the more widely known, but much less accurate, classical Kassel theory.

In both RRKM and QRRK theories the reaction rate for a molecule containing energy E is

$$R(E) = \frac{1}{2} k^\ddagger N^\ddagger(E^\ddagger) / N(E), \quad (1)$$

where k^\ddagger is the barrier crossing rate, $N^\ddagger(E^\ddagger)$ is the density of states of the activated molecule (molecule with m quanta fixed in the reactive coordinate), and $N(E)$ is the density of states of the molecule. In QRRK theory, k^\ddagger is taken as twice the rate of vibration of the molecule, i. e., $k^\ddagger = 2 \times 10^{13} \text{ sec}^{-1}$, which is a reasonable estimate of the rate of vibrational rearrangement within the molecule. The density of states is calculated by consider-

ing the molecule as a system of s degenerate harmonic oscillators and asking how many states are available to the molecule at an energy $E = nh\nu$, where ν is the frequency of the CO₂ laser pulse, i. e., $\nu = 943 \text{ cm}^{-1}$, and n is the number of photons absorbed. The answer, given by a combinatorial argument, is the binomial coefficient

$$N(nh\nu) = \binom{n+s-1}{s-1}. \quad (2)$$

This count of the number of states available to the molecule appears to be somewhat crude. However, it is justified because it is like a one-frequency grouping in the RRKM calculation where Whitten and Rabinovitch¹⁰ have shown that this grouping is in good agreement with an exact count at the energies we are considering here.

The density of states available to the activated complex is similarly calculated. We require that a minimum of m excitations are in the bond corresponding to the reaction coordinate, while the remaining $n - m$ excitations may be in any of the s oscillators. (Remember $mh\nu$ is the critical energy required before unimolecular dissociation can occur.) The activated complex density of states is again given by combinatorial theory as

$$N^\ddagger(E^\ddagger = (n - m)h\nu) = \binom{n - m + s - 1}{s - 1}. \quad (3)$$

By definition, m excitations must be fixed in the reactive coordinate in order to form the activated complex; thus the activated complex has much less energy (only $n - m$ excitations) available to redistribute over the complex. It turns out¹⁰ that for such low energies, treating the complex as a collection of s equivalent oscillators is a fairly crude approximation and is responsible for most of the discrepancy between the QRRK and the RRKM reaction rates.

The final step in calculating the QRRK reaction rate for the specific case of SF₆ is to realize that there are six equivalent S-F bonds which may be severed in the dissociation, and therefore a symmetry factor of 6 should be included. Thus, the QRRK reaction rate is

$$R_n = 6A \frac{(n - m + s - 1)! n!}{(n - m)! (n + s - 1)!}, \quad (4)$$

where the subscript n denotes that this is the rate of reaction for a molecule containing n excitations, and $A = \frac{1}{2} k^\ddagger$.

Reaction rates calculated using Eq. (4) are plotted in Fig. 1 as a function of energy above the critical energy, which we have taken to be equal to 30 photons in agreement with earlier thermal measurements.¹⁴ Figure 1 also compares the QRRK reaction rates with an RRKM calculation.⁹ An important point to be noted is that the two calculations are in qualitative agreement, i. e., the reaction rate rises sharply as a function of excess energy. In the final section of this paper we shall show that this behavior is all that is required to calculate the yield. In fact, a major conclusion of this work will be that efforts to improve agreement between experimental and theoretical yields should concentrate on determination of the molecular distribution function, because that

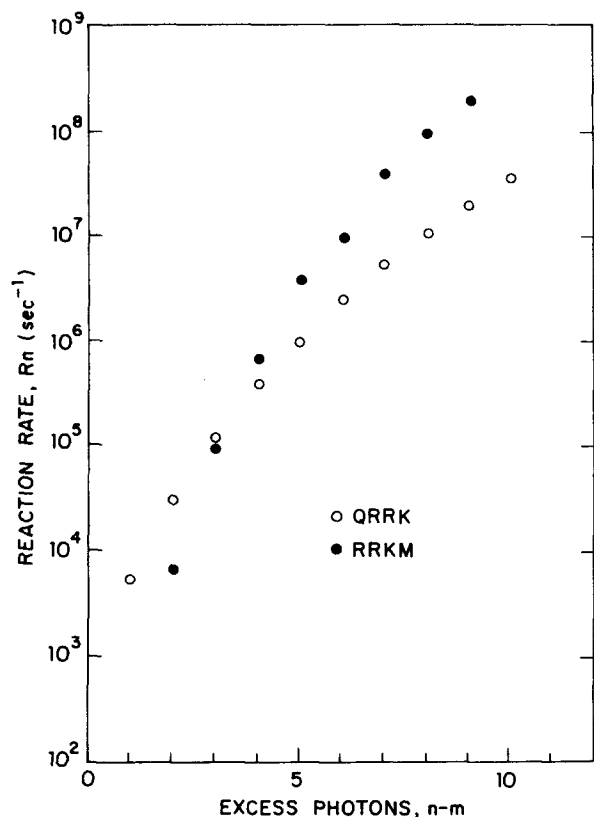


FIG. 1. Reaction rate as a function of the number of photons, $n-m$, above the critical energy, $mh\nu$. (RRKM calculation is from Ref. 9.) $m=30$ was used for the purposes of this calculation.

function has a much larger effect on the yield than the detailed behavior of the reaction rates.

At this point it is instructive to make a qualitative comparison with the results of Grant *et al.*,⁹ in which they found an experimental estimate for the dissociative lifetime to be 100 nsec. This is a reasonable lifetime because when the lifetime becomes this short, the molecule dissociates during the laser pulse. Figure 1 indicates that a lifetime of 100 nsec corresponds to an average energization of 6 photons above the dissociation limit for the RRKM model, while the simpler QRRK model predicts 7–8. The difference between these results is within the experimental error, and both are in reasonable agreement with the experimental work of Grant *et al.*

B. Fractional dissociation

The aim of this work is to calculate the fraction of all molecules dissociated by a given laser pulse. This fraction is naturally the fractional dissociation for each level of excitation times the probability of occupying that level, summed over all levels. Thus it is necessary to determine the fractional dissociation from any given level.

This fractional dissociation is given as the ratio

$$f_n = R_n / R_n^{\text{tot}}, \quad (5)$$

where R_n is the rate of dissociation from level n [given

by Eq. (1) or (4)] and R_n^{tot} is the loss rate from level n . For the experiment that we are considering—very dilute gas, no competing chemical reactions—molecules leave level n either by dissociation or by collisional deactivation. Thus,

$$R_n^{\text{tot}} = R_n + D, \quad (6)$$

where D is the mean collisional deactivation rate. Under typical experimental conditions (SF₆ pressure below 1 torr) the collisional deactivation rate¹¹ is $D \approx 10^6$ sec⁻¹.

Therefore, the fractional dissociation is

$$f_n = R_n / (R_n + D). \quad (7)$$

Equation (7) implies that any molecule containing less than the threshold energy will not dissociate because for $n < m$, $R_n = 0$. Also, if $R_n \gg D$, $f_n = 1$, i. e., if the dissociation rate is very fast compared to collisional de-excitation, all molecules having that energy will dissociate. Conversely, if the molecule takes too long to dissociate, it will de-excite and not contribute to dissociation.

Figure 2 illustrates the dependency of f_n on the number of excess photons for both the QRRK and RRKM reaction rates. Two points should be noted: (a) the RRKM curve rises somewhat faster than the QRRK curve (owing mainly to a more realistic counting of the number of states available to the activated molecule by the RRKM model), and (b) the two curves are in fairly good qualitative agreement. Also note once the molecule absorbs ~ 7 photons above the critical number, it is very likely to dissociate rather than de-energize via another pathway. This is the basic reason for the insensitivity of our results to the particular values of the reaction rates.

C. Distribution over the energy levels

The final quantity needed to determine the total fraction of molecules dissociated is the distribution of the

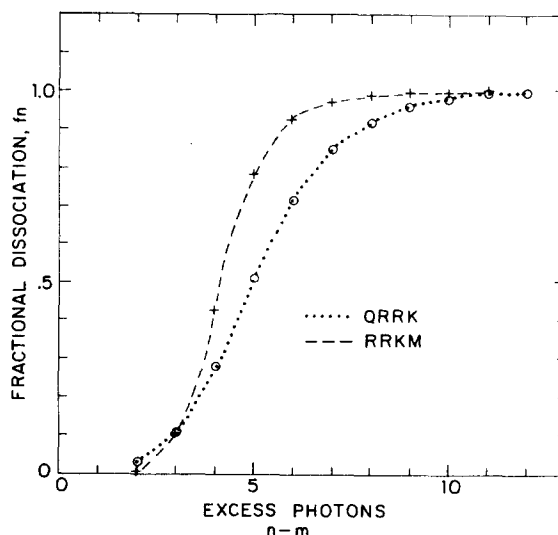


FIG. 2. Fractional dissociation as a function of excess photons, $n-m$. The critical number of photons is m .

TABLE. 1. Correspondence among the average number of photons absorbed, the temperature, and the classical equipartition temperature.

$\langle n \rangle$	11.2	12.3	13.4	14.5	15.5	16.8	18.0	19.4	20.7	22.1	23.5
T	1600	1700	1800	1900	2000	2100	2200	2300	2400	2500	2600
T eq. part.	1013	1113	1212	1312	1403	1520	1629	1755	1873	2000	2121

molecules over the levels of excitation. This distribution depends on the nature of the transitions in the quasi-continuum. We claim that transitions in the quasicontinuum are of an *incoherent* nature. That is, the molecular evolution is best described in terms of kinetic rate equations rather than the coherent Bloch-type equations.

This claim relies on an 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 evidence¹² shows that intramolecular VV times are in the 1 psec range for very highly excited polyatomics. In addition, absorption cross section measurements⁷ indicate that the rate of photon absorption is indeed slower than VV times for SF₆. Thus, transitions in the quasicontinuum are incoherent in nature.

It is well known in quantum electronics¹³ that an incoherently driven oscillator assumes a Planck distribution at a well-defined temperature. Therefore, statistical thermodynamics may be employed in the description of the population of the various levels of excitation.

Statistical thermodynamics gives the population of a narrow energy band about the energy E as

$$P(\delta E) = Q^{-1} N(E) \exp(-E/kT), \quad (8)$$

where Q is the molecular partition function, $N(E)$ is the density of states, and T is the vibrational temperature. Using Eq. (8) the correspondence between $\langle n \rangle$, the average number of photons absorbed, and T can easily be computed and is given in Table I. In Table I we have also listed the classical equipartition temperature (T eq. part.) corresponding to each $\langle n \rangle$. Notice that for each $\langle n \rangle$ the actual temperature is consistently higher than the classical equipartition temperature. This results from the fact that the condition $kT \gg h\nu_i$ is not satisfied by all vibrational modes of SF₆.

As indicated earlier, the density of states at energies near threshold is well approximated by QRRK theory; hence the density of states is given by Eq. (2). The vibrational energy for a molecule which has absorbed n photons of frequency ν is

$$E_n = nh\nu. \quad (9)$$

Therefore, the molecular partition function is

$$Q = \sum_{n=0}^{\infty} \frac{\alpha^n (n+s-1)!}{n! (s-1)!} = (1-\alpha)^{-s}, \quad (10)$$

where $\alpha = \exp(-h\nu/kT)$. Thus, substituting Eqs. (2), (9), and (10) into (8) yields the population of the n th level of excitation as

$$P_n(T) = \alpha^n (1-\alpha)^s \binom{n+s-1}{s-1}. \quad (11)$$

As Eq. (11) indicates, the precise shape of the probability distribution is a function of the temperature. Thus, as the temperature changes, $P_n(T)$ also changes. A typical distribution is shown in Fig. 3 for $T = 2000^\circ\text{K}$. At the end of the next section we shall discuss the effect of the thermal distribution assumption on our results.

As we mentioned earlier, the QRRK model gives good agreement with the actual density of states for energies near the critical energy and above. Therefore, this theory also gives an accurate picture of the probability distribution [see Eq. (8)] for energies greater than or equal to the critical energy. Since the total fraction dissociated depends only on the distribution at the critical energy and above, this model gives a reasonably accurate description of the distribution function.

III. RESULTS

As previously mentioned, the aim of this work is to calculate the total fraction of molecules dissociated with a given laser pulse. Since the absorbed energy is statistically distributed, the fraction dissociated is characterized by the vibrational temperature of the molecule. Thus, we will now calculate the fraction dissociated as a function of the vibrational temperature using three different theoretical models.

In all three models we assume that a critical energy $m h\nu$ is required for dissociation and that the molecular distribution function is characterized by the temperature. The three models differ in their treatment of the reaction rate as a function of the number of excess photons absorbed and thus give different results for the total fraction dissociated. However, we shall show that the results of the three models are in good agreement, indicating that the total fraction dissociated is insensitive to the model chosen.

A. Description of the models

As mentioned in the previous section, the total fraction dissociated is

$$F = \sum_{n=0}^{\infty} f_n P_n, \quad (12)$$

where f_n is given by Eq. (7) and P_n by Eq. (11). The three theoretical models we shall describe differ in their treatment of the reaction rate as a function of excess photons and therefore, they differ in the values for the fractional dissociation, f_n .

(a) The simplest and crudest model is to assume that the reaction rate R_n jumps from zero for $n - m < 0$ to infinity for $n - m \geq 0$. Then

$$f_n = \begin{cases} 0 & n - m < 0 \\ 1 & n - m \geq 0. \end{cases} \quad (13)$$

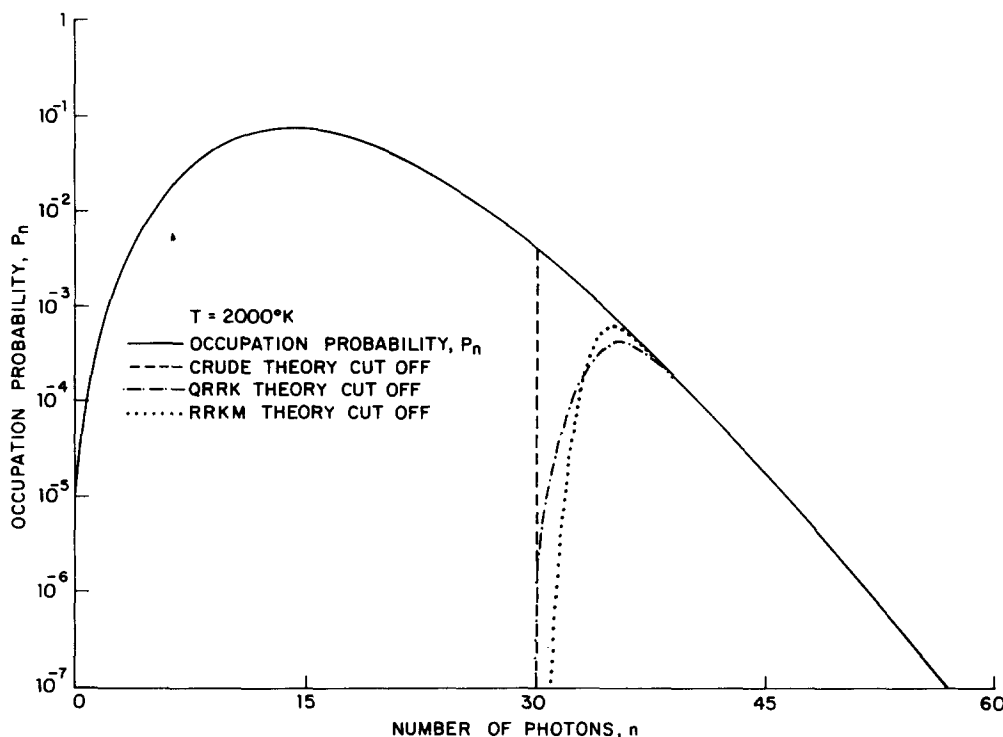


FIG. 3. The probability distribution P_n as a function of the number of photons absorbed, n . Also shown is the cutoff function for the three different theoretical models.

That is, every molecule that absorbs enough energy reacts. Here we take $m = 30$ as given by the thermal measurements of Bott and Jacobs.¹⁴

In this case, calculation of the total fraction dissociated is very simple, because Eq. (12) reduces to

$$F_{\text{crude}} = \sum_{n=30}^{\infty} P_n \quad (14)$$

In other words, the total fraction dissociated is the total probability for having absorbed 30 or more photons, i. e., the area under the probability distribution curve which is cut off vertically at $n = 30$. This cutoff is shown by the dashed line in Fig. 3.

The total fraction dissociated as a function of temperature calculated with this crudest model is shown in Fig. 4. We postpone discussion of this result until after presentation of the other two models.

(b) The second model, the QRRK model, is only slightly more complicated but is more realistic and accurate. The foundation of this theory has been presented earlier. In particular, the reaction rates are given by Eq. (4) and the fractional dissociation by Eq. (7). This model gives a more gradual cutoff of the probability distribution as shown by the dotted and dashed curve in Fig. 3.

This model is more realistic because it accounts for the fact that if the molecule has absorbed only 0, 1, or 2 photons more than required for dissociation, all or nearly all of the absorbed energy must be found in the reaction coordinate. Since this is a fairly unlikely distribution, it will, on the average, take a long time before it will occur. If it takes longer than the deactivation time, the dissociation will simply not be seen.

The total fraction dissociated as a function of temperature for this model is shown in Fig. 4. Again, we postpone discussion of these results until after presentation of the final model.

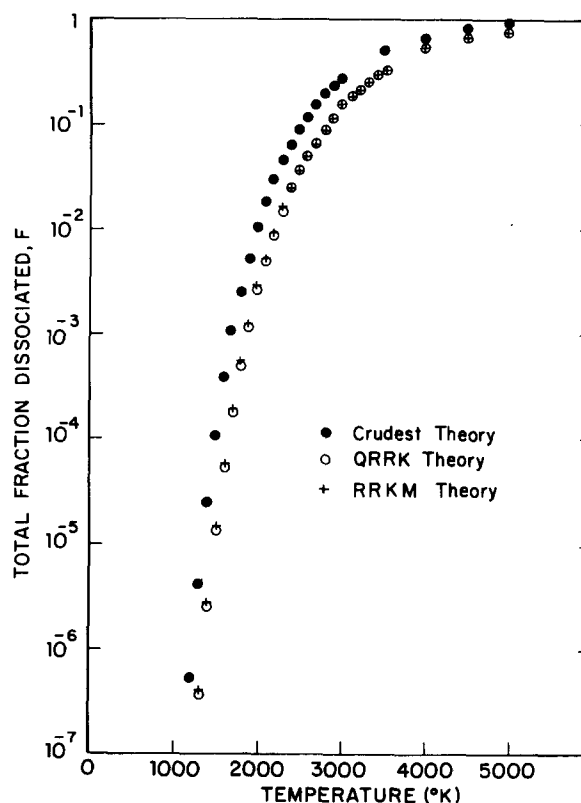


FIG. 4. Total fraction of molecules dissociated versus vibrational temperature for three different models: quantum Kassel model (QRRK), the more sophisticated RRKM model, and the crude model.

(c) The last model we will discuss is the RRKM model. This is the most sophisticated and accurate model which is widely used today. An extensive discussion of this theory is presented elsewhere,⁸ thus our discussion will be brief.

The reaction rate as a function of excess energy is given by Eq. (1). As previously mentioned, the main difference between RRKM and QRRK theory lies in the more realistic treatment of the density of states of the activated complex, $N^\ddagger(E^\ddagger)$ by RRKM theory. The RRKM reaction rates are given in Ref. 9 and displayed graphically in Fig. 1. These reaction rates will lead to the cutoff of the probability distribution as shown in Fig. 3.

We will now discuss the results of these three different cutoffs and will calculate the total fraction dissociated with each.

B. Fraction dissociated versus temperature

In all three models the total fraction of molecules dissociated is found by adding up the portion of molecules found under the tail of the probability distribution. As indicated in Fig. 3, the cutoff function for the three different models is not greatly different. Thus, we might expect that the total dissociated fraction F calculated from the crude cutoff would differ somewhat from that with the RRKM and QRRK cutoffs. However, the difference between the RRKM and QRRK results may not be noticeable.

These results are compared in Fig. 4, where we find that the crude model gives results which are somewhat different from the RRKM and QRRK results. However, the RRKM and QRRK calculations are virtually indistinguishable. We therefore conclude that provided the reaction rates are a fairly rapidly rising function of energy, the calculation of the fraction dissociated is fairly insensitive to the specific rates used. This result is quite reasonable because it implies that processes which compete with dissociation are not very significant, which is exactly what one would expect in a very dilute gas.

At this point we would like to comment on the thermal distribution assumption. Preliminary results indicate that dissociation yields calculated assuming a thermal distribution give results which are in reasonable agreement with experimental measurements. Thus, this assumption is fairly good. However, it is interesting to ask how these results would change if one assumed a different distribution—say a broader or narrower one keeping the same average excitation. If the distribution were broader, the yield at any $\langle n \rangle$ would be higher; and since the high energy tail would be longer, the yield near threshold would rise somewhat more slowly as a function of excess energy. For a narrower distribution, the converse would hold. The important point is that a fairly small change in the size or shape of the molecular distribution function will have a fairly large effect on the area under the tail and thus will have a large effect on the calculated yield. Hence, we conclude that al-

though QRRK theory is crude compared to the more widely used RRKM theory, it is useful in light of the large uncertainties which remain in other parts of the theory of laser induced unimolecular dissociation.

IV. SUMMARY AND CONCLUSION

We have presented a statistical theory for calculation of the dissociation efficiency of SF₆ by infrared radiation. We have compared this theory (the QRRK theory) both to a more complex and accurate theory (the RRKM theory) and to a much simpler theory. We find that the three models differ greatly in their determination of the reaction rate as a function of excess photons absorbed (i. e., the inverse of the lifetime of a molecule containing a specific number of photons). Nevertheless, all three give comparable results for the total fraction of molecules dissociated. In fact, RRKM and QRRK give virtually identical results.

This result indicates that at low pressures and for low yields, the dissociation probability F depends on the properties of the reactant molecule (e. g., the number of vibrational modes, existence of a quasicontinuum, and $V-V$ transfer rates) and on the critical energy $mh\nu$, but not on any details of the activated complex.

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