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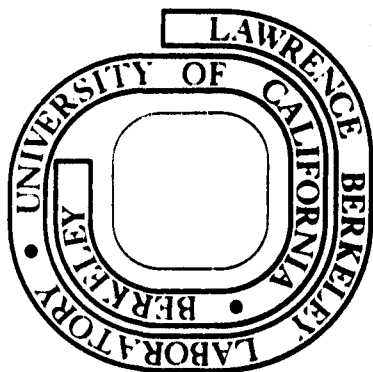
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Collisionless multiphoton dissociation (MPD) of polyatomic molecules is now a well-known subject in quantum electronics. The process has been shown to be isotopically selective and rather efficient. It has also been suggested as a potential method for exciting mode-control unimolecular reactions for chemical synthesis. Since there already exist a number of extensive review articles on the subject [1], we shall not discuss here in any detail on what has already been established, but shall limit ourselves to the most recent progress on our understanding of the subject.

Among the many problems of MPD, the following are most important:

1. How can a molecule absorb several tens of infrared photons from a moderately intense laser field with a high probability? In other words, what is the physical mechanism responsible for such an efficient multiphoton excitation?
2. Is the multiphoton excitation of a molecule mode-selective or non-selective, or is the laser energy deposition into the molecule randomized among all vibrational modes?
3. For each molecule dissociated, how many photons (or how much laser energy) does it absorb? How does the molecular structure limit the laser energy deposition?
4. What is the dynamics of multiphoton dissociation? Is the dissociation always dominated by the lowest dissociation channel? How does the molecular structure affect the dynamics of dissociation?

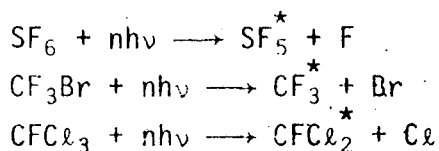
The first question has already had a qualitative but reasonable answer [1]. A polyatomic molecule has discrete states at low energies, but the density of states increases very rapidly with increase of energy and soon forms a quasi-continuum. It is believed that a moderately strong laser field can selectively excite the molecule over the discrete states via a near-resonant multiphoton transition and then through the quasi-continuum via resonant stepwise transitions to and beyond the dissociation threshold. This explanation is strongly supported by the results of the two-laser experiments of AMBARTZUMIAN et al [2].

The other questions, however, have not yet received satisfactory answers. The main difficulty of the usual experiments on MPD of molecules in a gas cell is that molecular collisions during and after the laser pulse excitation and the chemical reactions following the collisionless unimolecular dissociation often make the experimental results very confusing and sometimes even inconsistent. Then in these usual experiments, study of dissociation dynamics is

also impossible. It is clear that in order to be able to understand a collisionless process, one must first eliminate molecular collisions in the experimental investigation. The best way to achieve this is to use a molecular beam. With an appropriately designed molecular beam apparatus, the dynamics of dissociation can also be studied [3-5]. In this paper, we shall describe and discuss the preliminary experimental results on MPD of polyatomic molecules obtained from our recent crossed laser and molecular beam experiments. We show that with the help of a phenomenological model for multiphoton excitation and a statistical model for molecular dissociation, we can essentially answer all those important questions posted above.

Our experimental arrangement has been described elsewhere [3]. Briefly, a Tachisto CO₂ TEA laser was used to produce a laser beam which crossed with a molecular beam at the collision center in a molecular beam apparatus. The dissociation fragments from the collision center were detected and analyzed by a mass spectrometer rotatable around the collision center. A gated counting system attached to the mass spectrometer was used to obtain time-of-flight spectra of the fragments. Thus, both the angular distributions and the velocity distributions of the fragments could be readily obtained. From these results together with the measured velocity distribution of the primary beam, we could then deduce by deconvolution the kinetic energy distribution of the fragments.

We have so far studied MPD of three different polyatomic molecules: SF₆, CF₃Br, and CFCℓ₃. In all three cases, we found from mass spectroscopy that MPD occurred through the lowest dissociation channel



where * denotes internal energization of the dissociation products. The case of SF₆ turned out to be much more complicated than the others. First, the fragmentation pattern of SF₅^{*} in the ionization chamber of the mass spectrometer was not known and had to be established. Then, we realized that at higher laser energies SF₅^{*} produced during the laser pulse could absorb more photons and undergo a secondary dissociation SF₅^{*} + n'hν → SF₄^{*} + F [4]. Why we have found no similar secondary dissociation in MPD of CF₃Br and CFCℓ₃ is of course a rather interesting question. We shall see later that the question can be answered by the statistical theory of molecular dissociation with its explicit dependence on the molecular structure.

As was mentioned earlier, we can deduce, from the measured angular and velocity distributions of the fragments, the kinetic-energy (or recoil-energy) distribution g(ε) for the fragments. We show in Fig. 1 an example of SF₆ obtained with ~10 J/cm² of laser excitation. One can readily draw several conclusions from the results in Fig. 1. First, the average recoil energy of the fragments is only 2.5 KCal/mole (~0.11 eV), suggesting that if a molecule absorbs more than one photon above the dissociation threshold, then a large fraction of this excess energy must be retained by the SF₅ fragment in its internal degrees of freedom. Second, g(ε) strongly peaks at zero kinetic energy, indicating that there is little energy barrier for dissociation of SF₆ and the laser energy deposition in the molecule before dissociation must be randomized in many accessible states.

We believe that because of the very strong coupling among the vibrational

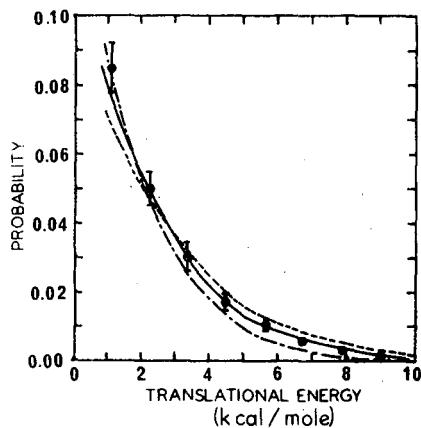


Fig.1 Fragment recoil energy distribution for $\text{SF}_6 \rightarrow \text{SF}_5 + \text{F}$. Experimental data points are denoted by the dots. Curves are calculated from the RRKM theory assuming a molecular excitation of $E = E_0 + n h \nu$ with $n = 7$ (- · -), $n = 9$ (—), and $n = 11$ (---) where E_0 is the dissociation threshold energy and $h \nu$ is the CO_2 laser photon energy.

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modes of a highly excited polyatomic molecule, the excitation energy deposited in the molecule is likely to be randomized in all vibrational degrees of freedom. Then, the well-known RRKM statistical theory for unimolecular dissociation [6] which assumes complete energy randomization can be used to calculate $g(\&)$. We may assume that the molecules are initially excited to an energy $E - E_0 = n h \nu$ above the dissociation level where E_0 is the dissociation threshold energy, $h \nu$ is the CO_2 photon energy, and n is an integer. Knowing the molecular structure, we can then calculate $g_{n h \nu}(\&)$. In Fig. 1, three theoretical curves with $n = 7, 9$, and 11 are shown; the $n = 9$ curve is in fair agreement with the experimental results. Actually, because of the statistical nature of the laser excitation process, there should be a significant spread of populations in different n levels before dissociation with $n = 9$ being the average. This will be seen more clearly later in our model calculation. The RRKM calculation also predicts a laser energy dependence of $g(\&)$ which agrees well with our experimental results.

From the good agreement between theory and experiment, we can then conclude that (1) the laser energy deposited in SF_6 before dissociation is completely randomized in all vibrational modes, (2) mode-controlled dissociation of SF_6 does not occur with nanosecond pulse excitation, and (3) each SF_6 molecule absorbs on the average 36 to 40 CO_2 laser photons before dissociation, assuming that absorption of 29 photons is needed to reach the dissociation threshold. The RRKM calculation also yields a dissociation rate corresponding to each specific level of excitation. As shown in Fig. 2, the dissociation rate in-

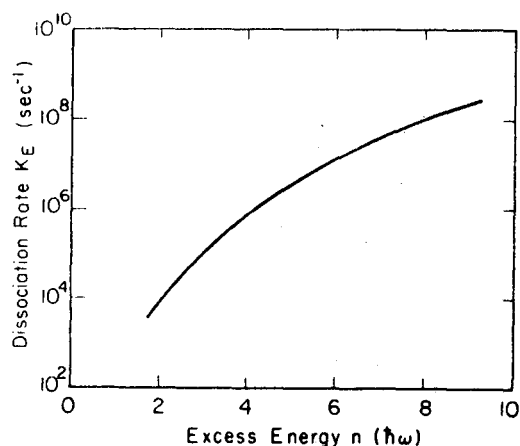


Fig.2 Dissociation rate of SF_6 calculated from the RRKM theory as a function of level of excitation $n h \nu = E - E_0$.

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creases very rapidly with n , and for $n = 7$ to 11 , it varies from 2×10^9 to $2 \times 10^7 \text{ sec}^{-1}$. This explains why on average, the dissociation seems to have initiated from the $n = 9$ level of excitation. For $n < 7$, the up-excitation rate is much larger than the dissociation rate so that only a small fraction of molecules will dissociate. For $n > 11$, the reverse is true and only a small fraction of molecules can be excited to higher levels.

We have also obtained preliminary results of recoil energy distributions of fragments from MPD of CF_3Br and CFC_2Br under $\sim 10 \text{ J/cm}^2$ laser excitation. The RRKM calculations for these cases show the same qualitative behavior as in the case of SF_6 . In particular, the excitation energy in these molecules seems to be completely randomized in all degrees of freedom before dissociation, and only a small fraction of the excess energy appears in the form of recoil energy after dissociation. However, the observed recoil energy distributions in the cases of CF_3Br and CFC_2Br correspond respectively to an average excitation energy of 1-3 and 3-5 CO_2 laser photons beyond the dissociation level. This average excess energy seems to be quite different for different molecules, but actually, it corresponds to a dissociation rate from 10^7 to 10^9 sec^{-1} which is the same for all three molecules we have investigated. Clearly, the balance between the up-excitation rate and the dissociation rate is responsible for what we have observed. The dissociation thresholds for SF_6 , CFC_2Br , and CF_3Br are 76, 77, and 65 KCal/mole respectively. At a given energy above the dissociation threshold, the statistical rate for unimolecular dissociation is proportional to the ratio of the density of states of the critical configuration for dissociation to that of the energized molecule [6]. This ratio is smaller for larger or/and heavier molecules.

The difference in the excess energies in different molecules explains why SF_6 can undergo stepwise secondary dissociation while the others cannot. In all cases, a major portion of the excess energy appears as internal energy of the fragment after dissociation. Thus in the case of SF_6 , the dissociation product SF_5^* has an average internal energy of $6h\nu - 10h\nu$, and must have already been excited to the quasi-continuum states. It can therefore easily absorb more photons to and beyond its dissociation threshold as long as the laser field is present. Consequently, stepwise dissociation of SF_6 can be expected if the exciting laser pulse is sufficiently long and contains enough energy. This is however not true for the other molecules. Because of the lower excess energies, the fragments CF_3^* and CFC_2^* are not quite in the quasi-continuum states. As a result, they cannot resonantly absorb more photons and hence the secondary dissociation process becomes less probable. From these results, we can then predict that for MPD of polyatomic molecules, the larger and heavier molecules with a large excess energy before dissociation will most likely undergo stepwise dissociation.

To help our understanding of MPD, we have developed a simple phenomenological model which we believe is realistic enough to exhibit at least the qualitative behavior of the multiphoton excitation and dissociation process. We assume in the model that the molecular system can be described by a set of evenly spaced energy levels with the corresponding densities of states being the degeneracy factors. In this respect, we have neglected the possible initial multiphoton transition step or steps to reach the quasi-continuum by jumping over the discrete states. This is probably a good approximation as long as the laser intensity is much larger than the threshold intensity for overcoming the discrete state barrier, e.g., $\sim 30 \text{ KW/cm}^2$ for SF_6 [7]. We then assume that the transitions between levels are incoherent and the populations N_j of all levels are governed by the following set of rate equations.

$$\frac{d}{dt} N_i = C_{i-1}^a N_{i-1} + C_i^e N_{i+1} - (C_i^a + C_{i-1}^e) N_i \quad (1)$$

for levels below the dissociation threshold E_0 , and

$$\frac{d}{dt} N_m = C_{m-1}^a N_{m-1} + C_m^e N_{m+1} - (C_m^a + C_{m-1}^e) N_m - k_m N_m \quad (2)$$

for levels above the dissociation threshold. In the above equations, k_m is the dissociation rate of molecules in the m th level calculated from the RRKM theory, and C_j^a and C_j^e are respectively the absorption rate from level j to $j + 1$ and the emission rate from j to $j - 1$. For one-photon transitions, we have

$$C_j^a = \sigma_j I \quad (3)$$

$$C_j^e = (g_j/g_{j+1}) C_j^a$$

where σ_j is the absorption cross-section, I is the laser intensity, and g_j is the degeneracy factor of level j .

We can solve the above set of equations numerically for a given molecule with σ_j and $I(t)$ specified. Our results for SF_6 are shown in Figs. 3 and 4.

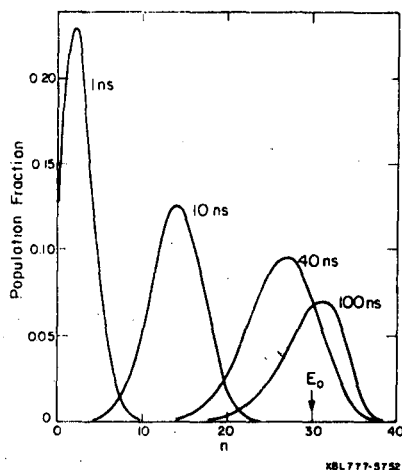


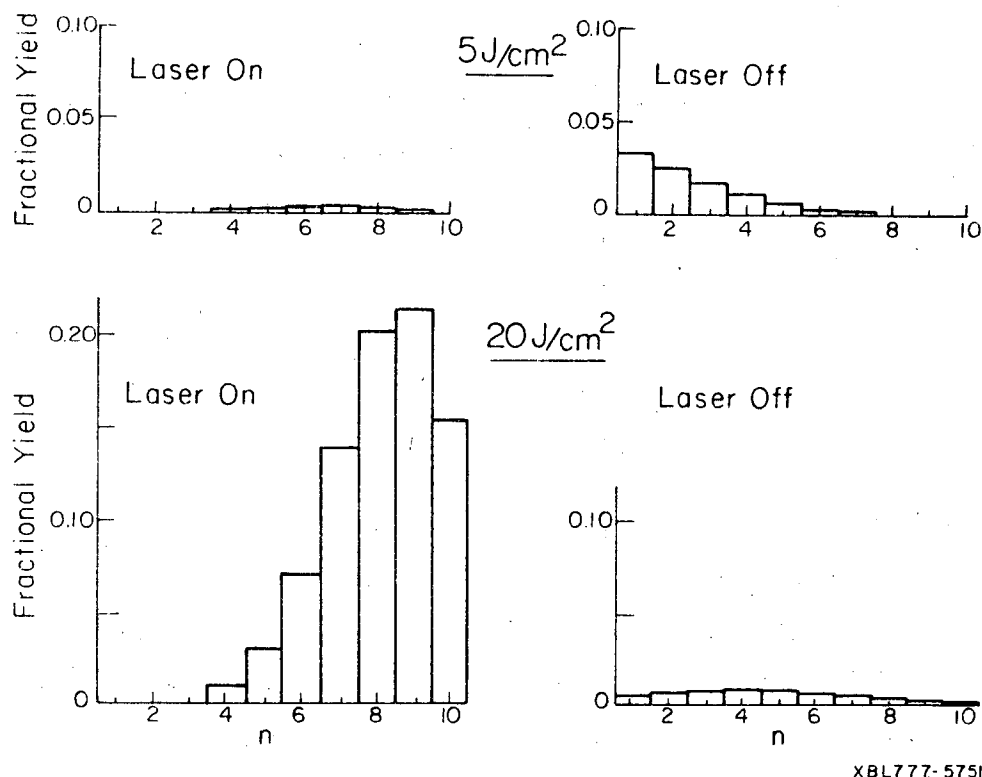
Fig.3 Calculated excited state population distributions of SF_6 for various times during a square laser pulse (200 MW/cm², 100 nsec.).

We used in the calculations a square laser pulse of 200 MW/cm² with a 100 - nsec duration, and an absorption cross-section

$$\sigma_j = \exp[-.02936 j - 42.93] \text{ cm}^2.$$

This relation for σ_j was chosen so that our numerical results yield both the observed dependence of average number of photons absorbed per molecule on laser fluence [8] and the observed dependence of dissociation yield on laser energy fluence [9].

Figure 3 shows that as time goes on, the laser excitation effectively drives the population distribution up to higher levels; the average number of photons absorbed per molecule of course increases correspondingly. Only after ~ 30 nsec, does the high-energy tail of the population distribution start to have a



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Fig. 4 Calculated dissociation yields during and after the 100 - nsec laser pulse for two laser energy fluences: 5 J/cm^2 and 20 J/cm^2

significant portion above the dissociation threshold (assuming $E_0 = 30 \text{ h}\nu$). Dissociation then occurs. The laser excitation continues to drive the population distribution further up, but the action is soon limited by the very high dissociation rates at higher energy levels which deplete the populations effectively. This is seen by the more abrupt cutoff on the high-energy side of the 100 - nsec population distribution curve.

Knowing the populations above the dissociation threshold, we can then calculate the dissociation yield as shown in Fig. 4 for two different laser energy fluences. We have calculated separately the yield during the laser pulse and the yield after the pulse is off. The total yield is of course the sum of the two. It is seen that with 20 J/cm^2 of laser excitation, already a large fraction of the molecules is dissociated during the laser pulse. Then, the fragments produced during the pulse can absorb more photons and undergo secondary dissociation if the laser pulse is sufficiently long and intense as we have experimentally observed.

Recently, BLOEMBERGEN et al have also concluded from their optoacoustic measurements that MPD is a statistical process [8,10]. They used the quantum Kasal theory to interpret their results. In their model, they assumed that the laser multiphoton excitation of a molecule is equivalent to a heating process. The population distribution is then governed by the thermal Boltzmann distribution characterized by an effective temperature T . To find T , they assumed that the classical equipartition relation $s kT = \langle n \rangle h\nu$ holds, where s is the total number of vibrational degrees of freedom ($s = 15$ for SF_6) and $\langle n \rangle$ is the average number of photons absorbed per molecule which can be obtained from the optoacoustic measurement. They also assumed that the thermal distribution is

not affected by dissociation. This limits the validity of their calculations to cases with low dissociation yield. Now, it is not obvious a priori that the above assumptions are correct. In particular, we wonder whether laser excitation will indeed yield a thermal distribution with an effective temperature $T = \langle n \rangle h\nu / sk$. Using our more realistic model calculations, we can now answer this question directly.

Figure 5 shows a population distribution created by laser excitation with an average number of photons absorbed per SF_6 molecule $\langle n \rangle = 20$. Two thermal distribution curves are also shown for comparison. Clearly, the one at $T = 1800^\circ \text{K}$ calculated from $T = \langle n \rangle h\nu / sk$ with $s = 15$ is very different from the laser-excited distribution. The other at $T = 2200^\circ \text{K}$ (corresponding to a reduced number of vibrational degrees of freedom $s' \cong 12$) has the same average excitation energy as that of the laser-excited distribution, but the thermal distribution curve is appreciably broader and has a longer high-energy tail.

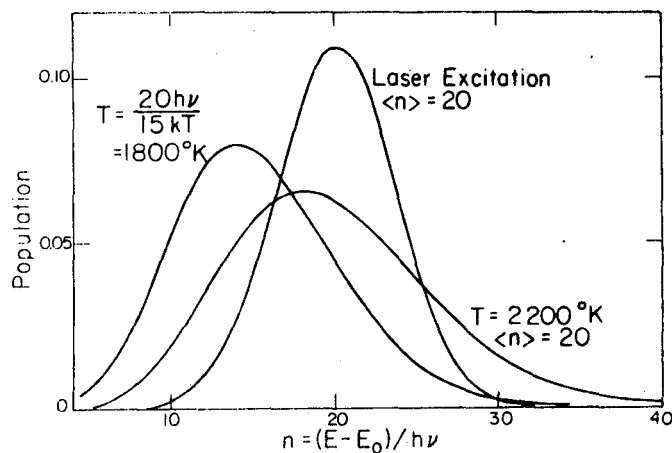


Fig.5 Comparison between population distributions obtained by laser excitation and by thermal heating. See the text.

Thus, we can conclude that a thermal distribution is only a rather crude approximation of the real distribution created by laser excitation, and the corresponding "temperature" is appreciably larger than the one calculated from $T = \langle n \rangle h\nu / sk$. The discrepancy in "temperature" comes in mainly because in reality different vibrational modes have different frequencies and the inequality $h\nu_j \ll kT$ necessary for the validity of equipartition theorem does not hold for all modes. However, if we consider only the population distribution near and above the dissociation threshold, then the $T = 1800^\circ \text{K}$ thermal distribution agrees better with the laser-excited distribution. In other words, the $T = 1800^\circ \text{K}$ curve gives a fair prediction of the dissociation yield. This is probably the reason why BLOEMBERGEN et al found that thermal distributions with $T = \langle n \rangle h\nu / sk$ seem to describe the observed dissociation yield near threshold fairly well.

We summarize here the most important results we have obtained from our studies. First, in MPD, the laser energy deposition into a molecule is quickly randomized among all vibrational degrees of freedom, suggesting that mode-controlled dissociation of molecules is not possible at least in the cases we have studied. Second, the number of excess photons absorbed per molecule above the dissociation threshold varies with molecules, ranging from 1-3 for CF_3Br , 3-5 for CFCl_3 , and 7-11 for SF_6 . The dissociation rate however ranges from 10^7 to

10^9 sec^{-1} for all these molecules and is the limiting mechanism for excitation to higher levels. Third, the primary dissociation of a molecule usually occurs through the lowest dissociation channel. A larger or heavier molecule such as SF_6 is more likely to undergo a secondary dissociation process. Fourth, during dissociation, only a small fraction of the excess energy appears as the recoil energy of the fragments; the rest is retained by the fragments in their internal degrees of freedom. We have developed a model calculation which exhibits the qualitative behavior of multiphoton excitation and dissociation and strongly corroborates our physical interpretations. In addition, we have shown that the population distribution obtained from laser multiphoton excitation is appreciably different from that resulting from thermal heating.

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