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MULTIPHOTON DISSOCIATION OF POLYATOMIC MOLECULES

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INTRODUCTION

In the activities of human society, the development of a new technology always leads to the discovery of some new phenomena. Since the invention of the laser in the early sixties, along with the arrival of various laser equipment and optical devices, there were significant advances in the understanding of the interaction of photons with matter. But, probably none of the phenomena discovered so far in the general area of laser chemistry and quantum electronics is as exciting as the infrared multiphoton excitation and dissociation (MPE and MPD) of polyatomic molecules.[1-10] The motivating idea behind laser chemistry is its potential for modification of chemical properties of molecules through the absorption of laser photons.[11-14] UV and visible photons are most effective in fulfilling this purpose by causing electronic transitions in molecules and there has been much interesting work in recent years, especially using tunable dye lasers. The absorption of an infrared photon by a molecule is not likely to induce as drastic a change in the chemical properties as UV or visible photons but, on the other hand, it offers an exciting possibility of promoting one specific reaction channel over others by exciting a particular mode of molecular vibration which is directly or closely related to the motion along the reaction coordinate. Many attempts at carrying out mode controlled chemistry by infrared laser excitation in the gas phase have only enjoyed limited success so far. After all, the relatively small amount of energy contained in one infrared photon usually does not induce sufficient increase in the reactivity. Very often one observes that the energy deposited in a specific mode is mostly drained away by collisions through intermolecular energy transfers rather than being used effectively in the chemical reactions. The discovery of the phenomenon that an intense infrared radiation of correct frequency can selectively and efficiently deposit tens of photons in isolated molecules and cause dissociation is certainly one of the most exciting breakthroughs. Not only has it changed the perspective on the infrared laser chemistry, but it also has far reaching scientific and practical significance.

The possibility that a polyatomic molecule placed in the intense field of an infrared laser can absorb enough photons to dissociate in a very short time span was first suggested, in 1971, by Isenor and Richardson[15] based on their experimental observation of luminescence from dissociation products. In 1973, Isenor[16] and Letokhov and coworkers[17,18] found that the luminescence contained an instantaneous and a delayed component, suggesting that the absorption of many photons and the subsequent molecular dissociation could take place under isolated, collision free conditions. This infrared multiphoton dissociation (MPD) process was subsequently shown to be isotopically selective in 1974 by Ambartzumian et al.[19,20] and Lyman et al.[21] High efficiency and high selectivity of the process, as manifested by actual separation of isotopes, gave tremendous impetus to an unprecedented rapid growth in this new area of research. Actually, a considerable amount of interest and excitement was also generated with the suggestion that multiphoton excitation (MPE) could be a novel method for energizing molecules, one that offered the potential for vibrational mode control of molecular decomposition. In other words, by depositing energy into particular vibrational modes, one hopes to dissociate molecules along certain reaction pathways different from those of thermal decomposition.[22] Initial experimental results appeared to support this hypothesis: the first reported primary product analysis for the multiphoton dissociation of SF_6 [7a] indicated that this molecule dissociated into SF_4 and F_2, bypassing the lower energy SF_5 and F fragmentation channel. Results of gas cell experiments with $CFCl_3$ [23] were interpreted to evidence direct dissociation into CFCl and Cl_2. However, in later experiments with molecular beams, these interpreted results were not substantiated, as we shall see.

It is now generally understood that although a polyatomic molecule has discrete states at low energies, the density of states increases very rapidly with increase of energy and the states soon form a quasi-continuum.[16,24,25] It is believed that a moderately strong laser field can selectively excite the molecule over the discrete states via a resonant multiphoton transition and even through the quasi-continuum via resonant stepwise transitions to and beyond the dissociation threshold. The initial excitation over the discrete states depends not only on the frequency and the power of the laser, but also on the rotational quantum states and the excitation of hot bands,[26-30] and is mainly responsible for the high selectivity of the process. Once the molecules are excited to the quasi-continuum, the energy fluence, not the power of the laser, was shown to be responsible for driving the molecules through the quasi-continuum and determining the yield of dissociation. For molecules lying above the dissociation level, the rate of decomposition competes with the rate of excitation,[31,32] and then the power of the laser should determine the average level of excitation (or energy deposition).

As more definitive experiments on dissociation dynamics, such as the measurement of the fragment translational and internal energy distributions of multiphoton-excited molecules[33-40] were carried out, it became clear that the energy deposited in the molecules is completely randomized before dissociation. SF_4 and CClF observed in the multiphoton dissociation of SF_6 and CCl_3F respectively, which provided the basis for speculation of mode-controlled chemistry, was found to be due principally to secondary multiphoton dissociation or chemical reactions involving the primary products SF_5 and CCl_2F.[35,41]

The fact that energy randomization among vibrational modes is faster than the rate of excitation near dissociation implies that many important aspects of the dissociation dynamics can be understood from the application of a statistical theory of unimolecular dissociation, such as RRKM theory.[42,43] Using such a statistical theory, the dissociation rates and yields from various dissociation channels as well as the fragment energy distributions can be easily estimated for a given level of excitation from the known dissociation energy and vibrational frequencies of the molecule. In addition, the higher the molecule is excited, the faster the rate of dissociation becomes and the maximum number of infrared photons which can be absorbed by a molecule is eventually limited as the rate of dissociation becomes faster than the rate of excitation. A statistical theory can again be used for the estimation of the level of excitation.[31,32] For example, with a typical CO_2 TEA laser pulse of ~50 nsec duration and an energy fluence of 10 J/cm^2, many molecules are found to dissociate from energy levels with dissociation lifetimes of 1 to 10 nsec. For N_2F_4 and SF_6, that corresponds to the absorption of 1 and 9 excess photons, respectively, beyond their dissociation energies.[35,32]

In the following, we shall first review the various experimental techniques used and the most significant results obtained so far in the understanding of the dynamics of MPE and MPD. We shall then discuss some theoretical model calculations describing the multiphoton excitation and dissociation process. Finally, some possible applications of MPE and MPD and a number of unsolved problems are stated. In a field which has been advancing rapidly and has provided scientists with unprecedented opportunities of strong interactions along the way, sometimes, it is not easy to give proper credit to the individuals or groups of scientists who have made more original or more substantial contributions to some aspects of the problems. Some omissions and mistakes are inevitable. The readers will find that this is one of the joyous occasions in the history of science, that a new field has been developed so quickly in such a short time by scientists from many countries and disciplies working closely together. The field of infrared multiphoton dissociation and its application to isotope separation has been reviewed quite frequently in the past, and some of the more recent reviews are listed in Refs. 1-10.

EXPERIMENTAL

I. Experimental Techniques

(A) MESUREMENTS OF THE EXCITED MOLECULES We consider here measurements of polyatomic molecules which have been excited via a multiphoton process, but have not yet been dissociated. The most desired experimental result on the excited molecule is of course the time evolution of the vibrational-rotational population distribution $P(v,J)$ resulting from the multiphoton excitation, hopefully as a function of the input laser power P, energy fluence J and frequency ν. Certainly these results are rather difficult to get and most experiments are devoted to the easier measurements of quantities such as the total energy absorbed, $\langle n \rangle h\nu$, the gross multiphoton absorption cross section, σ, or the incremental single photon absorption cross section. $\langle n \rangle$ stands for the average number of CO_2 laser photons absorbed.

To date, all the measurements on the excited molecules can be classified as direct or indirect. The direct techniques, mostly intended to probe the population distribution in the excited molecules, include measurements of emission from the excited molecules, induced absorption, temperature rise or acoustic waves generated from the "hot" molecules, and photoionization or electron ionization. The indirect techniques deduce information about the state of the molecules from data deduced from the attenuation of the laser beam, namely <n> and σ. Measurements on the multiphoton excited molecules have so far been done mostly in gas cells. In all cases, the energy fluence J, and/or the frequency ν can be varied to obtain results important for understanding the mechanism of MPE. In a two laser beam double resonance experiment, the time delay between the pulses can be varied to obtain the time resolved information which is essential in understanding the dynamics of MPE. We shall review the various experimental methods below along with some comments on their relative merits.

Direct emission from the excited molecules has been observed by Frankel et al.[44] and Bott.[45] Frankel et al measured the 16μ fluorescence from the ν_4 mode of SF_6 as a function of multiphoton pumping at the ν_3 mode. Bott measured the ν_3 emission from the hot molecules. The ν_4 fluorescence experiment has a potential of furnishing the time-resolved information about the intramolecular energy transfer between ν_3 and ν_4 modes. However, the measurement of Frankel et al. had only a μsec resolution which was clearly inadequate for study of intramolecular dynamics. Bott measured the ν_3 emission at the dissociation threshold and it was not clear whether there was contribution from the dissociation products. Although laser induced fluorescence has been applied to reaction products to obtain internal energy distributions in the reaction products, no such experimental information has been obtained yet with the excited polyatomic molecule itself.

The optoacoustic technique was proposed by Bragratashvili et al.[46] as a direct way of monitoring the energy absorbed by SF_6 and OsO_4. The measurements on SF_6 were repeated by Black et al.,[47] and by Deutsch.[48] The same technique has been applied to other polyatomic molecules by Lussier et al.[49a,b] and by Reddy et al.[10c] in the measurement of single photon absorption. This technique depends on the fact that the vibrationally excited molecule will release its energy to the translational degrees of freedom via V-T relaxation. Then, after MPE, the temperature rise in the interaction region of the gas cell will set up acoustic waves with which the absorbed energy will eventually be relaxed to the cell walls. It is assumed that the acoustic signal is directly proportional to the energy absorbed. This method has the merits of simplicity and general applicability, but suffers from the disadvantages of low sensitivity and nonlinearity in the acoustic signal. Moreover the data will be difficult to interpret if there exists a fair amount of dissociation such that the constituents of the absorbing medium change during the laser excitation. Bolometric measurements can in principle yield the laser energy absorbed in a molecular beam[10d] or in a gas cell directly, but again the sensitivity problem is severe.

Sudbø et al.[50] recently used a photoionization technique to probe the population distribution in the vibrational states of SF_6. They used dispersed vacuum UV photons and measured the photoionization spectra of laser irradiated SF_6 molecules in a molecular beam and succeeded in deducing qualitative information about the population distribution. Brunner et al.[51a,b] had done a similar experiment with electron bombardment ionization mass spectroscopy, but their results are not as conclusive and some of their data analysis was doubtful. Nevertheless, it is still a viable method of probing the average amount of vibrational energy within a molecule.

There has been a prolific amount of measurements on $\langle n \rangle$ or σ as a function of J or ν of the laser by measuring the attenuation of a laser beam passing through a gas cell.[52-56] This method is however limited in accuracy. For obtaining better accuracy the gas cell must be optically thick. This leads to varying fluences along the gas cell which makes the analysis difficult. In order to have more or less constant laser fluence in the cell, the laser beam should also be fairly uniform inside the gas cell. This means that the cell windows experience the same high laser fluence as the gas molecules. Laser breakdown of the windows then limits the maximum laser fluence that one can put through the cell. Results of a lot of earlier experiments can be discarded because of the focusing geometry employed inside the gas cell. Even with an unfocused beam, the measurement still suffers from the ever present transverse spatial variation of the laser intensity which must be accounted for.[56,57] In absorption measurements, a tacit assumption is made that multiphoton absorption is the only process occurring in the cell. This of course may not be true, especially when the dissociation of molecules becomes significant.

In a two beam pump and probe experiment, the spatial correction problem can be eliminated provided the probe pulse has a much smaller cross-sectional area than the pump pulse. Moreover, the probe pulse can be time delayed,[55,56] and/or at a different frequency than the pump pulse.[30] In principle, one can measure the time dependent excited state absorption spectrum of the polyatomic molecule using this method.

Almost all of the experiments performed so far on MPE and MPD employed uncontrolled CO_2 TEA lasers in which mode beating caused undesirable intensity spikes. A low pressure gain tube which acts to smooth out the laser pulse is preferred.[58] As shown by Lyman et al.[59a,b] and Black et al.,[53] the mode beating or self mode-locking in the laser pulse can make a significant difference in the experimental results.

(B) MEASUREMENTS OF DISSOCIATION PRODUCT In the measurements of dissociation products, it is desirable to obtain information on the identity, yield and energy distribution of fragments as a function of frequency, power and energy fluence of the laser as well as other experimental parameters. These results are necessary for the understanding of many important aspects of the dynamics of unimolecular dissociation and for obtaining information concerning the excitation of the molecules prior to dissociation.

The molecular beam method gives clean collisionless conditions. Detection of dissociation products in a molecular beam apparatus is usually via electron impact ionization[33,61,51] or chemi-ionization[62] in conjunction with a quadrupole mass filter and ion detector. Coggiola et al.[33] were the first to demonstrate directly the collisionless multiphoton dissociation of polyatomic molecules by measuring the translational energy distributions of the fragments of SF_6 in a crossed laser-molecular beam arrangement. The method is generally applicable to the study of MPD of a wide variety of polyatomic molecules.[34,35,60] Using chemi-ionization as a method of detection of fragments, the number of chemical species which can be measured is often limited. Detection by electron ionization, on the other hand, is more general and was the method used in most of the experiments carried out so far. However, very often many ion fragments are produced from a molecule in the ionizer. This requires careful analysis of the results.

A number of research groups have used the molecular beam method to study MPD. Brunner et al.[51] have used a fixed detector on the beam axis to measure only the total dissociation yield. The Berkeley group[33-35,41,60] has used a rotatable detector to obtain high resolution angular and velocity distributions of the fragments. Similar information was obtained by Gentry and Giese[61] recently using a pulsed rotatable beam source.

Besides the molecular beam method, measurement of products from collisionless MPD can also be performed in a gas cell with time resolved detection of laser induced fluorescence (LIF) from the fragments. The technique has the advantage of being able to detect the internal energy distribution in the fragments. The major disadvantage of LIF is that the optical spectroscopic properties of only a few of the radical fragments are known and suited for LIF detection. Such a technique has been used by a number of researchers to detect C_2,[38,63,64] CH,[64] CN,[40,64] NH_2,[65] CF_2,[36,66] and OH[67] in the studies of MPD. Time resolved luminescence, both visible and infrared, has also been observed from dissociation products. The instantaneous luminescence presumably comes from products undergoing collisionless MPD. However, since the dissociation products are not likely to be in highly excited electronic states, it is not yet completely understood how instantaneous visible luminescence is generated. Measurements of infrared luminescence from vibrationally excited molecules provides another method of fragment detection and it has been used to detect the fragments HCl and HF[39,68] in MPD of halogenated hydrocarbons. Of course, if only ground state molecules are formed in the dissociation no collisionless infrared luminescence should be observed. Hartford,[69] for instance, estimates an upper bound for the production of vibrationally excited NO from MPD of CH_3ONO by the lack of luminescence.

Most experiments in gas cells reported so far were, however, carried out under the influence of molecular collisions. Molecular collisions during the laser excitation or collisions of excited molecules after laser excitation affect the dissociation yield in many ways: 1) Intermolecular energy transfer can change drastically the energy distributions in molecules and affect the effective absorption coefficient in the multiphoton excitation. 2) Collisional excitation and deexcitation of laser excited molecules can effectively modify the unimolecular dissociation process. 3) Collision of radical molecules can result in chemical reactions which lead to a final product completely different from the primary dissociation product.

It is often argued that if a laser with a pulse duration much shorter than the collisional dephasing time, τ_c, is used for multiphoton excitation, then the MPD process can be regarded as collisionless (in SF_6, $\tau_c \sim 13.5$ nsec-torr[55]). This, however, may not be true. In particular, at lower laser fluence with small dissociation yield, the average dissociation lifetime can be much longer than both the pulse duration and τ_c. Thus, even though the pulse duration is much shorter than τ_c, collisional effects may still dominate the dissociation process. In particular, a check for linearity of the MPD yield versus pressure ensures that the MPD occurs under collisionless conditions.

It is thus seen that the molecular beam method is more suitable for the study of collisionless MPD. However, the sensitivity of the molecular beam technique still leaves us much to desire. At present, experiments in gas cells can clearly yield important complementary information on MPD and especially on MPE.

II. Experimental Results

(A) INITIAL EXCITATION OVER THE DISCRETE LEVELS There are two types of experiments dealing with the discrete levels. One may study the discrete levels by measuring the spectroscopic properties of the polyatomic molecule, or one may study the effects of the discrete levels on multiphoton absorption and dissociation. Let us focus our attention on SF_6, the most studied polyatomic molecule. Its spectroscopic properties have been studied long ago by Steinfeld et al.[70] and Brunet.[71] In fact, because of its strong IR absorption around 10μ, it has often been used with the CO_2 laser in the study of coherent optical processes, such as photon echoes,[72-74] and self-induced transparency.[75] Even the red-shift of the ν_3 hot-band absorption spectrum has been discussed by Oppenheim in 1971.[76]

Due to the upsurge of interest in the study of the infrared laser induced chemical reaction, the spectroscopy of SF_6 has been under renewed scrutiny. Most of the work has been carried out at Los Alamos Scientific Laboratory and at Lincoln Laboratory using high resolution tunable diode lasers. These spectroscopic studies reveal the fine splittings and shiftings of the vibrational-rotational manifold. From comparison of theory and experiment, the force constants and interatomic potentials etc. can be obtained. These spectroscopic details about the discrete levels are of course essential not only for full appreciation of MPE but also for doing laser isotope separation at low laser power.

Aldridge et al.[77] published a series of high resolution spectra of SF_6 in 1975. They were supplemented by the theoretical calculation of Cantrell et al.[78] with assignment of proper nuclear spin statistical weights to the various symmetry substates. The resolution of the diode laser was in some cases better than 100 kHz or 3×10^{-6} cm^{-1}. With such resolution, it was possible to find the resonant frequencies and the line strengths of the SF_6 transitions near most of the CO_2 laser frequencies.[4b,79] As expected, the frequency mismatch between a laser line and the nearby absorption lines of SF_6 was of the order of MHz which is less than the laser linewidth. Knowing these transitions is of course essential to the interpretation of the multiphoton absorption data.

However, these high resolution spectra were obtained at low intensity and hence revealed only the $v = 0$ and $v = 1$ vibrational transitions of the ν_3 mode of SF_6. To map out resonances of higher vibrational transitions, the molecule has to be prepared in a higher vibrational state. Moulton et al.[80] used a double resonance method to study the $v = 1$ to $v = 2$ transition. They pumped with a broad band Q-switched CO_2 laser and probed with a weak cw diode laser in a low pressure cell. Unfortunately, no spectroscopic data was discussed in that paper. They measured a collisional relaxation time of the excited rotational levels of 36 nsec-torr in the ground state and 32.5 nsec-torr in the $v = 1$ state. This should be compared with the collisional deexcitation rate of a highly vibrationally excited molecule of ~13 nsec-torr.[5] This indicates that the vibrational energy transfer cross section depends strongly on the level of excitation.

Instead of looking at transitions with $\Delta v = 1$, Kildal[81] measured the $\Delta v = 3$ overtone spectrum with a 1 m grating spectrometer. The results were later corroborated with the higher resolution (0.04 cm^{-1}) results by Ackerhalt et al.[82] and Fox.[83] The $3\nu_3$ Q branch and the $(3\nu_3 + \nu_6) \leftarrow \nu_6$ hot band could be clearly resolved and the rotational structures observed. These measurements have provided valuable information about the anharmonicity of the ν_3 mode and the possible hot band structures on higher vibrational transitions.

As mentioned earlier, we can also observe the effects of the initial discrete levels in the dependence of MPE and MPD on laser power and frequency. Kolodner et al.[84] compared the multiphoton absorption of SF_6 using 500 ps, 10 nsec and 100 nsec CO_2 pulses of ~1.5 J/cm^2. For the same fluence, the dissociation yield changes only 20% even though the peak power changes by over a factor of 200. This implies that at such high laser powers there is little "bottleneck" effect in multiphoton excitation over the initial discrete levels due to frequency mismatch. The same conclusion was reached by Gower et al.[85] who varied the pulse duration by a factor of 5 and showed that the multiphoton dissociation of many polyatomic molecules had energy thresholds, but not power thresholds.

However, at low laser intensities, multiphoton absorption data show significant dependence on the laser peak power. Kwok[56] has measured the average number of CO_2 photons absorbed by SF_6, $\langle n \rangle$ versus the laser pulse fluence for CO_2 laser pulses of several different pulsewidths. He shows that there is significant difference in $\langle n \rangle$

for pulses with the same fluence but different pulsewidths of 30, 50, and 150 ps respectively. Together with the measurements of Black et al.[53] and Bagratashvili et al.,[46] Kwok's results show that for fluences less than 1 J/cm^2 there is a factor of 30 difference in <n> between pulses of 150 ps and 120 nsec. For higher laser fluence J (> 1 J/cm^2), the difference in <n> gets smaller as J is increased. These results again support the picture that the bottleneck effect of the discrete levels is significant only at low intensities.

The work of Beauchamp et al.[10a] is worth mentioning here. They irradiated proton-bound dimers of diethyl ether with a lower power CW CO_2 laser. At an intensity of 1 W/cm^2, they were able to dissociate the ions in 1 sec. This seemed to suggest that the ions were initially in the quasi-continuum and hence the observed multiphoton dissociation has an energy threshold, instead of a power threshold. It is possible that for a weakly bonded molecular ion with many atoms, the quasi-continuum begins at very low vibrational energy. In addition, such ions prepared by chemical reactions might be vibrationally excited, so that hot-band absorptions could be significant.

There have been a number of reports devoted to the frequency dependence of the multiphoton absorption and dissociation process. Letokhov et al.[28,46] have done extensive work on measuring the frequency dependences of the average excitation energy and the dissociation yield. They found that although at low laser power, absorption followed closely the linear absorption spectrum, it was not so at high fluences. The P, Q, R branch structure in the spectrum quickly disappeared as the power was increased, and the peak of the absorption spectrum progressively moved to the low frequency side. The same results were found by Deutsch[48] and Ham.[54] Similar conclusions were also reached for the dissociation yield by measuring the visible luminescence from the dissociation product.

The red shift of the absorption spectrum with increasing absorbed energy is expected because of the anharmonicity of the vibrational transitions. Less energetic photons are needed for excitation of more highly vibrationally excited molecules. This fact was demonstrated in the shock tube experiment by Nowak and Lyman[86] who measured the absorption cross section of SF_6 at various temperatures, Schulz et al.[27] who measured the MPD yield spectrum at various vibrational temperatures and Fuss et al.[30] who measured the MPD yield spectrum after initial excitation by a CO_2 laser.

(B) EXCITATION IN THE QUASI-CONTINUUM As discussed by Bloembergen and Yablonovitch,[1] the absorption in the quasi-continuum (QC) is energy fluence dependent rather than power dependent. To demonstrate this fact, <n> versus J with various pulsewidths should be measured on molecules pre-excited to the QC. Unfortunately, no such experiment has been performed yet. Instead, experiments have only been carried out at room temperature with molecules initially distributed in the discrete levels. The results show significant differences between laser pulses of different duration due to the power-denpendent excitation over the discrete levels.

One way of looking at the absorption properties of the quasi-continuum (QC) is to obtain the change of absorption cross section σ as a function of the laser energy absorbed by the molecule. This can be deduced from the $\langle n \rangle$ versus J curve through $\sigma = d\langle n \rangle/dJ$. The same value can be measured directly using two laser beams, one acting as a pump and the other acting as a weak probe. Comparison of σ at a certain internal energy deposited into the molecule by a laser pulse with a cross section σ_{th} measured with the same internal energy deposited as thermal excitation shows an interesting fact:[56] Initially, at low internal energies, σ is much smaller than the corresponding σ_{th}. However, at very high internal energies near the dissociation threshold, σ becomes the same as σ_{th}, within experimental error. This leads to the conclusion that the energy distribution among various modes near the dissociation threshold is close to random. The same conclusion has been obtained by Grant et al.[41] who observed the angular and velocity distribution of the reaction products (see the next section). If the molecules are preheated to the QC, σ measured with laser excitation then agrees qualitatively with σ_{th}.[56] This is consistent with the argument that the absorbed energy is more or less randomized in the QC. The time resolved measurement which will be discussed later in the section shows that this conclusion is justified.

Several experiments have been performed to investigate the spectroscopic properties of the absorption in the QC. Nowak and Lyman[86] have measured the absorption spectrum of the ν_3 mode of SF_6 with molecules heated to various temperatures in a shock tube. Their results agree with the band contour calculation except at the wings of the spectrum. The shock tube measurements is however hampered by the fact that the gas is not at a uniform temperature. Therefore, analysis of the experimental data is complicated by a complex weighted average over temperature.

Ambartzumian et al. conducted two–laser measurements on the dissociation of SF_6 and OsO_4.[87-89] Their experiments were designed to show improvement of the dissociation efficiency with two laser frequencies. The first laser pulse was somewhat weaker and was used to excite molecules over the discrete levels. The second laser pulse was a strong dissociating pulse which dissociates molecules excited to the QC by the first laser. Their results were interesting and gave some clue to the absorption characteristics of the QC. When the second laser pulse was tuned to the red side of the ν_3 resonance and held fixed, the dissociation as a function of the first laser frequency followed roughly the linear absorption spectrum but shifted slightly to the red resulting from anharmonic shifts of higher vibrational transitons. When the first laser frequency was fixed and the second was tuned, they found that the dissociation rose rapidly towards the red,[86] and fell to a constant value on the blue side of the linear absorption band. The results were interpreted as follows: When the molecules are in the QC, the absorption spectrum becomes very broad and shifts to the red because of vibrational anharmonicity. Some structure may remain in the spectrum due to hot band absorption.

These findings were corroborated qualitatively by Schulz et al.[27] in a molecular beam experiment and by Gower et al.[90] However, these authors did not vary the frequency of the second laser to obtain the absorption spectrum of the QC.

Two comments should be made for the experiments mentioned above. First, since they used dissociation as a probe, the second pulse is rather strong and therefore, the results obtained may not be correlated too easily with the absorption properties of the QC. Weak probe pulses should be used to measure the absorption cross section. This was done by Fuss et al.[30] in a double resonance experiment. The results were in qualitative agreement with what is stated above. However, that experiment is obscured by the fact that collisionless and collisional effects are mixed together.

Secondly, all of these experiments were carried out with the first laser pulse having a pulsewidth of ~100 nsec and an energy of ~1 J. With such an exciting laser pulse, the bottleneck effect of the discrete levels is still significant. Even with pumping strong enough to deposit $<n>\sim 8$ into the SF_6 molecules, approximately 50% of the molecules are probably still trapped in the initial discrete levels.[27] Therefore, the results obtained may not reflect truthfully the absorption characteristics of the QC. To overcome this difficulty, a short CO_2 laser pulse should be used as the first exciting pulse. Possible candidates are the picosecond OFID pulses,[91] and 2 nsec mode-locked pulses, and perhaps simply the truncated CO_2 laser pulses.

The temporal behavior of MPE in the QC can be measured either directly using a time-resolved method, or indirectly by measuring the absorption linewidth. Reddy et al.[10c] measured the absorption linewidth of a polyatomic molecule in the QC. They used a tunable dye laser to probe the absorption spectrum of the fourth, fifth and sixth overtones of the C-H stretching mode of benzene. They obtained a Lorentzian linewidth of 100 cm^{-1} from which they concluded that the broadening of the zeroth order local vibrational mode must be due to the vibrational heat bath with a relaxation time of 1 psec. Further work needs to be done to substantiate that claim.

There are several works intended to measure the time of energy flow between modes in the QC using time resolved double resonance. Frankel[92] found the "collisionless" energy transfer rate to be 3 $nsec^{-1}$ $torr^{-1}$! That experiment was, however, collisional in nature and the result is erroneous. Taylor et al.,[93] using mode-locked CO_2 laser pulses, found a rapid recovery of the absorption of the probe pulse which they could not resolve. Deutsch et al.[94] measured a "collisionless" intramolecular relaxation time of 3 μsec. That experiment is again doubtful because the molecules were pumped to about three CO_2 photons of energy which was clearly not in the QC. Those authors probably measured a collisional relaxation time or some coherence dephasing time of the discrete states.

Kwok and Yablonovitch[55] measured the time evolution of energy residing in the ν_3 mode of SF_6 using 30 psec CO_2 laser pulses. The intramolecular energy relaxation time was put within the limits of 1 psec and 30 psec. Moreover they found a collisional relaxation time of 13 nsec-torr which was smaller than any gas-kinetic time previously measured. In that experiment, a simple picosecond pulse was split into a pump pulse and a probe pulse. The pump pulse deposited energy into the molecule and the resulting change in the absorption was monitored by the probe. The magnitude of the change depends on how the deposited energy is distributed. It would be nice to extend this measurement to two different laser frequencies so that the entire QC absorption spectrum could be measured as a function of time. This type of measurement is presently being carried out by the Harvard group.

(C) THE UNIMOLECULAR DISSOCIATION OF EXCITED MOLECULES Since the first observations of visible luminescence from the dissociation products of CO_2 laser-irradiated gases,[16,18] a rich variety of unimolecular decomposition and isomerization reactions have been reported. Claims of "non-thermal" and "non-Boltzmann" reactions in gas cell experiments are common. Several experiments[23,95] have been interpreted to suggest that the primary reaction occurs while the excitation energy still resides in the vibrational mode into which it was absorbed. Other experiments, in particular the molecular beam work of the Berkeley group,[33-35,41] have shown that the collisionless unimolecular dissociation process is well described by a statistical model (i.e., one which assumes rapid redistribution of vibrational energy among all modes of the molecule). No convincing evidence for mode-selective dissociation of molecules exists yet, and the main features of all available experimental data are not inconsistent with the energy randomization hypothesis of statistical unimolecular reaction rate theory.

We will first discuss some results of experiments performed under collisionless or near-collisionless conditions. To begin with, some comments should be made concerning the observation of collisionless luminescence from the dissociation products of various molecules. Isenor et al.[16] distinguished between a fast luminescence produced by the dissociation of SiF_4 into electronically excited fragments during an intense CO_2 laser pulse and a pressure-dependent luminescence associated with collision-induced emission. Similar results were obtained by Letokhov and coworkers on many other molecules.[18,20,46] From physical arguments and from the experimental results accumulated so far, collisionless unimolecular dissociation is not likely to produce a substantial amount of fragments in excited electronic states. Thus, it is probable that the production of electronically excited fragments constitutes only a minor dissociation channel in most, if not all, cases.

Campbell et al.[65] have used laser induced fluorescence (LIF) to measure the amount of ground state NH_2 radical produced in 0.05 torr NH_3 at CO_2 laser intensities of ~10 GW/cm^2. The peak fluorescence intensity was observed to have a delay of ~700 ns relative to the CO_2 laser pulse due to the lifetime (radiative and collisional) of the excited state of NH_2. Given the time resolution and pressure used in the experiment, collisional formation of NH_2 cannot be ruled out, although it appears that at least some of the NH_2 $\tilde{X}(^2B_1)$ is produced by collisionless dissociation of NH_3. At pressures above 2 torr, fast-rising and decaying luminescence was observed above the background. Campbell et al.[65] were able to estimate that the ratio of population of NH_2 in the $\tilde{X}(^2B_1)$ ground state to the $(^2A_1)$ excited state is on the order of 10^6 for dissociation of NH_3 at 1 torr. While this is a crude estimate, it is clear that NH_2 is formed predominantly in its ground electronic state. In addition, Stephenson and King[37] have determined that the ratio of $\tilde{A}$ to $\tilde{X}$ state of CF_2 produced in the MPD of CF_2Cl_2 and CF_2Br_2 is less than 10^{-7}. Nevertheless, the production of small qunatities of electronically excited fragments has been useful experimentally, due to the extreme sensitivity of methods of detection of visible luminescence and the observed proportionality between luminescence intensity and dissociation yield in some cases.

Fragments from MPD of a large number of systems has been identified by mass spectrometric detection under the rigorously collisionless condition of a molecular beam.[33,60] By measuring the angular and velocity distributions of the products, information regarding the dissociation dynamics is also obtained. The Berkeley group has used this technique to study MPD of a variety of molecules including SF_6, N_2F_4, and a number of halogenated methanes, ethanes and ethylenes. In all cases dissociation proceeds into the statistically predicted channels.

For the molecules listed in Table I the lowest dissociation channel is a simple-bond rupture reaction.[35,41] Translational energy distributions calculated from the RRKM statistical theory corresponding to levels with dissociation lifetimes in the 1-10 ns range satisfactorily reproduce the experimental angular and velocity distributions. The translational energy distributions peak at zero and only a small fraction (less than 20-30%) of the excess energy enters translation. The actual level of excitation above the dissociation threshold depends on the size of the molecule and the magnitude of the dissociation energy. For small molecules like CF_3X (X = Cl, Br, I), the dissociation rate increases rapidly above threshold and only levels within a few kcal/mole of the dissociation energy are populated by the laser excitation. Because of its extremely low dissociation threshold (~21 kcal/mole), N_2F_4 has an even lower average excess energy and correspondingly less translational energy in the NF_2 fragments. For larger molecules like SF_6 and C_2F_5Cl, the dissociation rate increases much more slowly above threshold and a broad range of levels populated by the laser excitation contributes to the observed dissociation yield. For $SF_6 \rightarrow SF_5 + F$, the excess energy corresponds to 7-11 CO_2 laser photons.[27] Of the average excess energy of ~25 kcal/mole only ~3 kcal/mole enters translation, leaving the SF_5 radical fragment highly vibrationally excited in the quasi-continuum. The excited SF_5 can readily absorb more photon energy via stepwise resonant excitation. With energy fluences above 10 J/cm^2 the SF_5 is observed to undergo a secondary dissociation to SF_4 + F within the 50 ns laser pulse duration. Secondary dissociation of $CFCl_2$ produced in MPD of $CFCl_3$ is also observed (the $CFCl_2$ fragment has ~5 kcal/mole internal energy following the primary dissociation).

In the case of the four molecules listed in Table 2, the lowest dissociation channel is either three-center or four-center elimination of HCl.[34] In all cases the product translational energy distribution has its peak at a finite energy due to the presence of back-reaction barriers for these systems. The presence of such barriers, which are typical of many three-center and four-center eliminations, implies that there is considerable interaction between the fragments even after the crtical configuration is passed. The partitioning of the potential energy of the exit barrier between the vibrational, rotational, and translational degrees of freedom of the fragments cannot be predicted without further modeling of the potential energy surface along the exit channel. For molecules like CH_3CCl_3 and CHF_2Cl excited to levels with dissociation lifetimes around 10 ns, RRKM theory predicts product translational energies of the order of 2-4 kcal/mole. Experimentally the average translational energy for these systems is 8-12 kcal/mole. Evidently an appreciable fraction of the exit-channel potential energy barrier is converted into translational energy of the fragments.

Stephenson and King[37] used laser induced fluorescence to determine both the internal and translational energy distributions of the CF_2 fragment from MPD of CHF_2Cl. They used energy densities of 1.5-6 J/cm^2 and pressures of 0.5-100 m torr. Three nanosecond long pulses from a frequency-doubled N_2-pumped dye laser were used to excite specific $\tilde{A}$ CF_2 (v',J',K') ← $\tilde{X}$ CF_2 (v,J,K) transitions. Since the UV probe often excited more than one v' state, the fluorescence was dispersed in order to monitor single vibronic levels. They found that the vibrational energy distribution in CF_2 could be characterized by a vibrational temperature of 1160 K and that the rotational energy content was compatible with a temperature of about 2000 K. By measuring the rate of depletion of the CF_2 concentration in the radiation zone and assuming a Boltzmann velocity distribution for fragments, they calculated the average kinetic energy of CF_2 from CHF_2Cl to be 6.9 kcal/mole, making the total average translational energy of both CF_2 and HCl as high as 16.5 kcal/mole. Making a more realistic assumption that the fragment velocity distribution is sharply peaked due to the exit channel barrier, their derived average translational energy becomes a factor of two smaller, in good agreement with the molecular beam results. The high translational and rotational energy of CF_2 indicates that in the region of the exit barrier a repulsive non-central force exists between CF_2 and HCl. The comparatively low vibrational energy in the fragments indicates that the critical configuration of CF_2 and HCl is not greatly distorted from their equilibrium configurations.

There are numerous other examples of time-resolved spectroscopic detection of MPD products in the literature. Quick and Wittig[39] measured infrared spontaneous emission from vibrationally excited HF produced in MPD of vinyl fluoride and other fluorinated ethanes and ethylenes. Wurzberg et al.[66] used LIF to monitor production of CF_2 in MPD of CF_3Br and CF_3I. They argue that the CF_2 arises from secondary dissociation of the primary CF_3 proudct during the laser pulse. This may be possible even though CF_3 is only "born" with a few kcal/mole of internal energy, since it absorbs around the same frequency as CF_3Br and CF_3I. At the 1 μs time resolution of this experiment, collisional production of CF_2 cannot be ruled out, either. Bialkowski and Guillory[67] used LIF to measure the initial rovibronic distributions of ground electronic state OH and CH radicals produced in MPD of CH_3OH. Laser intensities in the GW/cm^2 range were used. Lesiecki and Guillory,[40,64] used similar techniques to study the time evolution of CH, CN and C_2 radicals formed from MPD of acetonitrile (CH_3CN). In these experiments collisional processes were important at pressures as low as 0.1 torr. Interestingly, isotopic substitution studies showed that at 0.1 torr C_2 is mainly formed via recominbation of single carbon fragments while at higher pressures appreciable amounts of C_2 derive from single CH_3CN molecules. However, Campbell et al.[38,63] have used LIF to detect C_2 produced in MPD of several molecules at pressures as low as 10^{-6} torr. They have even used optical time-of-flight spectroscopy to measure the recoil energy of the C_2 fragment from C_2H_3CN, which they interpret as arising from the collisionless sequential elimination of H, H_2 and CN. As in the case of luminescence from electronically excited fragments, the production of C_2 probably consitutes an extremely minor dissociation channel which is only observable because of the extreme sensitivity of the LIF technique.

While MPD tends to proceed through the lowest energy channel or the channel which is statistically more favorable, if a molecule has two (or more) low-lying dissociation channels close in energy, the molecule may be excited on average above the thresholds of all these channels. In such cases there will be competition between the various channels and the branching ratio will depend to some extent on the laser intensity. Such competition is expected to occur within the framework of statistical unimolecular rate theory. The situation is somewhat analogous to a pyrolysis experiment where at higher temperatures additional dissociation pathways may open up and branching ratios may change. Such competition has been observed in some cases. Using the LIF technique as described earlier, King and Stephenson[36] estimate that for CF_2Cl_2 about 15% of the molecules which dissociate yield Cl_2 and 85% yield Cl. Using a differentially pumped beam sampling mass spectrometer and energy fluences of 10-140 J/cm^2, Hudgens[97] measured the branching ratio of Cl versus Cl_2 elimination from CF_2Cl_2 to be greater than 33:1. In the molecular beam experiments of Sudbø et al.,[35] energy fluences of 5-10 J/cm^2 were used and again the atomic elimination channels were found to be the major channels for both CF_2Cl_2 and CF_2Br_2. The implication of the experiments is that the atomic elimination becomes more important relative to the three-center molecular elimination as the energy fluence is increased.

The above results reflect the differences in the critical configurations corresponding to the different dissociation pathways. In Cl elimination from CF_2Cl_2, the critical configuration should be characterized by a rather large critical bond extension along the reaction coordinates and by substantially lower vibrational frequencies compared to the molecule (a "loose" complex). The three-center elimination of Cl_2, on the other hand, should be modeled by a "tight" complex with relatively high vibrational frequencies in the critical configuration. As a result, the rate of the atomic elimination should grow faster with excitation energy than the rate of three-center elimination, which is what is observed experimentally for CF_2Cl_2.

We will now consider briefly a few examples of MPD studied in gas cells at relatively high pressures ($\geq$ 1 torr). Dever and Grunwald[23] irradiated CF_3Cl and $CFCl_3$ as pure gases at 60 torr and in the presence of 0-60 torr of H_2. Energy densities between 0.1 and 0.4 J/cm^2 were used. On the basis of the reaction products they concluded that the primary processes are $CF_3Cl \rightarrow CF_3 + Cl$ and $CFCl_3 \rightarrow CFCl + Cl_2$. However, the results of Hudgens[97] and Sudbø et al.[35] clearly demonstrate that under collisionless conditions $CFCl_3$ primarily dissociates into $CFCl_2 + Cl$ rather than $CFCl + Cl_2$. This illustrates the danger of drawing conclusions about the primary collisionless dissociation process from bulk gas cell experiments.

Dever and Grunwald[23] interpreted their data on the basis of an Arrhenius-type dependence of the conversion per laser flash (CPF) on absorbed energy (E_{abs}).

$$\ln(\mathrm{CPF}) \approx \ln A - \frac{E_{act}}{(E_{abs}/n)} \quad ; \qquad \frac{E_{abs}}{n} = RT_{vib} \quad ,$$

where n is the number of vibrational modes over which the absorbed energy is distributed and T_{vib} is the vibrational temperature of these modes. In this way they obtain values of n close to one, which they interpret as evidence that the primary reaction occurs while most of the vibrational energy resides in one vibrational mode. Preses et al.[95] used similar arguments to claim mode-selective decomposition of octafluorocyclobutane. Of many possible objections to such an analysis, the most obvious is the mounting evidence[50,89] that at moderate laser intensities only a small fraction of the molecules are coupled into the quasi-continuum where they can rapidly absorb energy and dissociate. The average energy absorbed per molecule, calculated assuming all molecules absorb equally, may grossly underestimate the average energy absorbed by the molecules which are actually coupled into the quasi-continuum (which are the ones that count). If this latter quantity could be determined experimentally and used in the Arrhenius-type expression, much larger values of n would be obtained.

Rosenfeld et al.[98] studied MPD of ethyl vinyl ether at pressures between 5 and 440 torr where the reaction is mainly collisional in nature. From the product yield branching ratio and known Arrhenius parameters they deduce an apparent "temperature" of ~1600 K assuming the applicability of RRKM theory. Brenner[99] also studied MPD of ethyl vinyl ether and found a different branching ratio when the laser pulses of different durations (0.2 and 2 μs), but constant energy fluence, were used. He suggests that the dynamics of multiphoton absorption may be different in the two cases. Although the absorption in the quasi-continuum seems to depend only on energy fluence, the level of excitation above the dissociation threshold does depend on laser intensity, and this may explain the observed changes in branching ratio.

Gas cell experiments involving focused beam geometries are particularly susceptible to misinterpretation. Colussi et al.[100] measured the ratio r = [HCl]/[DCl] in MPD of CH_2DCH_2Cl and found it to be independent of pulse energy (which is proportional to intensity for constant pulse length). This contrasts with the cases discussed earlier where it was shown that the excitation level and branching ratio may depend strongly on laser intensity. The reason no change in branching ratio is observed in the experiments of Colussi et al. is probably as follows. By attenuating the laser beam in a focused geometry the net effect is to cut down the sampling volume (due to the energy fluence requirement for dissociation), without changing the range of intensities seen by the molecules in the gas cell. Molecules in different parts of the converging laser beam see different intensities and dissociate from different levels, but the average excitation level and branching ratio should be (and are) constant, independent of the pulse energy.

In all gas cell experiments, it is necessary to distinguish between the "collisionless" laser-induced reaction and reaction resulting from thermalization of the absorbed energy by intermolecular V→V and V→T,R processes. Danen et al.[101] studied the laser-induced dissociation of ethyl acetate to acetic acid and ethylene. To evaluate thermal effects, they used a 1:3 mixture of isopropylbromide: ethyl acetate and monitored HBr elimination from isopropyl bromide. Since both reactions have similar activation energies, the ratio of the thermal rate constants is nearly temperature-independent. By comparing the observed product ratio to the thermal value, the extent of the non-equilibrium laser-induced reaction was determined as a function of reactant pressure and laser energy fluence. Similar experiments on CH_3CF_3 have been reported by Richardson and Setser.[102] Such "internal standards" should prove very useful in other gas cell experiments.

THEORY

In this section we will try to present some of the various theoretical approaches used to understand MPE and MPD. We will consider the problem of a single polyatomic molecule interacting with the strong infrared field of a laser beam. Additional complications arise when collisions between molecules cannot be neglected, as in most of the commonly performed gas cell experiments. We will only briefly mention the most important modifications in the theory necessary to account for the collisional effects.

Consider a molecule consisting of four or more atoms, irradiated by a laser field near resonance with one or more of the vibrational modes of the molecule. When the field is sufficiently intense, tens of photons may be absorbed by the molecule. This may eventually lead to dissociation of the molecule. In formulating a theory for the process, one is faced with a seemingly insurmountable difficulty, namely, the vast number of states needed to be included in a quantum mechanical treatment of the process. Classical approximations have been used in a few studies[4a,103-105] in an attempt to illuminate aspects of the process, but they have so far made rather limited contributions to the understanding of MPE. Numerical integration of the equations of motion for realistic models (i.e., systems with more than three atoms) is formidably time consuming. It is also unclear how good a classical approximation can be for a system in which the zero point vibrational energy is an appreciable fraction of the total energy.

Two distinctly different approaches for building simplified quantum mechanical models of a molecule have been used. In the first approach, attention is focused on the vibrational mode pumped by the laser field such that only energy levels attached to this mode are treated discretely. Hopefully, the number of states thus singled out is manageable, and as much as possible available spectroscopic information can be built into this simplified level diagram. The remaining vibrational modes of the molecule, coupled to the pumped mode by anharmonicities and Coriolis interactions, are considered to provide a heat bath for this mode. In this picture, the radiation first deposits energy into one particular mode, and then energy leaks gradually from this mode into the heat bath formed by the other modes. The bath heats up, increasing the total energy in the molecule. The interaction between the pumped mode and the bath then increases, leading to a red shift and a smearing out of the absorption spectrum of the pumped mode.

The other approach treats all vibrational modes on equal footing, and deals with transitions between true molecular eigenstates, induced by the laser field. The concept of intramolecular energy transfer does not apply here; the eigenstates are to various extents mixtures of the normal modes. For low excitation, the number of states involved is manageable. The transition frequencies and matrix elements can in principle be obtained from spectroscopic data, and a fully quantum mechanical treatment of the laser excitation, though cumbersome, is possible.[26,28] At higher excitation energies, the density of vibrational states may become so high that one speaks of a quasi-continuum. Once the molecules are excited to the quasi-continuum, they can easily absorb more photons through resonant incoherent transtions between levels. As we shall see, this can be described by a simple set of rate equations for the level populations.

For a molecule excited to a level around or above its dissociation energy, a theory has been well developed for the description of dissociation kinetics. This is the well-known RRKM theory of unimolecular reaction,[42,43] which can be directly applied to the collisionless multiphoton dissociation of molecules. The theory assumes a complete randomization of vibrational energy within experimentally resolvable energy intervals in the excited molecule. Only on a picosecond or shorter time scale is this a dubious assumption. The typical time scale for most MPE experiments is around tens of nanoseconds. The RRKM theory yields dissociation rates from given energy levels, and can therefore be easily incorporated into the rate equations. In the heat bath picture, however, incorporation of the RRKM theory into the calculation is more cumbersome, and has not been attempted so far.

The rate equations can, of course, be written down from the phenomenological point of view. They can, however, be justified in the microscopic derivation provided that certain approximations are satisfied. Complexity of the eigenstates involved in the transitions forbids a first principle calculation on the physical parameters in the rate equations. Hopefully, these parameters can be deduced from some experimental results and then the set of rate equations would properly describe the MPE and MPD process.

Before we proceed to review some of the work underlying the presently accepted picture of MPE, let us first mention one model which is attractive for its simplicity, but is definitely over-simplified.

This is the anharmonic oscillator model; degenerate[106-107] or nondegenerate.[103,108] The model neglects the rotational structure of the molecule even for the lowest levels, and ignores the presence of other vibrational modes at high levels of excitation. It may have looked like a way to explain the very high levels of excitation (more than twice the dissociation threshold) erroneously reported for SF_6.[28b] If it were true, very nonstatistical behavior of the dissociation process would be predicted, making selective bond breaking in molecules possilbe through MPE. Although this also has been erroneously reported to occur,[23] it is well established that in all cases studied so far, the dissociation is best described by standard statistical theories of unimolecular reactions.

The idea of a quasi-continuum to explain the high level of excitation was used already in the early work of Isenor et al.[16] The idea has later been extensively developed by many authors[7b,c,24,25,28,109-113] to explain phenomenologically the overall features of the excitation process. A rate equation approach with a few adjustable parameters determined from experiments,[27,31,32] can describe fairly well the dependence of dissociation yield and average energy absorbed on the laser energy fluence. Such an approach hs been justified by Bloembergen and Yablonovitch,[1] and more rigorously deduced from the Schrödinger equation of the process by Quack,[114] and Schek and Jortner.[115] The reduction of the Schrödinger equation to the rate equation is an old problem in statistical mechanics. However, the coherent part of the initial excitation over the discrete levels is neglected in this approach. Quack[114] has discussed how the discrete levels in principle can be taken into account, and has also shown by numerical examples that not a very large number of levels is needed in the lower end of the quasi-continuum for the rate equations to be a perfectly adequate description of the "leakage" from the discrete states into the quasi-continuum.

Initially in the history of MPE, it was somewhat of a puzzle how a molecule could be excited to the quasi-continuum by a moderately intense laser beam as was observed. The anharmonicity of a vibrational mode forbids successive resonant transitions leading all the way to the quasi-continuum. It was then shown[7c,28,112] that when the rotational substructure of the rovibrational levels was taken into account, resonance enhancement from intermediate levels can make coherent three- and four-photon transitions possible. For a while, anharmonic splitting of the degenerate modes was also believed to be important in bringing the stepwise transitions near resonance,[106,107] but both the observation of MPE in a number of molecules excited via nondegenerate modes, and the more recent detailed calculations on SF_6[26,29,116] show that the rotational substructure is the only really important feature. Initially, it was believed that the rotational compensation of anharmonic levels shifts could only occur for a limited number of the rotational states of the ground vibrational level. This is difficult to reconcile with the observation of close to 100% dissociation in sufficiently intense laser fields. However, Knyazev et al.[117] have pointed out that rotation-vibration interactions introduces level splittings which will allow the compensation to occur for more rotational states. Most of the transitions involved are weak, and only important at high laser intensities. Thus, at low laser intensities, only a small fraction of the population in the rotational states of the ground vibrational manifold can be excited into the quasi-continuum. As the laser intensity is increased, the weak transitions, together with power broadening of the strong transitions, allow more rotational states and thus a larger fraction of the molecules to be excited. This bottleneck effect at low laser intensities can also be strongly affected by collisions, since it can be partly offset by rapid intermolecular rotational energy transfer during interaction with the IR laser pulse.

The mathematical treatment of a multilevel quantum system interacting coherently with a strong electromagnetic field has received the continous attention of theorists ever since the birth of quantum mechanics, and a variety of techniques for treating the problem have been developed. Today, with the availability of high-speed computers and powerful numerical methods in linear algebra, the most commonly used method[26,29] is to reduce the time dependent Schrödinger equation to an eigenvalue problem by a "rotating wave approximation". Provided the number of levels is manageable, and the level properties are known, a numerical treatment is then straightforward. More general methods, based on the quasi-energy concept (for reviews, see Zeldovich[118] or Sambe[119]) or the "dressed atom" picture[3a] all lead to the same eigenvalue problem in the lowest order. For optical frequencies, this is usually an excellent approximation. Thus, it is possible that one can treat accurately the initial coherent excitation in MPE. The difficulties arise when the level complexity grows with excitation energy, or in the heat bath picture, the intramolecular relaxation becomes important. So far, no one has attempted such an all encompassing calculation on a real system.

The early treatment based on the heat bath picture used a simplified level diagram for the IR active mode. Interaction of the pumped mode with the remaining part of the molecule and the effects of molecular collisions were taken into account by phenomenological damping terms in the equations of motion.[108,110,120-122] Such equations of motion can be derived using the density matrix formulation[11,123] together with a few assumptions: The coupling between the heat bath and the pumped mode has to be weak or random, and there can be no interaction between the heat bath and the laser field. The validity of these assumptions is, however, disputable under at least some experimental conditions.

From what is said above, it should be evident that although a phenomenological approach with rate equations and experimentally determined parameters can be used to describe MPE and MPD qualitatively and semi-quantitatively,[27,31,32] a rigorous theoretical treatment is still not realized. It seems that by now all the important building blocks necessary for a theoretical understanding of the process are present. Thus, any given experimental observation can probably be reproduced by various models using the concepts and ideas presented above. In that sense, the process may be considered to be reasonably well understood. However, a reduction of this understanding into a calculable set of equations encompassing all experimentally relevant aspects of the process is still missing. Major reasons for this state of matters are the great complexity of and the lack of complete information about the quantum mechanical system involved.

APPLICATIONS

Of the possible applications for the MPD process, isotope separation has received the most attention. Isotopic enrichment of C,[124-127] H,[100,128-131] S,[21,52] Cl,[132-133] B,[124,134,135] Os,[20,87,96] Mo,[136] Si,[124] and Se[137] have been observed with enrichment of ^{2}H as high as a factor of 1400.[130] Many recently published articles and reviews give detailed discussions of isotope separation and its commerical feasibility.[5,8,9,11,13]

The efficient and inexpensive production of molecular radicals by MPD may stimulate further understanding of radical reactions. Laser control of the identity of and excitation in molecular radicals may be used to study radical reactions and provide some practical new synethic methods.

Multiphoton excitation of polyatomic molecules can complement conventional high temperature chemistry of polyatomic molecules.

The heating of a molecule via MPE is much more rapid (on a ns time scale) than under any other experimental conditions. Moreover, selected components of a reactant mixture can be singled out and heated without wall effect. Primarily internal vibrational energy, and little rotational and translational energy is given to the molecule. These salient features are peculiar to IR laser induced chemistry.

Purification of gases by MPD can be achieved by selectively dissociating impurities in a patently nonthermal manner.[138,139] The impurities 1,2-dichloroethane ($C_2H_4Cl_2$) and carbon tetrachloride (CCl_4) were removed from $AsCl_3$ by illumination from a CO_2 laser.[138] The dissociation products chemically reacted to form final products of C_2Cl_4, C_2Cl_6, C_2H_2, C_2H_3Cl and HCl. These final products can be more easily separated by physical methods than the initial impurities. Multiphoton excitation is used to eliminate hot wall reactions in pyrolysis studies because the excitation can occur far from walls which are relatively cold. Ultraviolet laser excitation or ionization of multiphoton excited molecules may also have a larger number of applications.[8] For example, Knyazev et al.[140] have recently achieved higher isotopic selectivity of carbon-13 with multiphoton infrared excitation followed by ultraviolet excitation to a dissociative state of CF_3I than has been achieved by infrared excitation alone.[126] The myriad uses of multiphoton excitation and dissociation of polyatomic molecules described here may not all be successful due to possible complications which arise in the application of any process. On the other hand, there may be a large number of applications which cannot be foreseen at the present time.

CONCLUSIVE REMARKS

As we have seen, the field of MPD has been moving very rapidly forward in the past several years. Most of the major aspects of the process are now qualitatively understood. However, there are still a number of very important questions yet to be answered more quantitatively. Here we mention only those which often come up in a discussion.

First, in the excitation process, how does the excitation over the discrete levels into the quasi-continuum depend on the laser frequency and intensity? This determines the fraction of molecules which enter the quasi-continuum and can then be resonantly pumped by laser fluence to and beyond the dissociation threshold. The transition between the discrete levels and quasi-continuum should in reality spread over a certain energy region. What the effective width of this transition region is, and how it would affect the excitation into the quasi-continuum are also questions worth considering.

Second, how does the intramolecular mode-mode coupling affect the multiphoton excitation in the molecule? This determines how fast and at what level the excitation energy will be effectively randomized in several or many vibrational modes, and whether mode-selective excitation and dissociation of moelcules are indeed possible. In this respect, it will be interesting to know how the absorption spectrum of the molecules changes and how quickly the intramolecular interaction among modes increases as the molecules are excited to higher and higher levels. A relatively simple, but rather intriguing question should also be answered: How well can a high-frequency mode ($\gtrsim 3000\ cm^{-1}$) couple with low-frequency modes ($\lesssim 1000\ cm^{-1}$), and hence can mode-selective excitation and dissociation be achieved by exciting a high-frequency mode?

Third, what does the population distribution look like in the quasi-continuum when the molecules are highly excited, in particular, close to or even beyond the dissociation threshold? This of course depends on the excitation in the quasi-continuum, but may also depend strongly on the excitation over the discrete levels. While there already exist a number of theoretical calculations on this subject, little experimental information is presently available.

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Table 1.* Simple bond rupture reactions

	Translational Energy Distribution	Best Fit RRKM Calculation	
Reaction	Average energy (kcal/mole)	Average excess energy available for the fragments (kcal/mole)	Corresponding life time for given excess energy (s)
$CF_3Cl \rightarrow CF_3 + Cl$	1.1	4	5×10^{-9}
$CF_3Br \rightarrow CF_3 + Br$	1.2	5	2×10^{-9}
$CF_3I \rightarrow CF_3 + I$	1.1	4	1×10^{-9}
$CF_2Cl_2 \rightarrow CF_2Cl + Cl$	2.0	10	5×10^{-9}
$CF_2Br_2 \rightarrow CF_2Br + Br$	1.6	7	5×10^{-9}
$CFCl_3 \rightarrow CFCl_2 + Cl$	1.2	5	12×10^{-9}
$N_2F_4 \rightarrow 2NF_2$	0.4	2	1×10^{-9}
$SF_6 \rightarrow SF_5 + F$	3.0	25	20×10^{-9}
$C_2F_5Cl \rightarrow C_2F_5 + Cl$	4.0	35	60×10^{-9}

*From references 35 and 41.

Table 2.* HCl elimination reactions

Reaction	Average translational energy (kcal/mole)	Average spread (FWHM, kcal/mole)	Energy barrier in the back reaction
$CHF_2Cl \rightarrow CF_2 + HCl$	8	6	6
$CHFCl_2 \rightarrow CFCl + HCl$	~8	~6	?
$CH_3CF_2Cl \rightarrow CH_2CF_2 + HCl$	12	8	55
$CH_3CCl_3 \rightarrow CH_2CCl_2 + HCl$	8	8	42

*From reference 34.

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