Infrared Laser Chemistry of Large Molecules

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Abstract: We have recently discovered a surprisingly efficient CO_2 laser-induced reaction in the largest and most complex molecular system studied to date. The results obtained in this work suggest that the multiple photon excitation that drives this reaction can be localized long enough to lead to a spatial and site-selective unimolecular dissociation. The experiments are performed on a volatile uranyl complex, $UO_2(hfacac)_2 \cdot THF$, which consists of 44 atoms and has some 126 normal modes. The dissociation products are $UO_2(hfacac)_2$ and THF. A model is proposed which requires T_1 of the pumped mode to be shorter than 10^{-9} s in order to absorb the five to ten photons required to overcome an approximately 30 kcal/mol activation barrier with laser intensities of only a fraction of a megawatt/cm^2. The observed absorption line shape appears homogeneous and the dissociative yield can be as high as 100%. The critical energy migration from the excited uranyl moiety to the bond broken probably occurs in a time longer than 1 ps and shorter than 1 ns. Collisions with argon during the excitation process are found to disrupt the process with extreme efficiency. Our results suggest that the reaction pathway induced by the laser can be predetermined by careful design of the structure and bonding in a molecule. This selective vibrational heating process is applicable to molecules which approach the size and complexity of molecules of biological importance.

Introduction

Infrared laser-induced multiple-photon unimolecular decomposition has been observed in almost every four- to ten-atom molecule which has been subjected to intense, resonant laser radiation.[1] Once the generality of the process for small- to medium-size molecules was demonstrated, attention focused on the extent to which infrared multiple photon laser chemistry was unique. One of the attractions of this form of laser chemistry is that, if energy can be deposited into a specified vibrational mode of a molecule and remain localized for a sufficiently long time, a selective reaction involving that mode may be realized. In addition, if the energy can be localized in the region around a specific bond, then selective reaction involving only that portion of the molecule may be obtained. Experimental results which support this concept are scarce. Instead the preponderance of experimental results on small- and medium-size molecules supports theoretical models which suggest that no bond or mode selectivity should be anticipated.[2] These models assume that when a molecule is excited beyond the first few vibrational levels the intramolecular energy randomization rates are extremely rapid, on the order of 10^{-12} s. Most of this work has been done on center-atom-symmetric molecules in which the intermode coupling is expected to be strong. There have been a few experiments on more complex molecules which suggest, on the basis of product branching ratios, that the excitation may not be randomized on the time scale required for reaction.[3]

There has only been one experiment reported on the infrared laser induced chemistry of molecules consisting of 30 atoms or more.[4] Based on measured vibronic relaxation rates in excited electronic states of large organic molecules, such as dyes, energy randomization and relaxation of vibrational excitation in the ground electronic state have been estimated to be on the order of, or faster than, 10^{-12} s.[5] Thus no selective multiple photon excitation leading to interesting and unique chemistry would be expected in such systems. Large molecules in general also fall beyond the degree of complexity considered in most theoretical models for the infrared multiple photon chemistry process. We have chosen to examine the infrared laser multiple-photon-induced unimolecular dissociation of a molecule consisting of more than 30 atoms to determine the validity of these assumptions.

A molecule suitable for this study should absorb CO_2 laser radiation for ease of experimentation. The molecule should be volatile, thermally stable, yet possess bonds which could be cleaved at a variety of energies with barriers ranging from 10 to 60 kcal/mol. It should be easily modified chemically and offer a number of chemically distinct energy input points in resonance with available laser sources. The molecule should be physically large with dangling extremities, such that regions of the molecule can be separated from the pumped moiety by more than one bond.

We have synthesized a novel, volatile uranyl complex in our laboratory which meets some of these criteria, and used it to demonstrate that vibrational energy in a complex molecule can be regionally localized long enough to lead to a spatial and site-selective unimolecular dissociation.

Experimental Results

The molecule we have synthesized is bis(hexafluoroacetylacetonate)uranyl–tetrahydrofuran, $UO_2(hfacac)_2 \cdot THF$, or $UO_2L_2 \cdot B$. The synthetic route and the chemical and spectroscopic properties of this molecule are described elsewhere.[6] This molecule is volatile at moderate temperatures; it sublimes at 50 °C and has about 1 Torr vapor pressure at 100 °C. Uranium in the +6 oxidation state prefers to be highly coordinated and many uranyl compounds such as UO_2F_2 exist in a polymeric network rather than an isolated molecular entities. To provide a volatile species, the polymerization has to be prevented by neutralizing the UO_2^{2+} ion and minimizing intermolecular attractions. This is accomplished by surrounding the UO_2^{2+} ion with chelating anionic ligands (hfacac) which tend to repel one another and tend to minimize intermolecular attraction. The final coordination site is occupied by a weakly bound neutral ligand, such as THF. The UO_2^{2+} moiety is nestled in the center of a planar pentagonal framework. This framework forms the first bonding sphere. It consists of the four oxygens of the (hfacac) groups and one of the THF ligand. The outer boundaries of the molecule consist of "Teflon shock absorbers" in the form of the CF_3 groups of the hfacac ions. These contribute to the isolation of the UO_2^{2+} moiety and to the volatility of the molecule. Figure 1 shows schematically the structure of the molecule.

The absorption band due to the asymmetric stretch of the UO_2^{2+} moiety in $UO_2(hfacac)_2 \cdot THF$ falls within the range of the CO_2 laser; it is clear of any other interfering absorption. It is most strongly resonant in the vapor phase with the P(6) CO_2 laser line at 10.6 μm. This band is relatively narrow, about 7.8 cm^{-1} fwhm. Excitation of the uranyl moiety by CO_2 laser radiation leads to a unimolecular dissociation of the molecule involving the loss of the neutral ligand. This laser-induced dissociation has been observed both in a static gas cell and in

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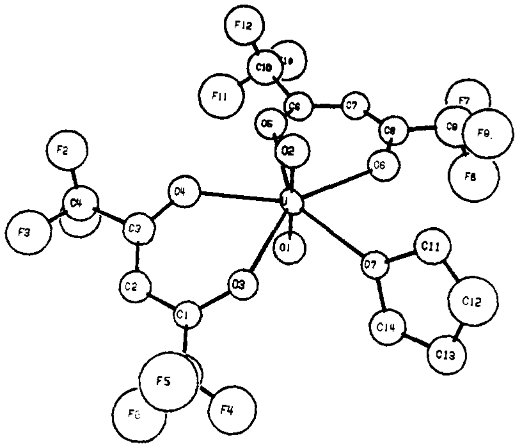


Figure 1. The structure of $UO_2(hfacac)_2$·THF.

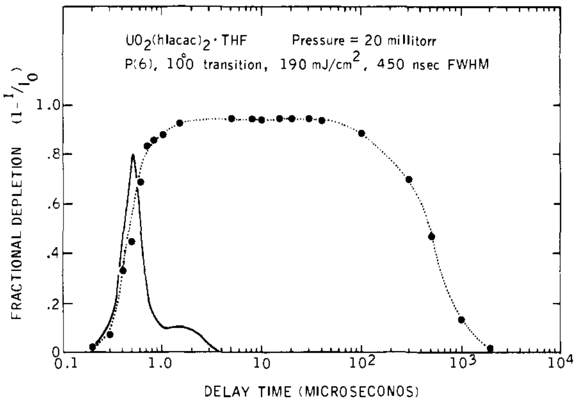


Figure 2. Time dependence of fluorescence depletion. Percent depletion vs. delay time where percent depletion is defined as $\{1 - I(t)/I_0\} \times 100$ with I_0 = fluorescence intensity in the absence of CO_2 laser irradiation, $I(t)$ = fluorescence intensity at delay time t following CO_2 laser pulse. The delay time is the time from the leading edge of the CO_2 laser pulse to the dye laser probe pulse. CO_2 laser characteristics: laser transition (P(6) 10.6μ; fluence 190 mJ/cm^2, TEM_{00}; pulse duration 450 ns fwhm. The long time return of the fluorescence signal reflects a diffusional refilling of the interaction volume.

a molecular beam. The results of the molecular beam experiments will be reported elsewhere.[7]

Static Cell Photodissociation Experiments

$UO_2(hfacac)_2$·THF is readily dissociated by radiation from an unfocused, pulsed CO_2 TEA laser. In a static cell at pressures below 1 Torr the dissociation is detected by monitoring the instantaneous concentration of the starting material using laser-induced fluorescence (LIF).[22] The CO_2 laser used in these experiments has a pulse width of 450 ns fwhm and a beam diameter of 0.85 cm at the $1/e^2$ point. A few experiments were also performed with a pulse width of 50 ns fwhm. The Molectron nitrogen laser-pumped dye laser has a 12-ns pulse width, a 10-Å bandwidth, and an output of 1 kW/pulse. The system was operated at 10 pps. Fluorescence of the starting material is induced by a counter propagating dye laser pulse at 4500 Å. The emission intensity at 5216 Å from the 0,0 band of the first excited singlet state serves as a monitor of the number density of reactant molecules. The diameter of the dye laser beam is approximately 1 mm and thus only the central portion of the volume swept out by the CO_2 laser beam is interrogated. No change is observed in the absorption of the 4500-Å radiation due to CO_2 laser excitation. By varying the delay time between the infrared pulse and the LIF interrogation pulse, the time evolution of the photoreaction is measured. The resolution is approximately 20 ns, somewhat poorer than the 12-ns width of the dye laser because of trigger uncertainties.

In Figure 2 we plot, as a function of delay time, the depletion of molecules induced by a CO_2 laser pulse at P(6) of the 10.6-μm transition with an energy fluence of 190 mJ/cm^2. The CO_2 laser pulse is also indicated in Figure 2 for reference. The rise time observed for the depletion follows the rise time of the CO_2 laser pulse. Therefore the sum of the rate of excitation to the critical energy level plus the rate of dissociation is faster than $(50\ ns)^{-1}$.[23]

The LIF signal returns to its initial intensity in a time characteristic of a diffusional refilling of CO_2 laser irradiation volume. This time increases as the pressure of the starting material is increased. At 500 mTorr, for example, the return time is on the order of 10 ms. At this pressure the molecules require roughly 5 ms to diffuse out of the interaction volume. This is roughly equivalent to 1000 collisions. Since we do not observe recombination within this time, if the recombination is a simple bimolecular reaction it must require more than 1000 collisions. Ultimately, however, the dissociation reaction is reversible. Although the CO_2 laser dissociates nearly all the molecules in its path and the volume swept out by the CO_2 laser is roughly 50% of the total cell volume, even after thousands of pulses there is no reduction in the LIF signal intensity. Regeneration is thought to occur on the wall of the stainless steel reaction cell, but some gas-phase exchange reactions are known to occur. The mechanism of regeneration is not yet understood and the reactions of photoproducts are presently under study.

The extent of dissociation is surprisingly large in view of the narrow CO_2 laser bandwidth of 0.1 cm^{-1} compared to the 7.8-cm^{-1} (fwhm) width of the UO_2^{2+} absorption band. Power broadening at the laser intensities used in these experiments may contribute about 0.1 cm^{-1} to the excitation linewidth but this is not enough to account for the observed dissociation yield. Thus the absorption band has to exhibit homogeneous-like behavior.[20]

At moderate laser energy fluence, around 50 mJ/cm^2, the wavelength dependence of the dissociation follows the small signal absorption profile. No dissociation was observed off-resonance, using, for example, the P(26), 10.6-μm transition. However at a higher energy fluence of 500 mJ/cm^2 we did observe about 10% dissociation using the P(26), 10.6-μm transition.

The dependence of dissociation yield on laser energy fluence is linear for all the laser transitions examined up to the point where 70% depletion is achieved. After this point the 100% level is approached with a roughly exponential dependence. Figure 3 shows the typical behavior on the P(6), 10.6-μm transition. No intensity threshold for the dissociation is observed within the sensitivity of the LIF technique. We extrapolate from these observations to predict that only the energy fluence and not the intensity of the laser radiation is important to the energy deposition process. The only constraint on the energy fluence is that the effective excitation period is limited by the transit time of the molecule in the laser beam. Indeed we observed, under collision-free, molecular beam conditions, CW laser-driven dissociation of $UO_2(hfacac)_2$·THF at intensity levels as low as 100 W/cm^2 with a contact time of 5×10^{-6} s; this corresponds to 0.5 mJ/cm^2 energy fluence.[7]

When both the fluorescence lifetime and intensity are monitored, information on the fluorescence quenching cross section of the photoproducts can be obtained. In this experiment the dye laser excites a small fraction of the UO_2L_2·THF molecules into the fluorescent state, prior to the CO_2 laser pulse. The CO_2 laser photodissociates molecules in the ground electronic state and an increased fluorescence quenching rate

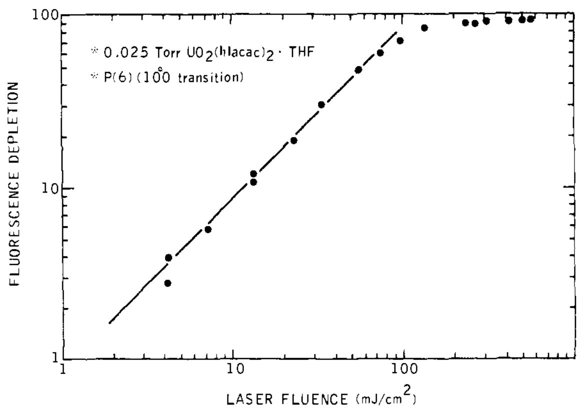


Figure 3. Extent of fluorescence depletion as a function of CO_2 laser fluence. Percent depletion is as defined in Figure 2 with a fixed delay time of 10 μs.

is observed. We observed that the molecules in the fluorescing, excited electronic state and the photoproducts do not absorb photons from the CO_2 laser transitions used to excite the molecule in the ground electronic state. The fluorescence quenching is caused by the CO_2 laser produced photofragments collisionally interacting with the electronically excited molecules. This data is shown in Figure 4. The self-quenching lifetime at the pressure used is 675 ns; the observed quenching rate is nearly doubled after the CO_2 laser dissociation of the sample. Because the quenching rate due to free THF has been measured to be negligible this increase is attributed to a long-range interaction between the coordinatively unsaturated uranyl photoproduct and the fluorescing species. These results indicate that dissociation occurs within 1 μs of the CO_2 laser pulse.

Mass Spectrometer Photofragment Identification Experiments

$UO_2(hfacac)_2$ and THF are identified as the primary photodissociation products when the parent molecule is irradiated by a pulsed CO_2 TEA laser at moderate laser energy fluence. This is demonstrated using time-of-flight (TOF) mass spectrometric detection in a scheme similar to that described by Kaldor and Hastie.[8] The sample is irradiated inside an oven behind a small pinhole at a pressure less than 0.01 Torr. The molecular species, parent molecule, and photofragments effuse from the oven, form a molecular beam, and are mass and time-of-flight analyzed. The experimental configuration is shown in Figure 5. The vapor density is controlled by the oven temperature and experiments are performed in the absence of hard-sphere collisions, i.e., the mean free path in the oven is large compared to the distance the irradiated molecules or photofragments must travel to escape through the pinhole. At 130 mJ/cm^2 on the P(6), 10.6-μm transition, we estimate that more than 50% of the molecules within the laser irradiation volume undergo unimolecular photodissociation. The laser irradiated volume represents about 25% of the total oven volume. The dc ion signal from the mass analyzer system is fed into a multichannel analyzer (MCA) triggered at each laser pulse.

Under these experimental conditions the parent uranyl molecular ion $UO_2(hfacac)_2 \cdot THF^+$ at 756 amu exhibits a typical time-dependent depletion in which a decrease of the ion signal due to the laser-induced dissociation of $UO_2(hfacac)_2 \cdot THF$ is observed. A qualitative representation of the TOF signal is shown in Figure 6A. The time evolution of the filling in of the dissociated volume reflects the thermal spread of the molecular velocities in the time necessary for the molecules to travel from the oven to the ionizer of the mass spectrometer and also the time delay in the onset of this signal due to the time necessary for the molecules to travel from the irradiation zone to the detector.

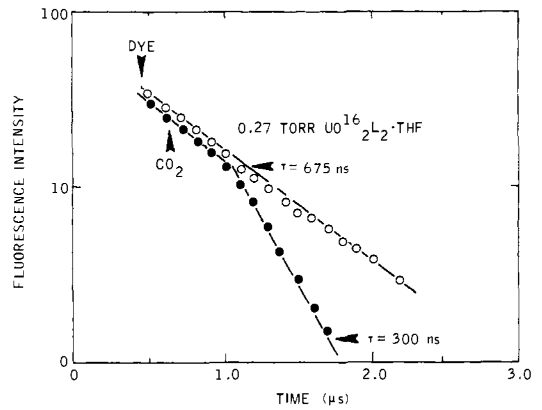


Figure 4. Enhanced fluorescence quenching by CO_2 laser photofragments. The logarithm of the fluorescence intensity is plotted vs. real time. In the upper curve (Δ) there is no CO_2 irradiation. The fluorescence is initiated at the time marked "dye" and the exponential decay of fluorescence due to self-quenching collisions is recorded. In the lower curve the CO_2 laser pulse follows the dye laser by 300 ns (indicated) and the change in fluorescence quenching rate is indicated by the abrupt change in slope. The effective quenching cross section is approximately doubled following the CO_2 laser pulse.

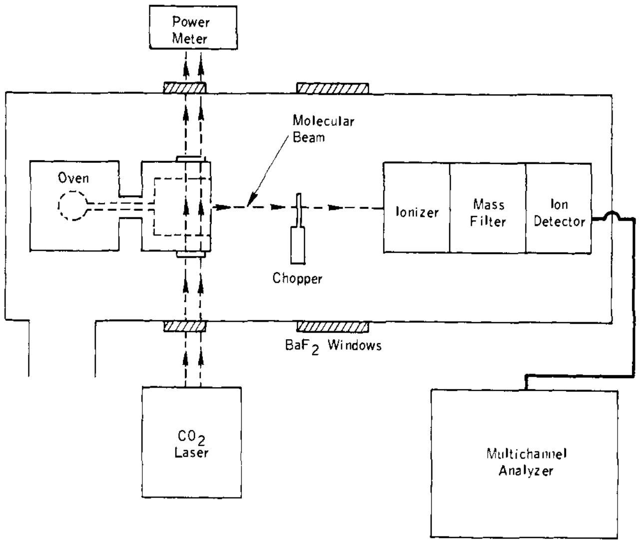


Figure 5. Schematic diagram of the experimental apparatus used in the photofragment identification experiments.

Alternatively a photodissociation fragment produced in the oven will give rise to a transient increase to the ion signal together with an earlier TOF arrival time because of the lighter mass and also, possibly, due to kinetic energy increase of the fragment through the photodissociation process.

Indeed, the highest mass fragment to exhibit an increased ion production and earlier arrival time was $UO_2(hfacac)_2$ at mass 684 amu. Similarly THF at mass 72 exhibited an arrival time even earlier than $UO_2(hfacac)_2$ together with increased ion production. From searching the mass spectrum only $UO_2(hfacac)_2$ and THF or their dissociative ionization fragments displayed increased ion production and earlier arrival times. The parent uranyl molecular ion $UO_2(hfacac)_2 \cdot THF^+$ or its directly produced dissociative ionization fragments such as $UO_2(hfacac) \cdot THF^+$ at mass 549 (the most intense high mass ion peak) all exhibited decreased ion signals with nearly identical arrival times. Some ion peaks had contributions from the dissociative ionization of both the parent uranyl molecular ion $UO_2(hfacac)_2 \cdot THF^+$ and the primary photoproduct

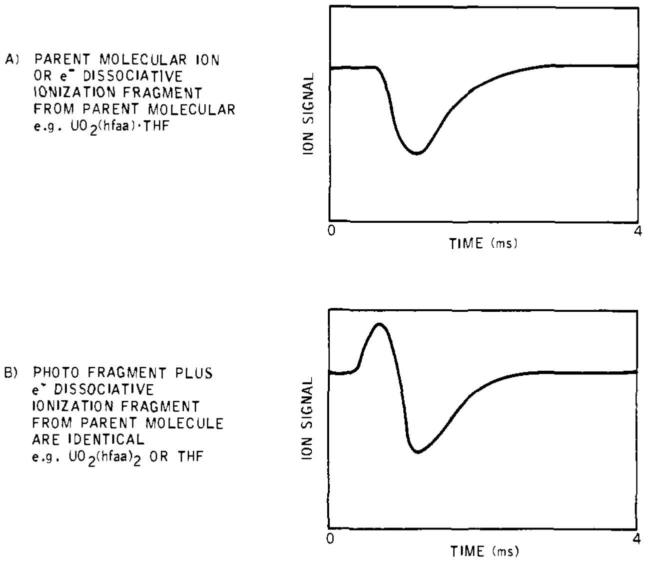


Figure 6. Typical time-of-flight responses for the parent molecular ion (A) and for a fragment ion (B). The fragment ion signal arises from two sources: one is the fragment produced by the dissociative ionization of the parent molecule (negative going signal) and the other ion is due to the directly produced photofragment (positive going signal and shorter TOF).

$UO_2(hfacac)_2$. In this instance both an increased ion signal at earlier times and a decreased signal at later times were observed. This behavior is shown qualitatively in Figure 6B. It should be noted that the mass fragmentation pattern of $UO_2(hfacac)_2{\cdot}THF$ in the absence of laser radiation exhibits a negligible $UO_2(hfacac)_2{}^+$ ion signal (less than 2% of $UO_2(hfacac)_2{\cdot}THF$ fragments to $UO_2(hfacac)_2{}^+$).

Based on the analysis of the transient behavior of many mass peaks we have been able to identify the photodissociation products from the IR laser induced unimolecular photodissociation of $UO_2(hfacac)_2{\cdot}THF$ as $UO_2(hfacac)_2$ and THF under the experimental conditions employed. The bond broken is not the bond pumped; it is the weakest bond in the molecule.

Discussion

These results demonstrate that multiple photon dissociation in large molecules can be a remarkably efficient process. How does multiple photon dissociation occur in large molecules and why is it so efficient? Very large molecules such as $UO_2(hfacac)_2{\cdot}THF$ have a number of characteristic features that do not exist in medium-sized molecules such as SF_6 and which indicate that the mechanism for multiple photon dissociation in large molecules may differ from that proposed for medium-sized molecules. In this discussion we propose a model for multiple photon absorption in large molecules and describe a computational study which indicates that the proposed model can account for absorption of several photons in the time scale of the laser pulse over the range of energy fluence used in these experiments. We then discuss the dissociation process in a vibrationally excited large molecule and show that in order to explain the dissociation on the observed time scale it is necessary to postulate that the energy deposited remains localized in a limited number of modes. An estimate of the number of photons actually deposited into these modes is obtained from the measured small signal absorption coefficient. Finally, we suggest possible extensions of this work to other systems.

Most theoretical treatments of multiple photon dissociation divide the manifold of vibrational energy levels into two regions: the first few discrete levels of the pumped mode and a quasi-continuum of vibrational levels starting at an energy of a few vibrational quanta.[9] Mixing the vibrational states of the quasi-continuum produces allowed transitions which are on or near resonance with the laser radiation. Once the molecule has reached the quasi-continuum, energy can leak out of the pumped mode into the other modes. The conditions under which this occurs have been discussed by Yablonovitch.[10] The molecule is usually assumed to reach the quasi-continuum through a multiphoton transition to some overtone level of the pumped mode. The spectroscopic structure of the first few vibrational levels may be important in providing a pathway to reach high overtone levels. Two kinds of structure have been put forward as being important: the rotational structure[11] and the anharmonic splitting of the vibrational levels of degenerate modes.[12] However, neither of these spectral features is available in very large molecules. The rotational constant of the $UO_2(hfacac)_2{\cdot}THF$ is ~0.003 cm^{-1} compared with 0.027 cm^{-1} for SF_6 (including the Coriolis interaction). The rotational structure collapses to a narrow region, about 1 cm^{-1} wide. In addition, such large molecules seldom possess the high degree of molecular symmetry required for degenerate vibrational modes. Multiphoton excitation of a single vibrational mode is therefore unlikely in large molecules except perhaps at certain specific frequencies for which an exact multiphoton transition to a given vibrational overtone level is possible. But for a molecule consisting of more than 30 atoms the density of states rises rapidly with energy and the thermal vibrational energy content (>10 000 cm^{-1}) is so high at room temperature that the molecule is already in the quasi-continuum. Therefore, after the absorption of a single infrared photon the absorbed energy can be rapidly transferred to other modes. The molecule can then return to the lower state of the pumped mode and absorb another photon. This process can be repeated many times during the laser pulse, and, if the energy transfer is rapid, can lead to multiple photon excitation. Tamir and Levine[13] have proposed a similar model for multiple photon dissociation. However, in their model there is leakage into a single mode only, because of strong Coriolis coupling between this mode and the pumped mode, whereas we propose that, in large molecules, leakage occurs into a set of modes through anharmonic coupling of the pumped mode to a quasi-continuum of vibrational levels. In order to explain our observations it is necessary to define the quasi-continuum as a regime where rapid coupling occurs to a limited number of states, followed by a somewhat slower coupling to the vibrational–rotational heat bath. A useful point of view is to consider the heat bath with discrete eigenstates within it.

The coupling of the pumped mode to the quasi-continuum can have a number of important consequences for the absorption of laser radiation. Firstly, it can lead to the very short dephasing time (τ_{phase}) of the phase coherent excitation of the pumped mode,[14] producing a fairly wide, homogeneously broadened absorption profile. All molecules will therefore interact with the laser field to some extent at all laser frequencies within this absorption profile. Secondly, a broadening mechanism may also arise because the inhomogeneous lines constituting the absorption band undergo a frequency precession due to the random fluctuation of the underlying dense hot band system in a period, τ_{hbp}.[15] As long as the laser pulse width, τ_p, or contact time with the laser radiation, τ_c, is longer than τ_{hbp}, the line will exhibit a temporal, homogeneous-like behavior. The random bond-breaking and bond-making lifetime in fluxional molecules, τ_f, may also contribute to a temporal homogeneous-like band shape behavior, as long as $\tau_p \geq \tau_f$. For large molecules we can invoke a composite of the different mechanisms discussed above, and add the effect of power broadening to establish the relationship

$$\tau_{\text{phase}} < \tau_f \approx \tau_{\text{hbp}} < \tau_p$$

which, when satisfied will lead to a homogeneous-like band shape. In the case of $UO_2(hfacac)_2{\cdot}THF$ irradiation experiments even the shortest pulse width used, $\tau_p = 50$ ns, satisfies this criterion and for this molecule a homogeneous-like behavior is observed. We plan to examine $\tau_p < 50$ ns behavior in an attempt to sort out the various contributions to the line shape.

We have carried out a computational study of the model proposed above using the generalized master equation (GME) formalism of Stone et al.[16] which describes the time evolution of the density matrix for a system of molecules absorbing radiation and undergoing phase and energy relaxation. We apply this formalism directly to the case of molecules undergoing (collisionless) intramolecular relaxation by taking the pumped mode to be the "system" and the remaining modes to be the "heat bath", as in ref 10. A similar GME formalism has been used by Hodgkinson and Briggs[17] to study multiple photon excitation in SF_6.

We considered only the first four levels of the pumped mode. Successive transitions were assumed to be shifted by 5 cm^{-1} due to the anharmonicity of the pumped mode. The dephasing time, T_2, was taken to be 5 ps for every pair of levels. Energy relaxation from the pumped mode into the heat bath was assumed to induce transitions only between adjacent levels of the pumped mode, and the energy relaxation time T_1 was assumed to be the same for each pair of adjacent levels. The rate of energy absorption by the heat bath is therefore

$$\frac{dE}{dt} = \sum_i \frac{\epsilon_i \rho_{ii}}{T_1}$$

where ϵ_i is the energy difference between levels i and $i - 1$. The transition dipole was taken to be $\sqrt{n} \times 0.1$ D where n is the quantum number of the upper level. The radiation frequency was resonant with the 0-1 transition.

Figure 7 shows the variation of the number of photons absorbed by the molecule in a 100-ns laser pulse as a function of laser power for a number of different values of T_1. The results show that, provided T_1 is less than a few nanoseconds and the laser power >500 kW/cm^2, it is possible to absorb at least five to ten photons during a typical 100-ns laser pulse. If T_1 is short ($<10^{-10}$ s), then for the range of laser powers shown in Figure 7 the rate of energy transfer is governed only by the rate at which photons are pumped up the excited vibrational levels. If T_1 is longer than a few nanoseconds, then the slow rate of energy transfer becomes a serious "bottleneck" and limits the multiple photon absorption process. Of course, the number of photons absorbed could be increased by simply increasing the pulse length, at constant laser power. For the range of laser powers shown in Figure 7 pumping to levels higher than $v = 1$ was found to be negligible.

Finally, we note that, if T_1 is sufficiently short ($<10^{-9}$ s), then five to ten photons can be absorbed in 100 ns with laser intensities of only a fraction of a megawatt/cm^2. This suggests that thresholds for multiple photon dissociation in very large molecules could be at least an order of magnitude lower than typical thresholds observed in medium-sized molecules. In fact, it is one of the consequences of our model that the number of photons absorbed is directly proportional to the pulse length at any given laser power (i.e., to the laser energy fluence). Hence, even at the very low laser powers attained with a CW laser, multiple photon dissociation will be observed for large molecules if the statistical probability for multiple photon absorption at the laser flux is satisfied and if there are no disruptive collisions in τ_c or τ_p.

The above model predicts boundaries to the number of photons required to drive the reaction, but it does not address the origin of the proposed bond, or site selectivity of the laser-induced chemistry. The absorption of a number of infrared photons is not sufficient to guarantee that dissociation will take place. The vibrational energy is introduced into the uranyl moiety, but the model requires that this energy be redistributed within the molecule. If the energy is spread over too large a number of modes, then, even if the energy absorbed exceeds the energy required to break one of the bonds, the lifetime of the molecule can be so long that collisions will remove the energy before dissociation can take place. The extent of this redistribution or partitioning of the energy and its effect on the reaction dynamics are some of the important aspects of this study.

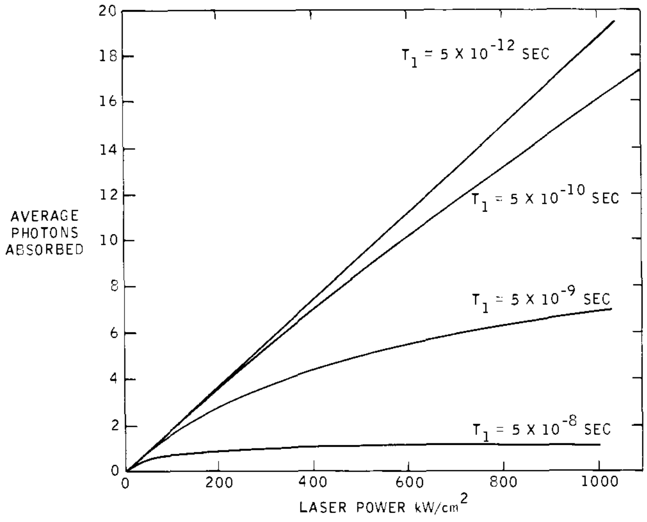


Figure 7. Calculated variation of the average number of photons absorbed in 100 ns with the incident laser power for a number of values of the leakage rate, T_1.

Using the known vibrational frequencies of the normal modes of THF, hfacac, and UO_2^{2+}, we can assign fairly accurate vibrational frequencies to most of the normal modes in $UO_2(hfacac)_2 \cdot THF$ and we can make reasonable estimates of vibrational frequencies of the remaining modes.[21] About half the vibrational modes have frequencies greater than 800 cm^{-1}, and the internal energy of these modes will be negligible at 100 °C. The average frequency of the remaining modes is about 250 cm^{-1} and we estimate that the total internal energy in these modes is 10 000 cm^{-1} at 100 °C. Each CO_2 laser photon absorbed contributes 950 cm^{-1} of additional internal energy. The calculated population distribution function with respect to internal energy is nearly Gaussian but has a slightly longer tail on the high-energy side. We have determined that the lowest energy barrier to the dissociation is about 30 kcal/mol.[18] This is about the estimated bond strength of the neutral base, THF, to the uranyl moiety. The bond strength of the chelating agent is estimated to be greater than 50 kcal/mol. The photons absorbed will contribute to overcoming this barrier, i.e., breaking the $U\text{-}OC_4H_8$ bond.

If the energy deposited by the laser were equally partitioned among the ~60 low-frequency vibrational modes of the molecule, the incremental excitation would be very small. It would be about 30 K temperature increase per photon absorbed. In order for the energy deposited in the uranyl moiety to be useful, it cannot be diluted throughout the molecule by intramolecular V-V processes, or degraded into heat by V-T processes. Both of these effectively cool the molecule and reduce the dissociation rate. If the collision rate with a second gas, such as argon, is comparable to the dissociation rate, then the collisions induce an intramolecular V-V redistribution process which does quench the unimolecular dissociation rate. When the argon pressure is high enough so that the collisions transfer appreciable energy from the $UO_2(hfacac)_2 \cdot THF$ to the argon, the yield is also proportionately reduced.

Our experiments suggest that the laser-driven dissociation rate has to be faster than 2×10^7 s^{-1}. An ergodic treatment cannot explain this fast rate. This reaction rate may be ex-

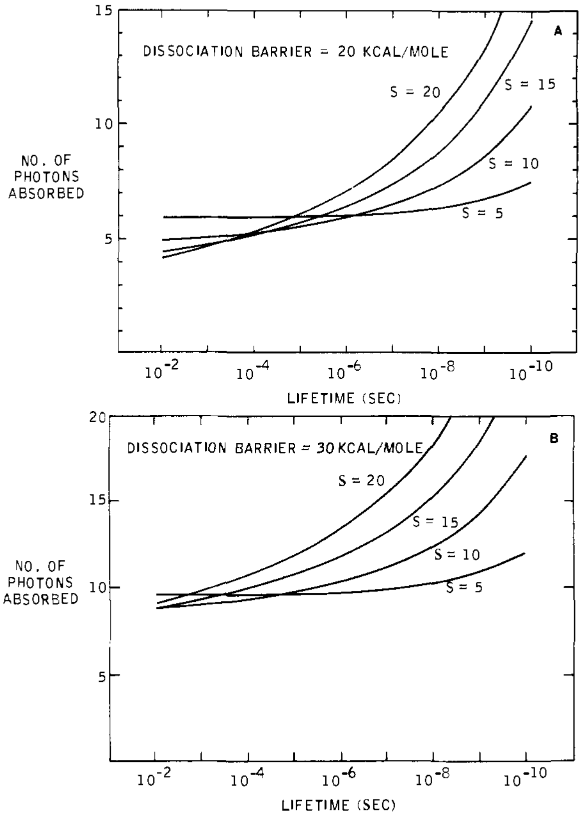


Figure 8. Calculated variation of the molecular dissociation lifetime with the number of absorbed photons (in addition to the thermal energy) for different values of the number of modes, S: (A) dissociation barrier = 20 kcal; (B) dissociation barrier = 30 kcal.

pected if the vibrational energy deposited by the laser is localized and is used in concert with the energy already in the intramolecular thermal bath. The first bonding sphere, including the uranyl moiety, contains 18 normal modes about half of which are low-frequency modes and we restrict our attention to this group. If energy equilibration is assumed only over these modes, a 150 K "temperature" increase per absorbed photon in the first bonding sphere of the molecule is possible. This "temperature", however, does not easily relate to the conventional definition of temperature and instead a kinetic analysis is preferred:

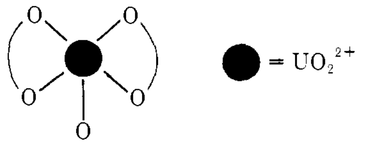
$$\tau = \frac{1}{k},\ k = k^0\left(\frac{E - E^0}{E}\right)^{S-1}$$

where E^0 is the dissociation barrier and k^0 is the frequency factor for the system, which we take to be $10^{13}\ s^{-1}$. Using this expression, we have calculated the number of CO_2 laser photons required in addition to the thermal energy, SkT, to obtain a given lifetime for different values of the number of modes, S. Figure 8 shows two sets of curves which give the dependence of the lifetime on the number of photons deposited for values of S in the range 5-20. The first set of curves was calculated assuming a dissociation barrier of 20 kcal/mol and the second set was calculated assuming a dissociation barrier of 30 kcal/mol. We estimate from the measured energy fluence and the absorption cross section that fewer than ten photons/molecule are absorbed when the dissociation yield is nearly 100%. Further, as stated above, the dissociation lifetime is less than 50 ns. It can be seen immediately from these curves that to obtain a lifetime of ~50 ns with less than ten photons the energy must be deposited in fewer than 20 modes. At least five photons are required to obtain this lifetime for any number of modes. These results do not appear to be sensitive to the choice of the frequency factor within the range 10^{12}-$10^{14}\ s^{-1}$. There is no single set of parameters which should be used in such calculations because the internal energy content of the molecule has a thermal distribution. It is reasonable to expect that those molecules in the high-energy tail of this distribution lie closer to the barrier and will undergo reaction with the introduction of less vibrational energy than those in the center, or the low-energy portion.

We must even consider the possibility that the molecules in this high-energy tail already possess enough thermal energy in the critical set of modes that a single CO_2 laser photon provides sufficient additional energy to cause dissociation on a time scale of 10^{-7} s. The laser-induced dissociation would then be a single-photon rather than a multiple-photon process. If the vibrational Boltzmann distribution were reestablished in a time that was short compared to the pulse length (although long compared to the dissociation lifetime) by intramolecular relaxation processes, then the high-energy tail would be continually removed and replenished during the pulse. In this way a substantial fraction of the molecules could be dissociated by a single-photon process. If we assumed that all the energy of a single CO_2 laser photon was available to drive the reaction, a simple Arrhenius treatment would predict a 150-fold rate enhancement over the thermal rate. While this simple treatment is certainly not quantitatively valid, it does suggest that the thermal unimolecular decomposition rate of UO_2L_2THF would have to be about $10^5\ s^{-1}$. This fast a rate is not compatible with the observed thermal stability of this system. Nevertheless, at low energy fluence a single photon process may not be incompatible with the thermal stability of the molecule because the laser-induced dissociation rate at low energy fluence could be considerably lower than $10^7\ s^{-1}$. The hypothesis that a single photon process predominates at low energy fluence does reconcile the observed yield at low fluence with the number of absorbed photons obtained from the absorption coefficient (less than one photon per molecule at fluences below 10 mJ/cm^2).

Using the measured absorption coefficient of 0.08 cm^{-1} Torr^{-1} we estimate that at an energy fluence of 100 mJ/cm^2 and a pulse width of 400 ns (fwhm), on the average five to ten CO_2 laser photons are absorbed per molecule, assuming that the absorption coefficient does not change during the energy deposition. At this energy fluence nearly 100% dissociation is observed. At a lower energy fluence, such as 10 mJ/cm^2, a lower yield is observed, and we estimate that on the average one CO_2 laser photon is absorbed per molecule (*not* per dissociated molecule). There are aspects of the energy deposition process which are not understood and require further experimental study. We postulate that on the average five CO_2 laser photons are deposited in the molecule, and this energy is localized over 5-15 modes of the first bonding sphere. The nature of the initial unimolecular energy redistribution from the uranyl moiety is delicate and fragile; it is a collisionless intramolecular process and collisions disrupt it severely.

The vibrational excitation in the uranyl moiety is rapidly redistributed in the first bonding sphere shown in i where the



i

induced moment due to the bending motion of the U-OC_4H_8 bond couples to the uranyl asymmetric stretch undergoing excitation.

The leakage rate from the UO_2^{2+} asymmetric stretch into this limited reservoir has not been determined, but in our computational model we allowed it to vary from 5×10^{12} to $5 \times 10^9\ s^{-1}$ with little effect on the energy deposited. In

$UO_2(hfacac)_2 \cdot THF$, we postulate that vibrational energy equilibration takes place in about 5 ns, or faster, because we are able to observe laser-induced chemistry on that time scale. The partial energy equilibration required can be achieved on a faster time scale, and this time scale is what is important in order to analyze the potential implication of this process. There is a limited time in which energy can migrate in the molecule, and if within this time energy is piled up in the U–THF bond, dissociation may occur. Thus in large molecules it is possible to discuss energy localization in a spatial sense due to temporal and communicational constraints imposed by the very size of the molecule. For example, we doubt if the energetics of the CF_3 group are significantly perturbed on the nanosecond time scale following the absorption of a large dose of vibrational energy by the uranyl moiety. Excitation (3 μm) of the THF group's C–H stretch by a 30-ns pulse width, 1-cm^{-1} bandwidth tunable OPO[19] has not produced measurable fluorescence depletion at laser fluences up to 10 mJ/cm^2. This can be rationalized, on the basis of an energy diffusion concept in the molecule. The CH stretch couples to the modes of the OC_4 ring of the THF more strongly than to the U–O bond. Thus some 33 modes are available to soak up energy in competition with the U–O bond. The energy is therefore so diluted that no dissociative reaction can occur before the system is vibrationally relaxed. If more energy were to be deposited into the CH stretch, at some critical energy the leakage rate into the U–O bond is expected to be adequate to yield observable decomposition.

The critical energy migration probably occurs in a time longer than 1 ps and shorter than or on the order of 1 ns. The range covers three orders of magnitude and, in the context of infrared laser chemistry, further refinement of this range is important. The energy leakage rate increases as the vibrational energy content of the molecule builds up, but it probably increases linearly tending toward the picosecond limit.

The intramolecular selectivity of the process described here has not yet been tested, but we have been able to abstract operating principles to guide the synthetic chemist. First a molecule has to be built which has more than one low-energy reaction channel to truly demonstrate the intramolecular bond selectivity postulated here. The results obtained so far indicate that site selective chemistry in complex molecules should be possible as long as the sites within the molecule are well segregated, i.e., the site one wants to operate on is beyond the bonding sphere of the sites to be discriminated against, and their characteristic infrared absorption spectra differ. An example may be the case of a multimetal cluster compound where a site near one metal cluster needs to be activated for use in synthesis or catalysis. In biochemical synthesis this technique may also be useful. Judicious selection of the molecular structure may allow laser-induced chemical surgery of undesired constituents of large molecules in a site-selective fashion. In addition, the opportunities are greater for inserting weak bonds into large, fluxional molecules than medium-sized molecules. The large thermal energy content of these molecules will also contribute to the energy required to break the bond, thus reducing the energy the laser radiation must supply.

Another implication of the results presented here is that, if adequate energy can be deposited in the molecule in 5–10 ps and can cause chemical conversion at that rate, then IR multiple photon laser chemistry in liquids should be possible.

The results presented so far only touch on one aspect of the utility of multiple photon infrared laser chemistry in large organometallic compounds. An IR-efficient, selective reaction has been demonstrated for a molecule with 44 atoms, the largest molecule examined so far. We continue our research on these systems in order to answer many of the questions raised in this report and to examine various other aspects of this chemistry.

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(20) A homogeneous absorption band is one where all molecules in the ensemble exhibit identical absorption bands.

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(22) Thermal chemistry experiments show that the dissociation products do not fluoresce. Further, on the basis of emission spectroscopy measurements, to be published, it is highly unlikely that the fluorescence depletion is due to vibrational excitation.

(23) We assume that the time dependence of dissociation is accurately monitored by that of the fluorescence depletion. However, the time evolution of the fluorescence depletion may monitor a sequence of reactions culminating in dissociation. Further experiments are underway to test this point.