quenching due to the crown ether ring which imposes a strictly defined compartmentalization of the probe and quencher within the aggregate.

The results for the 18-crown-6/SDS mixtures are less well defined. 18-Crown-6 binds to both sodium and cesium cations with binding constants of 6 and 10, respectively.²3 In both cases the bound and unbound forms of the crown ether are very water soluble. For the mixed SDS and 18-crown-6 systems the most likely explanation for the reduced quenching efficiency compared to SDS is the removal of cesium ions from the micelle into the aqueous phase as complexes with the crown ether. However, these effects are unlikely to be large since the association constant for cesium with SDS is so much larger than that for 18-crown-6.

Ouenching of 6-Indole-11. Since 6-indole-11 is located in a very hydrophobic environment in each aggregate, the quenching of this species could be different than that observed for pyrene. Additionally this probe does provide slightly different information than the pyrene probe since the "Stern-Volmer" analysis leads to association constants rather than dynamic quenching constants. The order of quenching efficiency in the aggregate systems is the same as that observed for pyrene (SDS > $C_{10}O18C \approx Brij 35$). However, the Stern-Volmer constant for SDS is smaller than the corresponding value in aqueous solution and thus quenching is observed to be less efficient. For the pyrene probe a higher quenching efficiency is observed in SDS compared to homogeneous solution. Although solubilization within an SDS micelle results in a higher effective cesium concentration for pyrene, the effective

concentration for the indole is evidently lower than that possible in homogeneous solution. The most likely reason for this is that the indole is located in the hydrophobic layer of the micelle and thus is protected from quenched by the cations which are associated with the outer layer. The quenching efficiency in both nonionic micelles is lower than in SDS presumably for the same reasons that pyrene is quenched less efficiently.

Conclusions

the quenching of the fluorescence of pyrene by cesium cations occurs via heavy atom induced intersystem crossing to the triplet state of this species. The efficiency of quenching is increased in SDS micelles compared to homogeneous solution for most of the pyrene singlets, and significantly decreased for C₁₀O18C and Brij 35. The quenching protection observed in C10O18C is due to an intramicellar sequestering of the cation which prevents contact between the probe and quencher, whereas the protection in Brij 35 is due to a simple lack of association between the micelle and cation. Similar results are obtained for 6-indole-11 after the effect of location of the probe within the aggregate is taken into account.

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Registry No. 6-Indole-11, 51097-79-1; C₁₀O₁₈C, 60742-60-1; SDS, 151-21-3; 18-crown-6, 17455-13-9; Brij 35, 9002-92-0; cesium chloride, 7647-17-8; pyrene, 129-00-0; water, 7732-18-5.

Photochemistry and Photophysics of Small Heterocyclic Molecules: 1. Multiphoton Ionization and Dissociation of N-Isopropyldimethyloxaziridine¹

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The resonantly enhanced visible multiphoton ionization spectrum of N-isopropyldimethyloxaziridine has been recorded over the wavelength region from 375 to 600 nm. Rydberg series have been observed and assigned to ns, np, and nd transitions, with n spanning the range from 3 to 6. These transitions are accompanied by changes in the vibrational energy of a ring deformation mode. The ionization potential for this molecule is estimated to be 8.84 eV from both the Rydberg series limits and the spectral changes accompanying the transition from a three- to a four-photon requirement for ionization. Preliminary gas-phase photochemical results indicate a sharp energy dependence in the mechanism for dissociation. A one-photon pathway leads primarily to simple ring opening and an amide final product, while a second, multiphoton channel leads exclusively to the severing of two bonds and an acetone fragment. These results are compared with earlier theoretical predictions and experimental results. The unique advantages of multiphoton photochemistry for the production of novel species are discussed.

I. Introduction

Prompted largely by practical considerations, inquiry into the chemistry of strained ring compounds has a rich history in the field of organic chemistry.² One reason for the interest in these molecules is their inherent instability, which enables them to be sources of highly reactive intermediates. The chemistry of heterocyclic compounds is equally interesting for its theoretical implications.² Due, in part, to a dipole moment created by the presence of one or more heteroatoms in the ring, small ring heterocycles exhibit physical properties distinct from their alkane analogues such as cyclopropanes and cyclobutanes.³ Hindered by the increased complexity of the heterocyclic systems in comparison to the hydrocarbon analogues, physical chemists were slow to systematically examine the intra- and intermolecular interactions associated with these molecules. However, a considerable body of data in such areas as reaction mechanism, bonding, equilibrium thermodynamics, and polymerization is now available for the single heteroatom molecules.4

We have begun a systematic study of the laser-driven, photochemical dissociation dynamics of small rings containing at least two heteroatoms. The goal of this research is a detailed understanding of the dependence of the reaction rate and dynamics on the nature of the heteroatoms and the quantum state of the molecule. Due to the lack of critical data, these goals will also require an examination of the electronic structure of the molecules from both experimental and theoretical viewpoints. Initial studies will concentrate on heterocycles in the gas phase at low pressures.

⁽¹⁾ Most of the research described in this report was contained in the Honors Thesis written by H. A. Michelsen in partial fulfillment of the requirements for receipt of the A. B. degree.

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The first molecule to be examined in this study and the focal point of this report in N-isopropyldimethyloxaziridine (I). This



has been chosen as an alternative to the parent molecule, since the synthesis of that compound is not feasible. The first synthesis of an oxaziridine was accomplished by Krimm⁵ in 1956 and independently by Emmons⁶ in 1957. Since that time many of the possible thermal and photochemical reactions of this interesting molecule have been explored, mostly in solution. Oxaziridines have been invoked as reaction intermediates in a number of organic reaction schemes.⁷ For example, this heterocycle was invoked as an intermediate in the photochemical isomerization of nitrones to amides.⁶ In addition, the aryl-substituted molecules have been shown to be precursors to the production of the nitrene diradical.8 Clearly, this heterocycle is an ideal starting point for a systematic study of this kind. Thermal decomposition of an oxaziridine was shown to result in production of both the nitrone precursor and the isomeric amide.⁶ Similar conclusions were drawn from photochemical⁹ experiments. Perhaps the most intriguing chemistry was the reaction of an N-substituted oxazirdine to yield arylor alkyl-substituted nitrenes.^{8,10} In these experiments, sensitized photochemical reactions yielded product molecules that could only evolve from a nitrene precursor. However, this product yield was quite minor and the amide isomerization channel dominated the rection. The small cross section reported for radical formation is most unfortunate, since reactive species such as diradicals are one of the areas in which a major contribution to understanding chemical reaction dynamics on a molecular basis may yet be made. Therefore, an attempt was made in the current study to develop a technique that would produce a large enough yield of nitrenes to allow an examination of the spectroscopy and rearrangement rate constants in a future molecular beam experiment. Multiphotonic effects have been employed to achieve these ends.

Multiphoton ionization (MPI) and dissociation (MPD) have become important new tools in electronic structure determination and reaction dynamics.¹¹ MPI may be used to observe molecular transitions which are forbidden in a one-photon spectrum due to symmetry constraints. Alternatively, this technique is a means of recording vacuum-UV spectra without the inconvenience of the usual vacuum-UV apparatus. In either case, high resolution and sensitivity are available to the experimentalist. This technique employs population of a resonance level with subsequent ionization occurring via absorption from this state. The multiphoton absorption occurs during the course of a single laser pulse, but the overall ionization is incoherent so that the molecule has some finite residence time in the intermediate resonance state prior to further absorption and ultimately ionization. Molecules in the resonance level may fragment or isomerize prior to, or instead of, further absorption. The MPI spectrum observed would then be that of the newly created species, rather than the parent molecule. Alternatively, the unimolecular reaction may occur from the ionized molecule, in which case, the MPI spectrum would reveal the resonance levels of the parent molecule and either multiphoton mass spectra or the time evolution of some spectroscopic property would be required to understand the mechanism of decomposition. In either case, MPD occurs with the production of fragments not easily obtainable by coventional means, due to the inaccessibility

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Figure 1. Two-photon resonant, three-photon MPI spectrum of the title molecule. Wavelengths are accurate, but intensities have not been corrected for laser intensity.

of the precursor electronic state. All of this chemistry takes place during a single laser pulse so that if one restricts the sample pressures to values ≤ 20 torr, the real time observations will be a result of unimolecular processes. The current report presents the results of multiphoton excitation applied to the target molecule, I. The carbonyl/nitrene channel is observed exclusively for multiphotonic excitation to selected molecular resonances. Also, preliminary results on the electronic structure determination are presented.

II. Experimental Section

Spectra were recorded in a conventional MPI static gas cell.¹² This consisted of a Varian "Tee", with an appropriate electrode system, connected to a rotary vacuum pump capable of reducing the background pressure to 10^{-3} torr. The electrode system was comprised of a cylindrical copper tube repelling electrode biased at -300 V running the entire length of the cell and a concentric stainless steel wire collecting electrode which was normally grounded. Sample pressures were typically 13 torr as measured by a capacitance manometer. These conditions did not result in electron avalanche amplification in the cell. The light source is a Lumonics EPD-330 dye laser pumped by the 308-nm beam of a Lumonics TE-861S-3 excimer laser. The dye laser beam was typically adjusted to an output of 1-2 mJ and passed through a 15-cm focal length lens resulting in a cross-sectional area of $\approx 10^{-5}$ cm^2 and a power density of the order of $10^9 W/cm^2$ at the focus. The MPI signals were detected and amplified via a Keithley Model 615 electrometer, digitized through an A/D interface and stored in a laboratory computer for later analysis. The laser energy was monitored by a Scientech Model 3 600 001 disk calorimeter with the results treated as above. The MPI spectra shown in this report are not corrected for the variation in laser intensity across a dye emission band. However, the laser power dependence of the bands was determined and this information employed in the assignments given in the subsequent sections. Laser calibration was effected via a neon optogalvanic (OGE) cell.¹³ The laser bandwidth determined with the OGE cell was 0.03 Å, but scans used 2-Å intervals.

The oxaziridine synthesis generally followed the imine oxidation procedure reported in the literature¹⁴ with the following modifications. Oxidation was accomplished by using m-chloroperbenzoic acid rather than peracetic acid. The reaction was also run in two steps rather than the single pot method described in

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⁽¹²⁾ Johnson, P. M. Acc. Chem. Res. 1980, 13, 20.

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Figure 2. Three-photon resonant, four-photon MPI spectrum of the title molecule. Wavelengths, but not intensities, are accurate. The bottom scale notes the coumarin laser dye employed and the wavelength region over which lasing action occurs.



Figure 3. MPI spectrum in the dye laser range 370–390 nm as a function of laser pumping time at 10 Hz and 1 mJ per pulse. The lowest spectrum was obtained for a purified acetone sample.

the earlier syntheses. This allowed purification of the imine intermediate and easy separation of the final material from side products. The latter step was accomplished via a spinning band column at 40 torr and 314 K. Subsequent GC, IR, and ¹³C NMR analysis¹⁵ indicated a purity of 99.99%. The IR spectrum is presented in section III of this report.

III. Results and Discussion

The MPI spectra were obtained through the use of eight laser dyes across the single-photon wavelength region from 375 to 600 nm. Spectra are presented in Figures 1 and 2, which represent two-photon resonant, three-photon (2 + 1) transitions and three-photon resonant, four-photon (3 + 1) transitions, respectively. The bands shown are not representative of the true spectral intensity since the scans have not been corrected for the variation of the laser intensity across a particular dye emission region. The wavelengths have been corrected by means of the OGE cell and are the true experimental values. Energies reported in wavenumbers are measured under vacuum.

The MPI spectrum in the wavelength region from 375 to 390 nm is shown in Figure 3 as a function of total laser pumping time. Figure 4 contains IR spectra of the oxaziridine (I) at similar time intervals for 385-nm pumping. For comparison, the gas-phase IR spectrum resulting from exposure of the oxaziridine (I) to a standard Hanovia quartz lamp is given in Figure 5. Differences



Figure 4. IR spectrum as a function of elapsed laser pumping time at 385 nm, 20 Hz, and 1 mJ per pulse. The lowest trace is that for a pure acetone sample.

Cm-1

1000

600

1400

1800



Figure 5. IR spectrum as a function of the total exposure time to a standard quartz photolysis lamp.

in these two sets of data are obvious. Although the two topics are related, as much as possible, the spectroscopic and photochemical experiments will be discussed separately below.

Spectroscopy. The oxaziridine molecule under study possesses C_1 symmetry. Since all electronic transitions not specifically spin forbidden are allowed, MPI is a tool by which the vacuum ultraviolet spectrum of the molecule may be readily obtained, rather than a means of circumventing one-photon selection rules. No single-photon vacuum-UV spectrum for any member of the oxaziridine family appears in the literature. However, a number of investigators¹⁶ report a near-UV absorption band in the region around 230 nm, primarily for solution studies. We have observed a weak, broad band, one-photon absorption in the same spectral region for a gas-phase sample. This absorption has been assigned to the $S_0 \rightarrow S_1$ transition as predicted by ab initio molecular orbital calculations.¹⁷ The one-photon spectrum also exhibits an additional band with maxima at 190.5 and 192.3 nm. This band has not been previously reported.

⁽¹⁵⁾ Copies of the spectra are available from the authors.

⁽¹⁶⁾ Splitter, J. S.; Calvin, M. J. Org. Chem. 1965, 30, 3427.

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TABLE I:	N-Isop	ropyldimethy	loxaziridine	Rydberg	Series
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assignment ^a	$\nu_{\rm calcd}, {\rm cm}^{-1}$	$\nu_{\rm obsd}, {\rm cm}^{-1}$	ΔG
	$\delta = 0.72$	38	
ns series			
3s	49 837	49 838	
4s	60 965	60914	
5s	65 235	65 288	
	$\delta = 0.38$	88	
np series			
3p	55 196	55 239	
3p + v		56 064	825
4p	62866	62788	
4p + v		63 640	862
5p	66117	66 094	
5p + v		(66 942)	
	$\delta = 0.02$	15	
nd series			
3d	58 959	58 904	
3d + v		59 773	869
4d	64 365	64 364	
4d + v		(65 288)	
5d	66 8 5 9	66 942	
5d + v		67 690	748
$a_n = 3, 4, 5.$			

The highest occupied molecular orbital for the parent oxaziridine molecule is best described as a linear combination of the oxygen and nitrogen lone pairs.¹⁷ Most of the observed structure can be assigned as Rydberg excitations or vibrational progressions of such processes out of this orbital. The series determined from the MPI spectra, along with the deviations from the calculated values, are presented in Table I. The series converge to a limit of 71 275 \pm 100 cm⁻¹. Since the photoelectron spectrum of this class of molecules is unknown, one must rely on the series convergence and observations with respect to the laser power dependence to obtain the ionization potential. The experimental quantum defects are 0.738, 0.388, and 0.015 for the ns, np, and nd series, respectively, resulting in term values of approximately 21 500, 16 000, and 12 350 cm⁻¹. It is impossible to fit the data to a Rydberg series by assuming that the transitions at ≈ 190 nm belong to a component of the 3p transition. Therefore, under the assumption that the spectrum is due primarily to Rydberg transitions with some vibrational structure, no other assignments are possible.

The 3s value is a reflection of the alkylation of the parent molecule.¹⁸ The parent oxaziridine is predicted, via the corrected Koopman's theorem¹⁷ and the empirical expression developed by Robin,¹⁸ to have an ionization potential of 11.08 eV and a 3s term value of 29560 cm⁻¹. The decrease in these two parameters for I relative to the parent oxaziridine is exactly what would be expected for a molecule reflecting the alkyl limit for Rydberg transitions; the alkyl substitution decreases the overall penetration of the molecular 3s orbital. This effect is most obvious for molecules in which the ionizing orbital is centered on the oxygen atom. Analogous behavior is observed in the spectra of substituted amides,¹⁹ which exhibit an effect of similar magnitude in going from formamide to N,N-dimethylacetamide. The ionization potential of the latter is comparable to I. The relative difference between the ionization potential of the target molecule and the corresponding amides is consistent with observations made on other heterocyclic molecules and their open-chain isomers.²⁰

The 2 + 1 spectrum in Figure 1 includes bands corresponding to two-photon excitation of the new, as yet unassigned, transitions observed in the one-photon spectrum. A laser power density study of these transitions confirms this assignment. There is approximately a 3 order of magnitude decrease in the intensity of the 3 + 1 bands in Figure 2 when compared to the spectrum in Figure 1. This observation, coupled with a careful examination of the spectrum in the intermediate region (405-430 nm), confirms the assignment of the ionization potential obtained from the Rydberg analysis. The transition from 2 + 1 to 3 + 1 ionization occurs in the region about 420 nm and, therefore, the ionization potential is estimated to be 8.84 eV. The only observed vibrational progression is of frequency 825 cm^{-1} . This vibrational mode was also observed in the gas-phase IR spectrum (see Figure 5) and, by analogy with other three-membered heterocycles, has been assigned to a ring deformation mode of the molecule. The np and nd Rydberg transitions have at least one quantum of this vibrational energy associated with the electronic excitation. We have not observed any vibrational structure accompanying the ns excitations.

Only one of the reported MO calculations has included a prediction of the spectroscopic energies associated with higher energy transitions of the parent molecule.²¹ Although the absolute values of the transition energies in that study are not applicable, two closely spaced valence excitations were predicted. These predicted transitions correspond, in our experimental results, to the $S_0 \rightarrow S_1$ transition and the band system observed to begin at approximately 190 nm, in the one-photon spectrum. The assignment of the Rydberg series leaves the remaining short wavelength features to be assigned to higher energy valence states.

Photochemistry. Figures 3-5 present the long-term spectral changes observed after pumping a gas-phase sample of I with a focused laser or a quartz Hanovia lamp. The progress of the reaction was monitored by IR and MPI spectroscopies. We have observed reaction channels leading to two different final products:

$$\begin{array}{c} CH_{3} \\ C \\ C \\ H_{3} \end{array} \xrightarrow{(n-1)-\hat{P}_{1}} CH_{3} - C - N \xrightarrow{(n-1)-\hat{P}_{2}} CH_{3} - C - CH_{3} + CH_{3} - C - CH_{3} - C - CH_{3} + CH_{3} - C - CH_{3} - C - CH_{3} + CH_{3} - CH_{3} - C - CH_{3} + CH_{3} - C - CH_{3} + CH_{3} - C - CH_{3} + CH_{3} - CH_{3} + CH_{3} - CH_{3} - CH_{3} + CH_{3} + CH_{3} + CH_{3} + CH_{3} +$$

Channel 1 is driven by photons of wavelength \geq 210 nm, but, just as in the earlier studies,^{8,10} a minor amount of acetone is also detected at these wavelengths. Channel 2 (with the nitrene fragment implied, but undetected) occurs for multiphoton pumping at 308 and 385 nm, but not for $\lambda \ge 400$ nm. Acetone is the exclusive product with no trace of amide detected. The rate of the second process, which is laser pumped, is considerably faster than the first.

Concentrating, initially, on channel 1 (Figure 5) one may determine the effect of UV wavelengths longer than \approx 210 nm. This figure compares a pure sample of the material to one which has been irradiated for 40 h. The disappearance of the ring modes (825 and 1240 cm⁻¹) and the appearance of an amide-type carbonyl absorption (1690 cm⁻¹) lead one to conclude that the S_0 \rightarrow S₁ transition results predominately in the breaking of the NO bond with subsequent migration of the methyl group. This conclusion is consistent with the theoretical predictions of Oliveros et al.¹⁷ with respect to the parent oxaziridine; assigning the lowest singlet transition to an $n \rightarrow \sigma^*$ band leading to dissociation via NO bond severance. Their analysis contends that the reaction is not concerted and that the barrier to migration of the proton (methyl group) is small or nonexistent. Other interpretations of the mechanism for this pathway have been proposed,²² but we have not attempted to resolve this mechanistic dispute.

Figures 3 and 4 present the progress of the second observed dissociation channel by means of MPI and IR techniques, respectively. These data were obtained by pumping at a laser wavelength of 385 nm, although similar effects were observed with the XeCl laser (308 nm) directly. In both figures, the time-dependent spectra are contrasted with the spectrum of a known acetone sample. The spectral changes are quite clear. Again,

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Figure 6. Multiphoton dissociation scheme for N-isopropyldimethyloxaziridine. The dissociation to acetone ions is symbolic. The energy of the acetone ion is approximately equal to that of three 385-nm photons minus the endoergicity of the cleavage reaction for oxaziridine. However, in most of the previously reported instances of dissociation from the molecular ion, absorption of additional photons by the ion was implied in the mechanism. The usual statistical model weights the reaction probability by the excess energy in the decomposing entity, and we would expect that the oxaziridine ion is also excited by further absorption.

the ring modes in the IR spectrum decrease, while bands associated with known acetone transitions grow in intensity. The MPI spectra present a similar story, with the long time behavior of the spectra taking on the appearance of the acetone two-photon resonant, three-photon spectrum. In neither case is there any evidence of an amide fragment. Other effects were ruled out by varying the laser intensity (to as low as 0.1 mJ) and laser wavelength and attempting to drive the reaction thermally. Heating the sample to 380 K produced no discernible change in the spectrum of the pure oxaziridine molecule. (It should be pointed out that, in his original paper, Emmons⁶ noted that trialkyl-substituted oxaziridines possessed a high thermal stability.) Oliveros et al.¹⁷ do not address the subject of this dissociation channel. A second theoretical paper by Bigot and co-workers²¹ involving a more qualitative analysis briefly considers it. These authors observed that the S_1 surface is inadequate for the decomposition of the parent molecule to formaldehyde and nitrene. Indeed, we do not observe any reaction from that state.

In terms of the MPI classification scheme advanced by Gedanken et al.,²³ this should be a class A molecule. The distinguishing feature of such a system is the production of the parent molecular ion prior to any fragmentation, which may occur due to subsequent absorption of additional photons. The oxaziridine Rydberg transitions obviously fall into this category. However, excitation to the S₂ and higher valence states results in a long time final product due to fragmentation. This does not represent a change in multiphoton mechanism, but is instead a result of the experimental technique (i.e., the time evolution of IR or MPI spectra). These products result from the preparation of an excited-state ion with sufficient energy for unimolecular decomposition, as shown in Figure 6. Direct fragmentation from the excited molecular resonance state would result in the production of the REMPI spectrum of acetone, rather than I. Further pumping, in that case, might fragment the acetone ion, but would show no evidence of I. The time lag prior to our observation of acetone in the MPI spectra is evidence for a gradual buildup of carbonyl concentration through eventual recombination of the unimolecularly produced ion, rather than direct MPD during the laser pulse.

Earlier reports list as minor photochemical products, molecules which are clearly a result of dissociation of a triphenyl- or a

monalkyl-substituted oxaziridine molecule into carbonyl and nitrene fragments.^{8,10} In each of these cases, the primary product was due to ring opening/rearrangement and the photochemical process was driven by a standard UV source, not a laser. Both of these studies found increases in the dissociation channel upon addition of a triplet sensitizer, such as acetone. The authors of both studies concluded that intersystem crossing was faster than the rearrangement to the amide. We have observed such a process for low energy, one-photon pumping; however, the mechanism for acetone (carbonyl) production must be different in the current multiphoton study, since at the proper wavelength it is only the acetone fragment (not the amide) which is produced. We have not been able to detect spectroscopic signals from the nitrogen fragment. This appears to be a result of the inherent weak intensity of the amine or imine final product bands in both techniques. Electron impact mass spectroscopy (30-eV electrons) shows almost complete fragmentation of the parent molecular ion, with the predominant signal due to acetone and a large collection of nitrogen-containing fragments. This is consistent with the general principles of mass spectrometry.²⁴ Cleavage of two bonds in an odd electron radical ion parent (such as that of the target molecular ion) results in production of an odd electron radical ion plus a neutral fragment. Since the highest occupied molecular orbital is best described as involving the oxygen lone pair, we postulate that the first ionization potential yields a parent molecular ion with the charge located primarily on the oxygen atom. Cleavage of two bonds would result in acetone ion plus isopropyl nitrene fragments. The complex nature of the mass spectral peaks due to nitrogen-containing species is a reflection of the reactivity of the diradical. The fragmentation and rearrangement of the nitrogen would also be occurring in the laser ionization measurements, further lowering the probability of detecting these products by IR spectroscopy. While MPI/MS does not necessarily lead to the same fragmentation pattern as electron impact ionization, it is possible in most cases to adjust the experimental conditions to obtain identical spectra. The results of this study appear to indicate that the adjustment is unneccessary for I. Thus, it appears that multiphoton dissociation of substituted oxaziridine molecules is a means of producing clean yields of alkyl nitrenes for spectroscopic and kinetic measurements. This is an organic analogue of the use of MPI/MPD to produce metal atoms from organometallic and inorganic compounds.²³

Further work, in particular the study of the time evolution of the dissociation process and the use of the collision-free regime of a supersonic jet, is now underway. Also, laser-induced fluorescence signals, attributed to acetone have been detected and will be explored in detail.

IV. Conclusions

The MPI spectrum of I corresponding to the vacuum-UV transitions has been recorded. The features in this spectrum are assigned as Rydberg series to ns, np, and nd molecular orbitals and three molecular valence states. Except for the ns Rydberg series, all transitions are accompanied by changes in the quantum state of a vibrational mode characterized as a ring deformation. Preparation of the molecule in any of the energy levels leads to ionization upon subsequent absorption of additional photons. However, population of these states above an energy threshold leads to photochemical fragmentation. The previously observed $S_0 \rightarrow S_1$ transition appears to promote ring opening with amide formation probably via the zwitterion mechanism usually invoked to explain the photochemistry of small ring compounds. The upper two valence levels result in exclusive formation of acetone and, by implication, at least initial formation of an alkyl nitrene. Although the mechanism for this latter process is still under study, it appears that dissociation occurs from the an excited state of the ion resulting from preparation of the oxaziridine molecule in the molecular valence levels. Our results are consistent with

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previous research on multiphoton dissociation which indicates that absorption of several photons may open a reaction channel not observed in one-photon experiments. Multiphoton pumping of small heterocycles may be a convenient method for the generation of reactive species which are difficult to obtain by conventional means.

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Coupled Equations Approach to Multiphoton Processes in Molecules. 1: **Time-Dependent and Scattering Formalism**

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A time-dependent treatment of direct photodissociation, resonance Raman scattering (RRS), stimulated RRS, and coherent anti-Stokes Raman scattering (CARS) via a dissociative state is presented for strong fields. In the weak-field limit, the usual Fermi golden rule expressions are recovered. The introduction of artificial channels is shown to lead to scattering (close-coupled) equations for calculation of the transition amplitudes of the above multiphoton processes. Such numerical methods can be applied to both weak- and strong-field cases, as shown by the time-dependent treatment. Finally, semiclassical methods are used to characterize dressed states in stimulated RRS.

I. Introduction

Models of traditional photochemistry and photophysics are based on applications of Fermi golden rule expressions for transition probabilities. In such treatments, one assumes that the excitation fields have no effect on the eigenstates of the system being probed. With the advent of powerful lasers, such perturbative treatments are no longer valid. Use of the dressed molecule picture,¹⁻³ where one adds photon energies to unperturbed electronic surfaces which are then coupled via radiative interactions, enables one to evaluate perturbations of molecular states by the incident fields to some degree. Thus new effects in strong fields can occur, such as laser-induced resonances, which cannot be described by the usual perturbation techniques.⁴⁻⁸ We have recently shown, using close-coupled equation calculations in the dressed molecule framework, that such resonances will affect drastically strong-field photodissociation⁹ and resonance Raman (RRS)^{10,11} cross sections.

In the present work we wish to present in detail the relation between time-dependent and scattering (close-coupled equation) approaches to calculating multiphoton transition probabilities. The latter approach enables one to perform precise numerical calculations and is most useful in treating bound and continuum states simultaneously. For initial bound states, one must introduce artificial continua in the coupled equations. This technique, first used in photodissociation,¹² has been extended to weak field multiphoton processes^{13,14} and to strong-field problems.⁹⁻¹¹ In the present paper, we develop for various field strengths the timedependent transition amplitudes for direct photodissociation (Figure 1), resonance Raman scattering (RRS) (Figure 2), photodissociation in the presence of stimulated emission or stimulated resonance Raman scattering (Figure 3), and finally coherent anti-Stokes Raman scattering (CARS) (Figure 4), for which the previously mentioned stimulated emission is an intermediate step. In weak fields, we recover the usual Fermi golden rule expressions. In strong fields, the mixing of bound states with continua introduces formal biorthogonal complex basis functions¹⁵ which are useful in discussing overlapping resonance effects in molecular multiphoton processes.¹⁶ We will show that the coupled equation approach follows from the time-dependent theory for both weak and strong fields for the four spectroscopies mentioned above.

Laser-induced resonances in bound to continuum photoabsorptions are known to alter considerably the photodissociation angular distributions.⁴⁻⁹ For such direct processes semiclassical methods were developed to characterize these resonance states in terms of diabatic (unperturbed) and adiabatic (field-induced) bound states.⁷⁻⁹ As mentioned in the previous paragraph, photodissociation in the presence of stimulated emission is an essential intermediate step in CARS. The semiclassical dressed states of this intermediate process will be derived and compared to the direct photodissociation dressed states.⁷⁻⁹ Finally, in the next paper of this series, we will present and analyze numerical calculations of a diatomic CARS spectrum at high fields with the aim of establishing the usefulness of intense field CARS as a means of probing dressed molecular states in photodissociation.

II. General Time-Dependent Formalism

The total Hamiltonian for a molecular system submitted to an electromagnetic field can be formally written as

$$\mathcal{H} = H_{\rm m} + H_{\rm R} + V \tag{1}$$

where $H_{\rm m}$ is the isolated molecule Hamiltonian, $H_{\rm R}$ is the free radiation Hamiltonian, and V stands for the radiation matter

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