

NANOSECOND *VERSUS*, PICOSECOND MOLECULAR MULTIPHOTON FRAGMENTATION OF KETENE AND CYCLOHEXANE

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Multiphoton dissociation of ketene was studied at 290.5 nm after irradiation of the first excited singlet state with two different laser pulsewidths of 4 ns and 10 ps. Analysis of the photofragment fluorescence spectra in the two time domains sheds light on the mechanisms that are responsible for the production of the observed $\text{CH}(A^2\Delta)$, $(B^2\Sigma^-)$ and $\text{C}_2(d^3\Pi_g)$ photofragments. Multiphoton ionization of cyclohexane induced by a visible laser at 581 nm and its second harmonic at 290.5 nm was measured in the above mentioned pulse duration regimes. Study of the dependence of the total ionization signal on pressure and laser energy helps to clarify the role played by the giant resonance of this molecule at 84000 cm^{-1} in the photoionization process.

Keywords: Multiphoton dissociation; multiphoton ionization; ketene; cyclohexane

1. INTRODUCTION

The use of short pulse lasers has activated the study and characterization of photofragmentation processes in molecules near the dissociation and ionization thresholds. The fragmentation mechanisms are discussed in reference to two possible pathways [1]. First the molecule, initially in its ground electronic state, absorbs several photons from the laser pulse reaching a dissociative state below the ionization limit. If the duration of the laser pulse is longer than the dissociative lifetime

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of the state, the neutral fragments produced in the dissociation of the parent can absorb further photons from the laser pulse, suffering dissociation or ionization. This process is called dissociation followed by ionization or ladder switching. However, if the laser pulse is shorter than the lifetime of the dissociative state, the parent molecule is preferably up-pumped to an ionization level from where it can ionize or dissociate producing ionic fragments. This second mechanism is called ionization followed by dissociation or ladder climbing. Some molecular systems show a propensity to fragment by one of these two mechanisms. Often both mechanisms compete, ladder climbing becoming dominant when the duration of the laser pulse is shorter than the dissociative lifetime of the involved molecular state. There have appeared in the recent literature a number of studies on the multiphoton fragmentation of molecular systems in which a comparison is established between the results obtained using laser pulses of nanosecond, picosecond and femtosecond duration [1–6]. The molecules range from small size, such as NO_2 , to large molecules of biological interest. It has been shown that often the molecular ion preserves its integrity even at high laser intensities making possible its detection by mass spectrometric techniques. This fact has important analytical applications and has given rise to the femtosecond laser mass spectroscopy (FLMS) technique [1, 7, 8]. The technique relies on the fact that the use of short laser pulses increases the possibility of producing molecular parent ions, as the dissociative states can be defeated by fast up-pumping of the parent ion state. This results in a large amount of high mass fragment ions making the interpretation of the spectra less ambiguous, simplifying the analysis of complex mixtures and providing information on the molecular weight, useful for sample identification.

In this article we present an overview of our recent work performed using laser pulses of nanosecond and picosecond duration in the molecules of ketene [9] and the cyclic saturated hydrocarbon, cyclohexane. Multiphoton dissociation of ketene at 290.5 nm was studied after irradiation of the first excited singlet state with laser pulses of 4 ns and 10 ps pulsewidths. Analysis of the photofragment fluorescence spectra in the two time domains with the help of a rate equation model [10] sheds light on the mechanisms that are responsible for the production of the observed photofragments. Cyclohexane is

one of the few reported examples of a molecule with a giant resonance [11]. This resonance appears in the absorption spectrum of the molecule as a broad absorption band in the vacuum ultraviolet region carrying out a very high oscillator strength. The total cyclohexane photoionization yield produced by a visible laser and its second harmonic was measured in the above mentioned pulse duration regimes. The resonant ionization processes were also evaluated through a population rate equation model. The role played in the photoionization process by the giant resonance of this molecule at 84000 cm^{-1} is discussed.

2. EXPERIMENTAL

The experimental system has been described in detail in [9]. Photolysis of molecular gas samples were carried out with laser pulsewidths of 10 ps and 4 ns. Laser pulses of 10 ps are provided by a synchronously pumped mode-locked dye laser (Rhodamine 6G) pumped by an active mode-locked Ar^+ ion laser. The dye oscillator output is amplified by a pulsed dye amplifier, the latter being pumped by a frequency doubled Nd-YAG laser operating at a repetition rate of 10 Hz. The system provides amplified pulses of 581 nm with a bandwidth of 2 nm and duration of 10 ps. The energy and polarization of the laser could be controlled by propagation through a half-wave plate and a polariser. Frequency doubling in a BBO crystal cut at 51° produced up to $50\ \mu\text{J}$ of 290.5 nm vertically polarized laser radiation. A UV cutoff filter (Schott UG5) could be used to eliminate the yellow fundamental beam before focalization in the photolysis cell. When required the above laser system could deliver pulses of 4 ns with the same energy and wavelength characteristics by switching off the RF signal of the mode-locker in the Ar^+ ion laser. This leads to a cw output in the dye oscillator, the finally amplified pulse having a duration close to that of the Nd-YAG pump laser.

Photolysis radiation was focused with a quartz lens (focal length ranging from 9 to 25 cm) at the centre of a glass cell fitted with quartz windows that contained the gas samples. Photofragment fluorescence detection was made perpendicularly to the laser propagation by an EMI 9816 QB photomultiplier. The spectral selection was performed

by a high intensity low resolution Bausch and Lomb monochromator. The cell could also be used to measure the laser induced ionization. For this purpose it was furnished with two parallel plate electrodes, one maintained at -60 V and the other at ground potential acting as an anode in collecting electrons [12]. The electric field between the electrodes is perpendicular to the polarization of the UV laser.

The above cell was connected to a glass vacuum system routinely operating at 10^{-5} Torr. Gas pressures were measured in the cell with a capacitance manometer (MKS Baratron $10^{-3} - 1$ Torr). Ketene was prepared by pyrolysis of acetic anhydride and purified twice by trap-to-trap distillation from 163 to 77 K. Cyclohexane was from Carlo Erba (purity $> 99.5\%$).

3. RESULTS AND DISCUSSION

a. Photodissociation of Ketene

A summary of results presented in [9] is given here. Photofragment fluorescence spectra following photodissociation of 700 mTorr of ketene at 290.5 nm were recorded in the 380 to 720 nm range. Photolysis with 4 ns pulses gives rise to CH ($A^2\Delta$) and ($B^2\Sigma^-$) emissions together with the C_2 ($d^3\Pi_g - a^3\Pi_u$) bands; however photolysis with 10 ps pulses only yields CH emissions. Table I compares the relative intensities of the CH ($A-X$) with both the CH ($B-X$) and C_2 ($d-a$) emissions.

The intensity of the CH($A-X$) $\Delta v = 0$ band, estimated by the height of the peak, increases by a factor of 5 when the pulse duration is reduced from 4 ns to 10 ps. On the other hand, shortening the duration

TABLE I Relative intensities of the observed emissions by photolysis of ketene at 290.5 nm with 4 ns and 10 ps pulses. The photon fluence is 3.7×10^{18} photons cm^{-2} in both cases. The numbers in parenthesis indicate the slope of the linear least squares fit of the logarithm of the fluorescence intensity as a function of the logarithm of the laser energy

Pulse duration	4 ns	10 ps
I (photons $\text{s}^{-1} \text{cm}^{-2}$)	1×10^{27}	4×10^{29}
CH($A-X$) $\Delta v = 0$ ^a	20 (2.0 ± 0.2)	100 (2.0 ± 0.2)
CH($B-X$) $\Delta v = 0$	8.3	6.6
C_2 ($d-a$) $\Delta v = 1$	1.6 (2.4 ± 0.2)	< 0.3

^a Intensity at the maximum of the band in arbitrary units.

of the pulse does not result in a substantial change in the ratio of intensities of the CH(A–X) and CH(B–X) emissions. The intensity of the C₂ emission relative to CH(A–X) is severely reduced to a value below the threshold of the detection system. To gain some insight into the mechanism of formation of each photofragment we determined the order of the multiphoton processes by measuring the corresponding fluorescence intensity as a function of laser energy. The slopes of the logarithmic plots, giving the apparent order of the process, are also shown in Table I.

As discussed previously [9], the different behaviour shown by the CH and C₂ emissions with laser pulse duration suggests that a different mechanism should be responsible for the formation of each fragment. The minimum energy required to produce CH(A) corresponds to the absorption of at least three photons. Therefore, the quadratic dependence observed in the CH emission could suggest that one absorption step is saturated. The two-photon absorption process by the parent molecule populating a Rydberg level is far from the saturation regime. Two different processes, indicated in Figure 1, would give account of the CH photofragments. First, in the molecular pathway, electronically excited CH could be originated by three-photon absorption by the parent molecule followed by dissociation. In the alternative pathway, involving the participation of an intermediate, dissociation from the two-photon excited molecular Rydberg state could compete favourably with up-pumping giving rise to a species that dissociates after the absorption of a third photon. To clarify this point a simple rate equation model has been employed to account for the variation of CH(A) intensity with the duration of the laser pulse [10]. Figure 1 shows the elementary processes considered in the model. Values of the cross sections for one-photon absorption by ketene, $\sigma_1 \approx 10^{-20} \text{ cm}^2$, and of the dissociative lifetime of the corresponding one and two-photon molecular excited states, $t_1 \approx 30 \text{ ps}$ and $t_2 \approx 1 \text{ ps}$, are from the literature [13–15]. The magnitude of σ_2 and σ_4 , corresponding to the absorption of a second photon by the parent molecule and to the absorption of a laser photon by the intermediate respectively, do not affect in a severe way the predictions of the model. These predictions are that, unless the cross section for absorption of the third photon by the parent molecule σ_3 is unreasonably high, above 10^{-13} cm^2 , the ratio of CH(A) emission intensities for the 10 ps

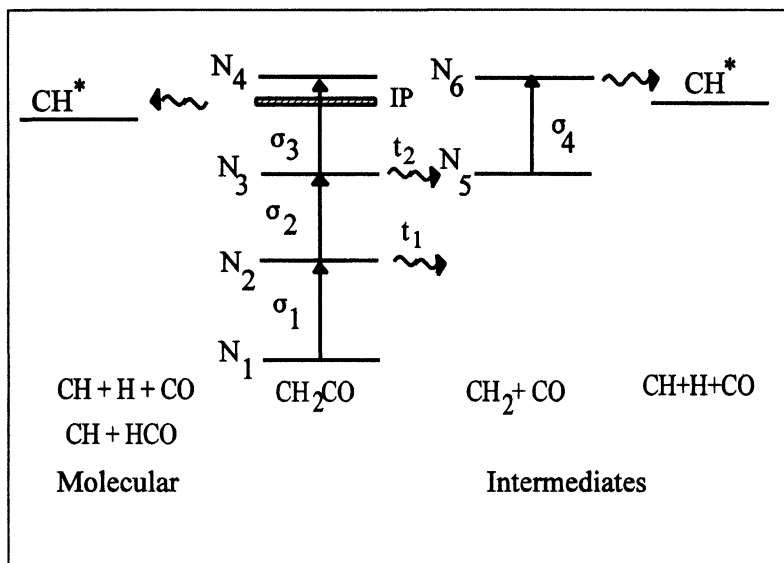


FIGURE 1 Scheme of molecular energy levels participating in the formation of electronically excited CH from UV multiphoton dissociation of ketene. The kinetic model mentioned in the text includes the states labelled N_i , σ_i are cross sections of the corresponding absorption steps and t_i dissociative lifetimes of the states. The population of the electronically excited methyldiene CH^* is proportional to the populations of states N_4 and N_6 in the molecular and intermediates pathways respectively.

and 4 ns pulses would be about 10^4 , several orders of magnitude above the experimental value of 5. However, for σ_3 ranging between 10^{-18} and 10^{-21} cm^2 , this ratio is of the right order of magnitude when dissociation from a two-photon excited Rydberg state is invoked. With respect to the nature of the precursor of the CH photofragments, arguments in favour of $\text{CH}_2(^1\text{B}_1)$ are given in [9]. The last absorption step by this intermediate would have to be saturated here to explain the observed quadratic dependence.

For $\text{C}_2(\text{d})$ the spin forbidden process leading to the carbon fragment and ground state H_2O requires three photons whereas all other possible processes require on additional photon. The fact that the Swan bands are not observed with 10 ps pulses could be an indication that this fragment is not formed by a molecular pathway through the spin forbidden process $\text{CH}_2\text{CO} \rightarrow \text{C}_2(\text{d}) + \text{H}_2\text{O}$. Alternatively the possible intermediate fragments, formed after one or two-photon

absorption by ketene, that could give origin to C_2 have to be considered. These are ketylenyl $CHCO$, ethynyl C_2H and C_2O radicals and the acetylene molecule. The fact that $C_2(d)$ emission is only observed in photolysis with 4 ns pulses, indicates that a relatively slow step is involved in the processes forming $C_2(d)$. Therefore, dissociation of the possible intermediates would proceed at a relatively low rate, making the formation of the final $C_2(d)$ precursor to compete unfavourably with up-pumping when the laser pulse duration is shortened to 10 ps. There are examples in the literature of such a delayed dissociation process [16], also involving formation of $C_2(d)$.

b. Photoionization of Cyclohexane

The total ionization signal was measured as a function of the pressure of C_6H_{12} in the 0 to 1 Torr range. The ionization signal induced by visible pulses of either 4 ns and 10 ps pulsewidths at 581 nm is very weak, even with the tightest focussing, achieved with a focal length of 9 cm. However, UV laser pulses at 290.5 nm give rise to intense ionization signals. Figure 2 shows the dependence of the photoionization signal with pressure for 4 ns and 10 ps UV pulses focussed with different lenses of $f = 9, 15$ and 25 cm. The highest ionization yield was achieved with 10 ps pulses at 290.5 nm. In the same focussing conditions, pulses of 4 ns at the same wavelength induce an ionization signal roughly one order of magnitude smaller. Tighter focussing in the two time domains seems to increase the ionization signal.

More information about the process is obtained by measuring the ionization signal as a function of laser energy. Two sets of experiments were performed by focussing the laser at the centre of the cell with a $f = 15$ cm lens. First we measured the ionization signal as a function of the UV laser energy when only UV light was allowed into the cell. The results are shown in Figure 3. Two regions with different slopes in the logarithmic plot can be distinguished. In the energy region below $7 \mu J$, corresponding to an intensity of $2.3 \cdot 10^{11} Wcm^{-2}$, the linear squares fit of the data gives a slope of 3.0 ± 0.2 . At higher energies the ionization signal follows the $3/2$ power law characteristic of the focussing conical geometry. Secondly, we measured the ionization signal again as a function of the UV energy, but in this case both fundamental and second harmonic beams, at 581 and 290.5 nm respectively, were

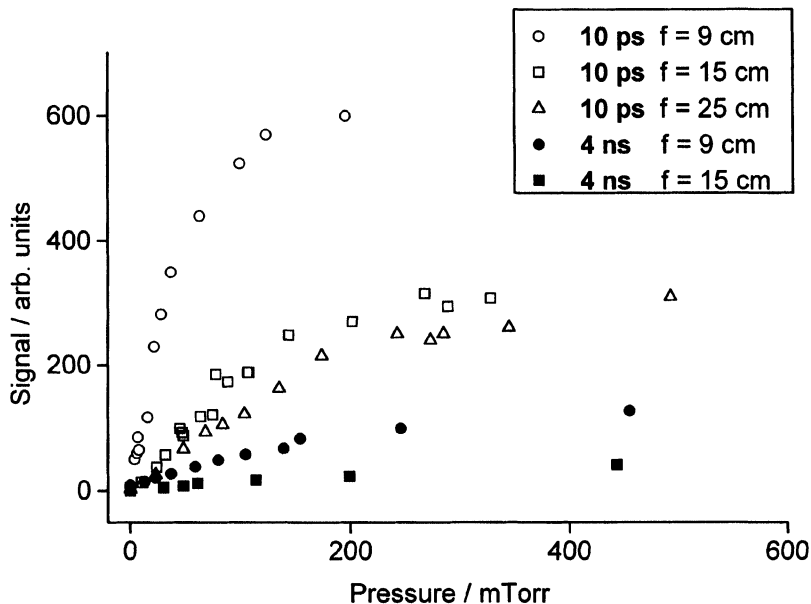


FIGURE 2 Ionization signal as a function of the pressure of cyclohexane induced by 290.5 nm laser pulse focused with different focal length lenses. Data taken with pulses of: a) 10 ps, open symbols, b) 4 ns, solid symbols.

propagating through the ionization cell. The dependence follows a quadratic law in the whole energy range with a slope of 2.1 ± 0.1 .

A saturated hydrocarbon such as cyclohexane has no singlet excited states lower than 55000 cm^{-1} above the ground electronic state. As indicated in the scheme of Figure 4, two or four-photon excitation at 290.5 and 581 nm respectively places the molecule in an energy region corresponding to a broad valence band absorption peak in the one-photon spectrum [11]. An additional photon of either wavelength sends the molecule above its 78000 cm^{-1} first ionization potential [17, 18]. The visible photon at 581 nm explores the energy region of the giant resonance of this molecule at 84000 cm^{-1} . The low probability expected for a five-photon process would explain the negligible photoionization signal measured at 581 nm with either 4 ns or 10 ps pulses. One and two colour three-photon ionization processes, $3\omega_{UV}$ and $2\omega_{UV} + \omega_{VIS}$, are expected to occur with higher yield. Photoionization induced by UV pulses presents a cubic dependence of the

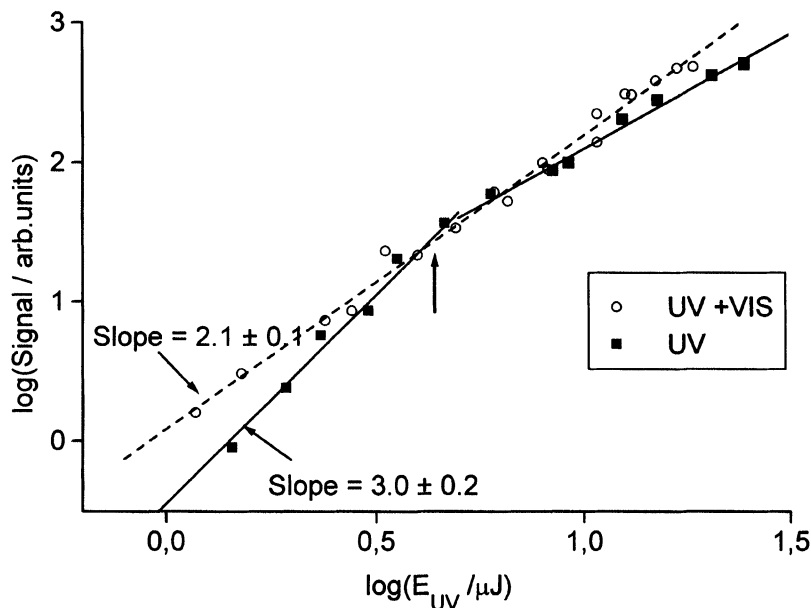


FIGURE 3 Plot of the logarithm of the ionization signal as a function of the logarithm of the UV laser pulse energy at 290.5 nm, focussed with a lens of $f = 15$ cm in 1 Torr of cyclohexane. Ionization is induced by: a) only UV beam, squares; the vertical arrow indicates the change of slope for energies above $7 \mu\text{J}$; b) UV and visible beams, circles. The slopes of the linear plots are indicated.

ionization signal with the UV laser pulse energy in the region below $7 \mu\text{J}$, indicating the absence of saturation in any of the steps of the two-photon resonant three-photon ionization process of the molecule [18]. In the two-colour experiments both $3\omega_{\text{UV}}$ and $2\omega_{\text{UV}} + \omega_{\text{VIS}}$ processes could be contributing to the measured total ion yield. The reduction of the order in the UV energy dependence in one unity could be a signature of the competition established between the two ionization paths. Dissociation from the excited valence state could take place competing with further up-pumping prior to dissociation. The radiationless processes that dominate the decay of singlet excited states of this alkane result in decomposition with detachment of H_2 and/or H and proceed with a rate of $10^8 - 10^9 \text{ s}^{-1}$ [19, 20]. For laser pulses of 10 ps this rate is very slow; dissociation should not compete favourably with up-pumping to a state above the ionization threshold.

Therefore, it should be reasonable to assume that the ionization signal measured with 10 ps laser pulses is due mainly to molecular parent ions. The photoionization processes taking place at the two studied wavelengths in the picosecond domain were treated by using a three level population rate equation model [10]. A proper description of the procedure and its extension to the nanosecond domain will be published shortly. The elementary processes included in the model appear in Figure 4. The observed energy dependences, shown in Figure 3, are satisfactorily retrieved by the model for a set of values of the cross sections: $\sigma_{2\gamma} \approx 10^{-52} \text{ cm}^4 \text{ s}$ and $\sigma_{\text{UV}}, \sigma_{\text{VIS}} \approx 10^{-20} \text{ cm}^2$, corresponding to the two-photon resonant excitation and one-photon ionization of the molecule at the UV and visible wavelengths respectively. In the presence of only UV pulses the last step towards the ionization of the

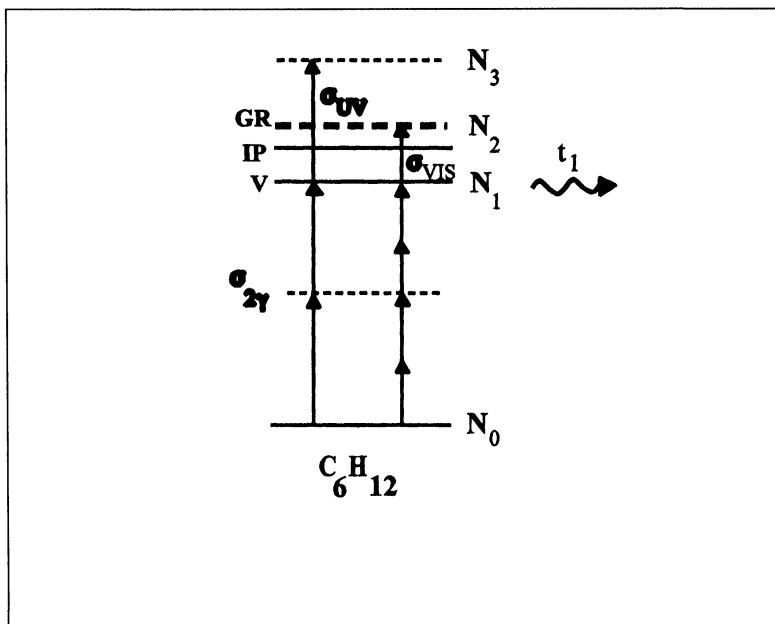


FIGURE 4 Cyclohexane energy levels involved in the multiphoton ionization process. V, IP and GR represent the two-photon resonant valence state, the ionization threshold and the giant resonance of the molecule respectively. The kinetic model mentioned in the text includes the states labelled N_i , σ_i are cross sections of the corresponding absorption steps and t_1 the dissociative lifetime of state V.

molecule involves the transition from a two-photon resonant valence state, V in diagram of Figure 4, to an energy region around 97000 cm^{-1} . In the presence of both UV and visible pulses, the total ionization process includes a contribution due to the visible laser. This contribution has its origin in the valence shell transition from V to the valence state associated with the giant resonance of the molecule. According to the above results the cross sections of these two processes, σ_{UV} and σ_{VIS} , are similar in opposition with what is found in transitions from the ground state, which carry out extremely high oscillator strength if the final state corresponds to the giant resonance of the molecule.

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