Effect of Cation Absorption on Ionization/Dissociation of Cycloketone Molecules in a Femtosecond Laser Field[†]

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The mass spectra of a series of cycloketone molecules, cyclopentanone (CPO), cyclohexanone (CHO), cycloheptanone (CHPO), and cyclooctanone (COO) are measured in a 788 or 394 nm laser field with 90 fs pulse duration and the intensity ranging from 5×10^{13} W/cm^2 to 2×10^{14} W/cm^2. At 788 nm, a dominated parent ion peak and some weak peaks from the fragment ions $C_nH_m^+$ are observed for CPO and CHO (a ratio P^+/T^+, the parent ion yield to the total ion yield, is 81.6% and 52.6%, respectively). But the extensive fragment ion peaks are observed with the greatly reduced parent ion peak for CHPO ($P^+/T^+ = 5.5\%$) and that are even hard to be identified for COO. These observations are interpreted explicitly in the frame of the significant resonant effect of their cation photoabsorption on ionization and dissociation of these molecules. The present work also suggests that a nonadiabatic ionization occurs with a nuclear rearrangement due to the H movement in these molecules during the ionization in an intense femtosecond laser field.

1. Introduction

The ionization and dissociation of polyatomic molecules in a femtosecond (fs) laser field within an intensity range of $10^{13}-10^{16}$ W/cm^2 show various novel phenomena. Many experimental and theoretical studies reveal the mechanism of ionization and/or dissociation of polyatomic molecules in an intense radiation field,[1−8] which is much more complicated than that of atoms or even small molecules. This complication is due to the multidimensional potential surfaces, a large number of available pathways for excitation and relaxation, and the strong coupling between the laser field and molecules, leading to a considerable variety of molecular dynamic processes. For example, in a femtosecond laser field, polyatomic molecules can be ionized to generate their parent ions with fewer fragment ions than that in the case that are ionized by a nanosecond pulsed laser.[4−8] But this is not universal and for some polyatomic molecules such as some hydrocarbons, aromatic, and chlorinated compounds, extensive fragment ions have been observed in such a femtosecond laser field.[9−16] Nakashima and co-workers[11,13,14] studied the ionization and dissociation of a number of organic molecules irradiated by a 120 fs, 800 nm laser with an intensity $\sim 10^{14}$ W/cm^2 and showed that the mass spectra of the molecules have a dominant contribution from the parent ion if their cation has not allowed electronic transition at the laser wavelength, and in contrast, the mass spectra of the molecules with a similar structure but their cations have the absorption at the laser wavelength, show a considerable contribution from the fragment peaks, and a negligible peak from their parent ion. Robson et al.[15] found that the resonance in cation absorption can also cause multiple ionization directly if the molecules have a more stable structure such as some aromatic molecules. Furthermore, Trushin et al.[16] studied the dissociation of metal carbonyls irradiated by the lasers with different pulse durations (30−110 fs), wavelengths (800 nm or 1.35 μm), and intensities in the range of 2×10^{12} to 2×10^{14} W/cm^2. They suggested that the dissociation phenomena could be rationalized if molecular intermediate relaxation, either neutral or ionized, was taken into account.

In the present work, we select a series of cycloketone molecules with similar molecular structure but different cation photoabsorption such as cyclopentanone (CPO), cyclohexanone (CHO), cycloheptanone (CHPO), and cyclooctanone (COO) for investigating the resonant effect in ionization and dissociation in an intense femtosecond laser field. The experimental observations are interpreted in terms of theoretical calculation for photoabsorption, explicitly demonstrating the significant resonant effect of their cation photoabsorption on ionization and dissociation of these molecules and the nonadiabatic ionization with a nuclear rearrangement due to the H movement in the molecular system during the ionization in an intense femtosecond laser field.

2. Experimental

Briefly, the mass spectra of gaseous cycloketone molecules are obtained by using a linear time-of-flight mass spectrometer with an ion optical system based on Wiley−McLaren design, giving an approximate mass resolution of 1000 at approximately $m/e = 84$. The commercial cycloketone samples (Aldrich Co. Ltd., CPO 99%, CHO 99.5%, CHPO 99%, and COO 98% purity) are used without further purification. The samples (400 Pa for CPO, CHO, and CHPO, 240 Pa for COO, with 4×10^4 Pa Ar as the carrier gas) are ejected through a pulsed nozzle (General Valve G9) into a vacuum chamber (background pressure of 3×10^{-5} Pa). A 90 fs, 788 nm or its second-harmonic, 394 nm, linearly polarized laser beam from a Ti:sapphire chirped-pulse amplifier laser system (Spectra-Physics) is focused by a lens ($f = 350$ mm) onto the molecular beam in the vacuum chamber. A half-wave plate and a Glan prism are placed in front of the lens for the purpose of varying laser intensity continuously and ensuring the direction of laser polarization parallel to the flight axis of the time-of-flight mass spectrometer. The estimated laser intensities are in the range

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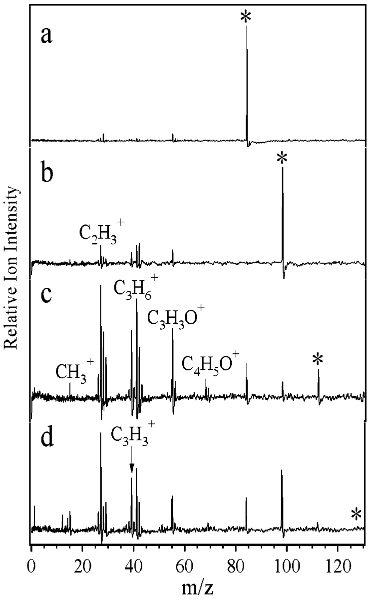

Figure 1. Mass spectra of cycloketone molecules at 788 nm laser with 90 fs pulse duration and intensity of 6 × 10^{13} W/cm^2. (a) Cyclopentanone (CPO); (b) cyclohexanone (CHO); (c) cycloheptanone (CHPO); (d) cyclooctanone (COO). The parent ions are denoted by asterisks.

from 5 × 10^{13} to 2 × 10^{14} W/cm^2. The produced ions in the femtosecond laser field are collected by a dual MCP detector at the end of the flight and the detected signal is sent to a digital oscilloscope (Lecroy 9361). All experimental data are normally averaged over 1000 laser shots.

3. Results

The mass spectra of CPO, CHO, CHPO, and COO are presented in Figure 1 for a 788 nm femtosecond laser with an intensity of 6 × 10^{13} W/cm^2. Parent ion peak is dominated in the CPO and CHO mass spectra, and all the rest of the peaks from the fragment ions are with relatively small intensities (a ratio P^+/T^+, the parent ion yield to the total ion yield, is 81.6% and 52.6% for CPO and CHO, respectively), although the CHO mass spectrum shows relatively increased fragmentation and observable $C_nH_m^+$ ($n = 2-3$) compared with that of CPO, as given in Figure 1a,b. Differently, the parent ion peak is greatly reduced in intensity for CHPO ($P^+/T^+ = 5.5\%$) and even hard to identify for COO. The mass spectra of CHPO and COO give the extensive fragment ion peaks, assigned as $C_nH_m^+$ ($n = 1-6$), as seen in Figure 1c,d. It is noticed that no peak can be assigned to the multicharged ions for the cases of these four molecules, and Coulomb explosion is also absent because of no mass peak splitting observed.[17,18] For comparison, the mass spectra of CPO, CHO, CHPO, and COO are also measured by using a 394 nm femtosecond laser with the same intensity, given in Figure 2. The results exhibit more fragments, $C_nH_m^+$, and less parent ions for all four molecules in this UV radiation field, and the most contributing fragment ions are CH_3^+, $C_2H_3^+$, $C_3H_3^+$, $C_3H_6^+$, and $C_3H_3O^+$. A clear H^+ peak is also observed in these mass spectra, which is almost negligible in case of the 788 nm laser field.

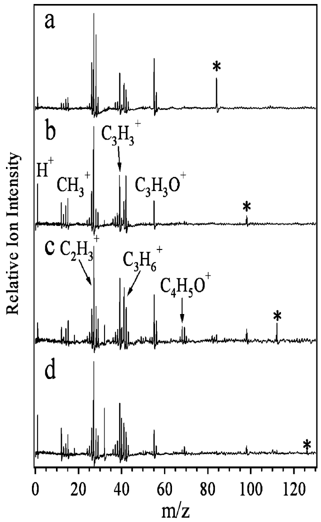

Figure 2. Mass spectra of cycloketone molecules at 394 nm laser with 90 fs pulse duration and intensity of 6 × 10^{13} W/cm^2. (a) Cyclopentanone (CPO); (b) cyclohexanone (CHO); (c) cycloheptanone (CHPO) (d) cyclooctanone (COO). The parent ions are denoted by asterisks.

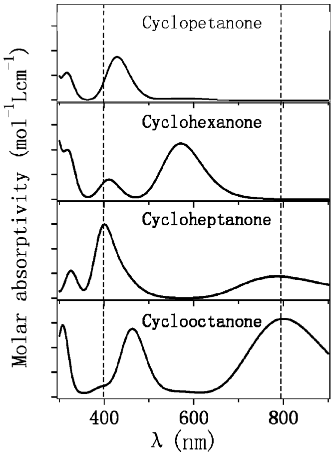

Figure 3. Photoabsorption spectra of cycloketone cations convolved by the SWizard program from the excitation energies and oscillator strengths of electronic transitions calculated by a time-dependent DFT method with 6-31G++(d,p) basis set. The broken lines indicate the positions of the femtosecond laser wavelengths used in the experiments.

The absorption spectra of the neutral and single charged ions of these cycloketones are calculated using the Gaussian03 program. A DFT calculation of B3LYP method with 6-31++G-(d, p) basis set has been carried out to determine the optimized geometric structure of the molecular systems first. Then a time-dependent DFT of UB3LYP method with the same basis set is used to calculate the transition energies and the oscillator strengths between their ground and excited states based on the optimized molecular geometric structures obtained. Finally, the optical absorption spectra are drawn from these calculated results with the help of SWizard program.[19] For the neutral molecules, it is known that there is no single photon absorption in the spectral region interested here. For the molecular cations, there is no experimental absorption data available, and the calculated spectra are given in Figure 3. These spectra show different absorption features for different cycloketone molecules, depending on the nature of the HOMO−LUMO transitions, in the spectral region of 300−900 nm. The calculated wavelengths (λ), oscillator strengths, and molar absorptivities for the assigned cation transitions nearby 394 and 788 nm are listed in Table 1, together with the ratios of P^+/T^+ from the measured mass spectra, for these molecules. These results exhibit that there is almost no absorption for CPO^+ and CHO^+ near 788 nm, but the absorption are obvious for $CHPO^+$ and COO^+. According to the assignment of the calculation, the absorption is formed from the convolution of the transitions HOMO → LUMO, HOMO-1 → LUMO, and HOMO-2 → LUMO for $CHPO^+$, and the strong absorption is originated mainly from the HOMO → LUMO transition for COO^+. Also, in the case of the 394 nm

TABLE 1: Photoabsorption of the Different Cycloketones Cations Calculated by Using B3LYP Method with 6-31++G (d, p) Basis[a]

	laser wavelength (nm)	λ (nm)	oscillator strength	excited states	electron transition assignment (coefficients)	molar absorptivity (mol^{-1} L cm^{-1}) contribution	total	P^+/T^+ (%)
CPO	394	448.5	0.0055	3^1A	HOMO-3 → LUMO (0.776) HOMO-2 → LUMO (0.596) HOMO-7 → LUMO (0.196)	20.429	520.17	5.33
		425.2	0.0205	4^1A	HOMO-2 → LUMO (0.779) HOMO-3 → LUMO (−0.558) HOMO-5 → LUMO (−0.237)	499.741		
	788							81.6
CHO	394	410.8	0.0110	4^1A	HOMO-3 → LUMO (0.977)	566.002	570.56	1.62
		359.1	0.0004	5^1A	HOMO-5 → LUMO (0.828) HOMO-6 → LUMO (0.461) HOMO-10 → LUMO (0.235) HOMO-8 → LUMO (−0.202)	4.558		
	788	615.5	0.0034	1^1A	HOMO → LUMO (0.98) HOMO-2 → LUMO (0.163)	5.119	6.743	52.6
		597.5	0.001	2^1A	HOMO-2 → LUMO (0.978) HOMO → LUMO (−0.163)	0.478		
		567.2	0.0284	3^1A	HOMO-1 → LUMO (0.958)	1.146		
CHPO	394	440.8	0.0117	5^1A	HOMO-4 → LUMO (0.98)	87.597	2846.74	2.5
		398.3	0.0391	6^1A	HOMO-5 → LUMO (0.823) HOMO-3 → LUMO (0.404) HOMO-7 → LUMO (0.282)	2758.715		
		342.5	0.0005	7^1A	HOMO-6 → LUMO (0.994)	0.428		
	788	907.8	0.0036	1^1A	HOMO → LUMO (0.987)	108.832	880.096	5.5
		784.6	0.0043	2^1A	HOMO-1 → LUMO (0.979)	311.408		
		762.2	0.0067	3^1A	HOMO-2 → LUMO (0.974)	459.856		
COO	394	462.8	0.0376	6^1A	HOMO-5 → LUMO (0.924) HOMO-8 → LUMO (0.226) HOMO-10 → LUMO (−0.182)	32.407	429.203	0.75
		394.4	0.0054	7^1A	HOMO-6 → LUMO (0.983)	391.096		
		349.8	0.0018	8^1A	HOMO-7 → LUMO (0.989)	5.700		
	788	962.5	0.0001	1^1A	HOMO-1 → LUMO (0.99)	1.399	3139.132	0.1
		801.4	0.0427	2^1A	HOMO → LUMO (0.918)	3048.093		
		741.2	0.0015	3^1A	HOMO-2 → LUMO (0.992)	89.640		

[a] The wavelength (λ), transition oscillator strength, and molar absorptivity for each transition involved in the spectral convolution nearby 394 and 788 nm are given from the analysis using the SWizard program. The measured ratio of parent ion yield to total ion yield (P^+/T^+) is also listed.

excitation, the absorption of all four molecules are strong and resulted from the transitions HOMO-2 → LUMO, HOMO-3 → LUMO, and HOMO-5→LUMO for CPO^+, the transition HOMO-3 → LUMO for CHO^+, the transitions HOMO-5 → LUMO, HOMO-8 → LUMO, and HOMO-10 → LUMO for $CHPO^+$, and the transition HOMO-6 → LUMO for COO^+. Furthermore, the ionization potentials for forming their doubly charged ions are also evaluated from the single-point energy calculation using the B3LYP method and 6-31G(d, p)++ basis set, giving the values of the ionization potentials roughly about 17 eV for these cycloketone cations.

4. Discussion

In general, ionization of atoms and molecules in an intense femtosecond laser field can be through the mechanism of multiphoton ionization and field ionization, depending on the radiation intensity and the atomic or molecular properties. For atoms, a Keldysh parameter γ have been introduced for determining whether the ionization process was in the field ($\gamma \ll 1$) or multiphoton ionization ($\gamma \gg 1$) regime. For molecules, the influence of molecular behavior such as the electronic orbital shape, size, and polarization should be considered in evaluating the Keldysh parameters of different ionization mechanisms.[1,9,20−23] This modified adiabatic parameter shows that the probability of field ionization is largely increased for polyatomic molecules compared with atoms. It leads to a tunneling ionization of polyatomic molecules that can take place normally in a relative weak laser field (e.g., a field ionization mechanism, rather than a multiphoton process, for benzene in a laser field of 3.8×10^{13} W/cm^2).[9] Thus, it is reasonable to believe that the ionization of the neutral cycloketone molecules in a laser field of 6×10^{13} W/cm^2 in the present experiment is mainly through a tunneling ionization, although the multiphoton mechanism cannot be excluded. The produced parent ions should be able to gain more excitation energy by further photoabsorption in the same laser pulse. Considering a high threshold for further ionization (17 eV approximately), the probability to form multicharged species should be negligibly small. Thus, the energetic cations should decay through a nonergodic decomposition into different fragment ions.[24,25] Taking this sequential model of the molecular ionization/dissociation in a femtosecond laser field into account, the influence of cation photoabsorption is expected to be significant.

The importance of the cation photoabsorption is explicitly convinced by our experimental observation. The mass spectra for different cycloketones exhibit quite different characters (see

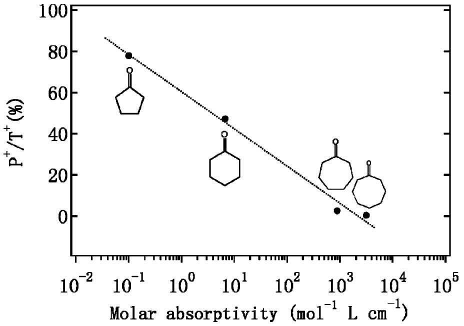

Figure 4. Measured ratios of the parent ion yield to the total ion yield (P^+/T^+) at the 788 nm laser with the intensity of 6 × 10^{13} W/cm^2, plotted as a function of molar absorptivities for cyclopentanone (CPO), cyclohexanone (CHO), cycloheptanone (CHPO), and cyclooctanone (COO).

Figures 1 and 2). Comparing the features of their cation absorption with the mass spectra, it is clear that the appearance of a parent ion peak is related clearly to the absence of the resonant absorption of a single photon by the cations and the fragmentation of the molecular cations increases significantly in the case of resonance. For example, when the molar absorptivity is smaller than 6.27 mol^{-1} L cm^{-1}, such as in the cases of CPO and CHO in the 788 nm laser field, the only strong mass peak is from parent ions and other fragment ion peaks are much smaller. On the contrary, the molar absorptivity of CHPO$^+$ and COO$^+$ are 880.096 and 3139.132 mol^{-1} L cm^{-1}, respectively, showing the intense resonance with the 788 nm laser field and, therefore, the mass spectra of CHPO and COO given in Figure 1c,d show a number of fragments. For the case of the 394 nm laser, because the molar absorptivities of all four cycloketone cations are relatively large (520.17, 570.56, 2846.74, and 429.203 mol^{-1} L cm^{-1} for CPO$^+$, CHO$^+$, CHPO$^+$, and COO$^+$, respectively), indicating the resonant absorption of these cations to some extent in the 394 nm laser field, their mass spectra obviously exhibit more fragments, as shown in Figure 2.

It is worthy to note that the absorption spectra used in interpreting the resonance effect above are calculated by taking the optimized ionic molecular structures. According to our calculation, the strong vibrational intensities of cycloketone cations are mainly contributed by the H atom movement, including stretching and torsional vibrations. In CPO$^+$ and CHO$^+$, the largest vibrational intensity is the stretching vibration of the C-H bond, which is on the carbon of a vicinal carbonyl. For CHPO$^+$, the stretching vibrations of the H atoms are on the meta position carbon of the carbonyl. It is noticed that the stretching of C−O bond of the carbonyl is the strongest vibration in COO$^+$, although all of the H atoms have also modest vibration intensities. These H atom movements should result in the nuclear rearrangement from the equilibrium structure of the neutrals into an optimized ionic molecular structure. This rearrangement is believed to be performed in a pulse duration of the femtosecond laser, as it has been demonstrated by Fuss et al.[16,26,27] and Yamanouchi et al.[28−30] that this kind of H migration in organic molecules is as fast as several tens of femtoseconds. This process is more like that described by the nonadiabatic multielectron (NME) model of dissociative ionization.[31] As shown in Figure 4, for different cycloketones, the ratio P^+/T^+ decreases with increasing molar absorptivity in the 788 nm laser field. It implies that the resonant absorption enhances the dissociation of the molecular cation because the yield of fragment ions increases when the molecular molar absorptivity gets larger. This suggests that the resonance effect should be considered in this nonadiabatic process, consistent with the discussion in the NME model by Trushin et al.[16]

In addition, although Harada et al. has suggested that multicharged ions can be produced when a molecular cation has no resonance with the femtosecond laser wavelength,[11,13] the multicharged parent ions are not observed in our mass spectra of CPO and CHO at 788 nm (Figure 1a,b). This is due to a high ionization threshold for further ionizing, as mentioned above, a relative low laser intensity used (6 × 10^{13} W/cm^2), and less stability of these molecules in structure (the cycloketone ions should dissociate as increasing the laser intensity). This has also been observed in previous studies in which the multiply charged CPO and CHO ions did not appear when using a 790 nm femtosecond laser even when the intensity is higher than 4 × 10^{15} W/cm^2.[17,18]

5. Conclusions

The mass spectra of a series of cycloketone molecules, CPO, CHO, CHPO, and COO, have been measured in a 90 fs 788 nm or 394 nm laser field in the intensity range from 5 × 10^{13} to 2 × 10^{14} W/cm^2. For analyzing them, ab initio calculation of the molecular photoabsorption in visible and near UV spectral region has also been done by DFT methods. It is found that the existence of parent ions in the mass spectra is related clearly to the absence of resonant absorption of a single photon by them and the fragmentation of the molecular cations increases significantly in the case of resonance because the yield of fragment ions increases with increasing molar absorptivity, as shown by the measured ratio P^+/T^+ for different cycloketones. We conclude, by combining the experimental observation of these mass spectra with the theoretical calculation of the absorption spectra, that the resonant photoabsorption of the molecular cation plays an important role in the ionization and dissociation of these cycloketones. It is also suggested that, for these cycloketone molecules, a nonadiabatic ionization occurs, resulting from the nuclear rearrangement due to the H movement during the ionization in an intense femtosecond laser field.

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