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Photodissociation of Cycloketones by Ultraintense Femtosecond Laser Pulses

Cheng Yin WU, Yi Jia XIONG, Jin Xiong WANG, Fan Ao KONG*

Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080

Abstract: Photodissociation of cyclopentanone (C_5H_8O) and cyclohexanone ($C_6H_{10}O$) was studied with 800nm, 50fs laser pulse at intensities of 5.0 — 13.0×10^{13} W/cm^2. A time of flight mass spectrometer was employed to detect the ion signals. Parent ions dominated at lower laser intensities. Fragmentation of the parent ions increases with increasing laser intensity and molecular size. The fragmentation mechanism was discussed.

Keywords: Intense field, femtosecond laser, fragmentation mechanism.

The study of photoionization and photodissociation processes induced by intense femtosecond laser pulses (>10^{13}W/cm^2) with polyatomic molecules becomes of interest because some new phenomena have been observed[1-3]. So far, most of the investigations focus on the experimental exploration of photoionization processes[4-7]. But the photoionization mechanism of polyatomic molecules in an intense fs laser field is still ambiguous[8,9]. In contrast to the photoionization processes, the understanding of fragmentation of molecular ion is even poorer. Corkum *et al.*[10,11] reported the first observation of infrared multiphoton dissociation of HCl^+ in intense ultrashort laser pulse and attributed the fragmentation to the charge-resonance of molecular ion. Recently, Talepour *et al.*[12] studied the fragmentation of ethylene in an intense femtosecond laser pulse and proposed that the fragmentation of molecular ion is the result of multiphoton ionization of the inner-valence electron.

Zewail *et al.*[13] measured the photodissociation time of cycloketones using femtosecond time-resolved method and found the photodissociation behavior to be non-RRKM (Rice-Ramsperger-Kassel-Marcus). In this letter, we will concentrate on the dissociation dynamics of cyclopentanone and cyclohexanone also by femtosecond laser pulses but with much higher laser intensities.

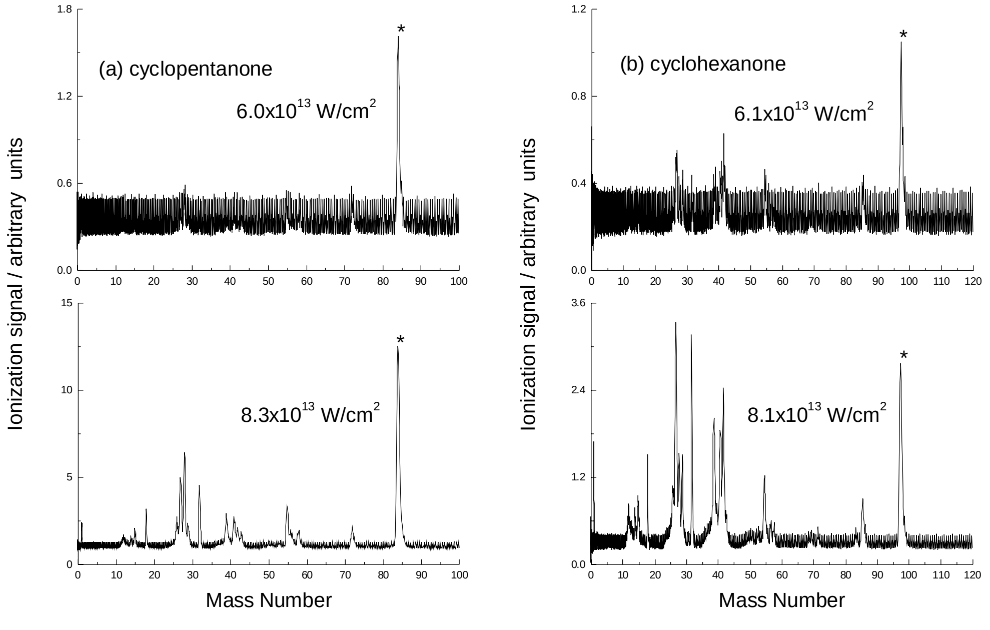
Experimental

A home-built mode-locked femtosecond Ti:Sapphire oscillator is pumped by an all-lines Beamlok argon ion laser (Spectra Physics). The 800 nm, 30 fs oscillator pulse is stretched and then led to a multipass Ti:Sapphire amplifier (Odin) as a seeding pulse, which is pumped by the second harmonic of a Nd:YLF laser (Quantronix DPH-527) operating at 1K Hertz. The amplified pulse is compressed to 50 fs. The laser beam was focused by a lens with f=150 mm and led into a chamber of a linear time of flight mass spectrometer. The laser intensity varied from 5.0×10^{13} W/cm^2 to 13.0×10^{13} W/cm^2 through an aperture in this experiment. The gaseous sample was continuously effused into the chamber through a Φ=230 μm orifice. The ions produced by the interaction of laser field and molecules were accelerated by a two-stage ion electric field and then went through a 50 cm free flight path. A dual micro channel plate (MCP) was used to detect the ions. The signals were acquired through a 100M Hz high-speed transient recorder (USTC) and then transferred to a PC-586 computer for storage and analysis.

Results and Discussion

Figure 1 (a) and (b) show the mass spectra of cyclopentanone and cyclohexanone at two typical intensities. The threshold ionization intensity for detecting ion signal is 5.3×10^{13} for cyclopentanone and 6.1×10^{13} for cyclohexanone. At lower laser intensities, the parent ions dominate for both molecules. At higher laser intensities, these molecules dissociate to copious amounts of fragment ions.

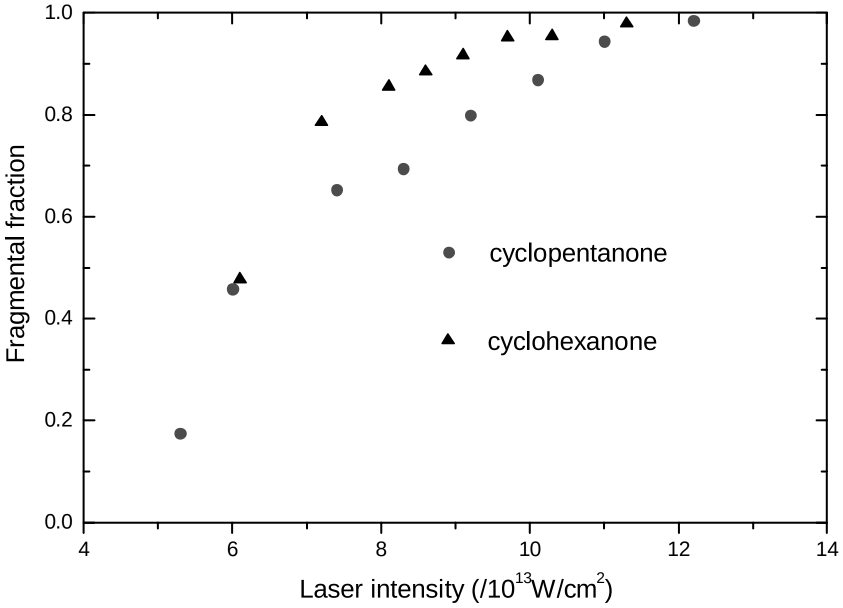
Figure 1 Time-of-flight mass spectra of (a) cyclopentanone, (b)cyclohexanone induced by 50fs laser pulse at 800nm. The asterisk represents the parent ion.



The ratio of total fragment ions to total ions is expressed by fragmental fraction. **Figure 2** plots the fragmental fraction *versus* laser intensity. It can be seen that the fragmental fraction increases with increasing laser intensity. For instance, the fragmental fraction is 13.6% at 5.3×10^{13} W/cm^2 and 94.6% at 12.1×10^{13} W/cm^2 for cyclopentanone. While in the case of cyclohexanone, the fragmental fraction is 47.6% at 6.1×10^{13} W/cm^2 and 97.8% at 11.3×10^{13} W/cm^2.

Because of the high laser intensity ($>5.0\times10^{13}$W/cm^2), the optical pumping rate is higher than the dissociation rate of the neutral molecule. Besides, the dissociating time is much longer than the laser pulse width. In the present case, the dissociation times are 125 fs for cyclopentanone and 180 fs for cyclohexanone[13], much longer than the laser pulse width (50 fs). Thus, the neutral fragments cannot be further ionized within the same laser pulse. The fragment ions we observed, therefore, should be produced through the fragmentation of parent ions.

Figure 2 The ratio of total fragment ions to total ions *versus* laser intensities for cyclopentanone (circle) and cyclohexanone (up triangle)



It also can be seen from **Figure 2** that the fragmentation increases with increasing molecular size at the same laser intensity. For instance, the fragmental fraction is 65.6% for cyclopentanone and 85.5% for cyclohexanone at intensity of about 8.2×10^{13} W/cm^2. This fragmentation pattern is quite different from that of thermal decomposition. In the thermal decomposition, a larger molecule should have less fragmentation because of rapid internal energy redistribution. Cyclohexanone is therefore expected to suffer less fragmentation than cyclopentanone if assuming equivalent excitation energy. But we observed more fragmentation for cyclohexanone than cyclopentanone. The result implies that the fragmentation of these cycloketone ions was non-statistical or cyclohexanone deposited more energy than cyclopentanone. Certainly, further evidences are needed. To clearly understand the fragmentation mechanism of cycloketone parent ions in an intense femtosecond laser field, some theoretical analysis is being carried out in our laboratory.

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References

1. H. S. Kilic, K. W. D. Ledingham, C. Kosmidis, *et al.*, *J.Phys.Chem.*, *A* **1997**, *101*, 817.
2. M. J. Dewitt, D. W. Peters, R. J. Levis, *Chem. Phys.*, **1997**, *218*, 211.
3. K. F. Willey, C. L. Brummel, N. Winograd, *Chem.Phys.Lett.*, **1997**, *267*, 359.
4. M. J. Dewitt, R. J. Levis, *Phys.Rev.Lett.*, **1998**, *81*, 5101.
5. M. J. Dewitt, R. J. Levis, *J.Chem.Phys.*, **1999**, *10*, 11368.
6. K. W. D. Ledingham, D. J. Smith, R. P. Singhal, *et al.*, *J.Phys.Chem.*, A **1999**, *103*, 2952.
7. M. Castillejo, S. Couris, E. Koudoumas, M. Martin, *Chem.Phys,Lett.*, **1999**, *308*, 373.
8. R. P. Singhal, H. S. Kilic, K. W. D. Ledingham, *et al.*, *Chem.Phys.Lett.*, **1998**, *292*, 643.
9. G. R. Kumar, D. Mathur, *Chem.Phys.Lett.*, **1998**, *292*, 647.
10. P. Dietrich, P. B.Corkum, *J.Chem.Phys.*, **1992**, *97*, 3187.
11. A. Conjusteau, A. D. Bandrauk, P. B. Corkum, *J.Chem.Phys.*, **1997**, *106*, 9095.
12. A. Talebpour, A. D. Bandrauk, J. Yang, S. L. Chin, *Chem.Phys.Lett.*, **1999**, *313*, 789.
13. E. W. G.Diau, J. L. Herek, Z. H. Kim, A. H. Zewail, *Science*, **1998**, *276*, 847.

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