Field Ionization of Aliphatic Ketones by Intense Femtosecond Laser

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Field ionization of acetone, butanone, and 3-pentanone in an intense laser field is experimentally investigated by using a femtosecond laser and a time-of-flight mass spectrometer. Theoretically, the ionization process is treated by using a molecular orbital-based model. The nonbonding P_x electron in the oxygen atom is considered as the most feasibly ionized electron and the x axis as the most feasibly ionized vector. The electrostatic potential is obtained by combining the ab initio potential of the molecule and the external potential. The tunneling probability of the P_x electron through the potential barrier is numerically calculated by the transfer matrix method. The ionization probability is modified by the spatial and temporal corrections for a pulsed laser beam, and the total ion yields can thus be obtained. The calculated laser power dependence of the ion yield agrees well with the experimental data measured in the range of $3.5 \times 10^{13}-1.2 \times 10^{14}$ W/cm^2.

Introduction

The interaction of intense laser radiation with a molecule leads to some new phenomena, such as high harmonics generation,[1−2] above threshold ionization,[3] above threshold dissociation,[4] Coulombic explosion,[5] multiple charged ion formation[6,7] and field ionization.[8−11] Among these phenomena, the field ionization has attracted particular attention in recent years.[12−17]

In 1964, Keldysh[18] first proposed a theoretical model to explain the field ionization for an atom in a strong electrical field. The model considers an electron being trapped in a potential well of an atom. The external field asymmetrically distorts the potential and forms a potential barrier on one side of the atom. The electron can penetrate through the barrier, which leads to the ionization of the atom. The process is called tunneling ionization (TI). Later, Chin et al.[19] found that the barrier height could be lower than the energy of the valence electron if the external laser field is extremely intense. Thus, the valence electron can freely escape over the potential barrier. This ionization process is called barrier suppression ionization (BSI). Both TI and BSI belong to field ionization (FI).

The field ionization of small molecules is originally explained by atom-based theories.[20,21] The coulomb potential with some adjustable parameters is used for calculating the tunneling probability.[22] However, molecules have a variety of geometries, the field ionization of polyatomic molecules cannot be simply treated by atom-based model. But the theoretical study on the field ionization mechanism of polyatomic molecule is poor. Recently, Levis et al. proposed a structure-based model to explain the photoionization of a series of organic molecules with conjugated bonds: benzene, naphthalene, anthracene, and tetracene.[13−16] Using the Wentzel−Kramers−Brillouin (WKB) method, they calculated the field ionization probability. But the WKB approximation is not valid in higher laser intensities.[23] Besides, the structure-based model only deals with highly symmetric molecules.

We propose a molecular orbital-based field ionization model. In principle, using this theoretical model one can calculate the field ionization probability of any molecules in arbitrary high laser intensity. In this orbital-based model, we assume that only the electron in the highest occupied molecular orbit (HOMO) is pulled out from the molecule. We further assume that the electron is drawn out along a vector of the densest distribution of the electron charge. The electrostatic potential along the vector is calculated by the ab initio method. When the laser field applies on the molecule, the electrostatic potential will be distorted and a barrier will be formed on the one side of the potential. The ionization probability is the tunneling efficiency of the electron through the barrier, which can be accurately calculated by the transfer matrix method.[24]

In this paper, we report the results of our study on the photoionization of acetone, butanone and 3-pentanone in intense laser field. The laser intensity dependences of the ion yields are obtained by theoretical calculation and experimental measurement, individually. The theoretical curve, which is derived from the orbital-based model, agrees with the experimental data very well.

Experimental Section

A home-built mode-locked femtosecond Ti:sapphire oscillator is pumped by an all-lines argon ion laser (Spectra Physics, Beamlok). The 800 nm, 30 fs laser pulse is stretched and then led to an amplifier as a seeding pulse. The multipass Ti:sapphire amplifier (Quantronix, Odin) is pumped by the second harmonic of a Nd:YLF laser (Quantronix, DPH-527) operating at 1 K Hz. The amplified pulse is compressed to 50 fs.

The amplified laser beam is focused by a lens with $f = 150$ mm and led into a chamber of a linear time-of-flight mass spectrometer (TOF-MS). The gaseous molecules are continuously effused into the chamber through an orifice with $\Phi = 230$ μm and crossed with the focused laser beam. The ions produced in the laser beam are accelerated by a two-stage electric field and then pass through a 50 cm free flight tube. The extracted voltage is 200V and the accelerated voltage is 900V. A dual microchannel plate (MCP) is used to detect the ions. The signal is acquired by a 100 M Hz high-speed transient recorder and then transferred to a PC-586 computer.

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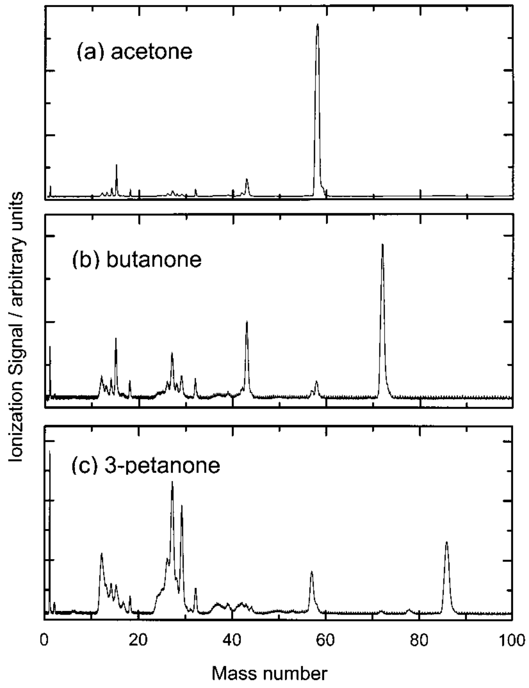

Figure 1. Mass Spectra for (a) acetone, (b) butanone, (c) 3-pentanone induced by 800 nm, 50fs laser pulse at intensity of 9.2×10^{13}W/cm^2.

Results and Discussions

1. The photoionization of three aliphatic ketones: acetone, butanone, and 3-pentanone, are experimentally investigated with the femtosecond laser pulses at 800 nm. Each molecule is studied at eight different laser intensities in the range of 3.5×10^{13}—1.2×10^{14} W/cm^2. The ion signal appears when the laser intensity increases to 4×10^{13} W/cm^2. At low laser intensity, the parent ion dominates. The phenomenon is different from the case of nanosecond laser excitation and ionization, where no parent molecular ion can be detected for all these molecules.[25] Figure 1 shows the mass spectra of acetone, butanone, and 3-pentanone at the laser intensity of 9.2×10^{13} W/cm^2. Only single charged ions are found in the mass spectra. The contribution of the fragmental ions becomes important when the molecular size increases. Because the laser pulse width (50 fs) is shorter than the dissociation time of these aliphatic molecules, which is about a few hundred femtoseconds.[26−28] The fragmental ions thus should originate from the parent ion. The total ions produced in the laser beam, including parent ion and fragmental ions, are therefore taken into account for the ion yield. Figure 2 denotes the logarithm of the measured total ion yield versus the logarithm of the laser intensity.

2. The field ionization probability of the ketones can be theoretically calculated. According to the orbital-based field ionization model, only the electrons in HOMO are ionized by the external field. The photoelectron spectroscopic data show that the nonbonding P_x orbit of the oxygen atom is the HOMO of these ketones. The lowest ionization potential are 9.7, 9.5, and 9.3 eV for acetone, butanone, and 3-pentanone, respectively.

The ionization probability also depends on the orientation of HOMO toward the external field. In gaseous phase, the molecular orientation is randomized. The molecules only with suitable orientation are taken into account for the field ionization. The optimal orientation is that the vector of the electronic charge distribution in HOMO is parallel to the external electric field. For example, the densest charge distribution of the P_x electron in HOMO of acetone lies on the skeleton plane of the heavy atoms and perpendicular to the C═O bond.

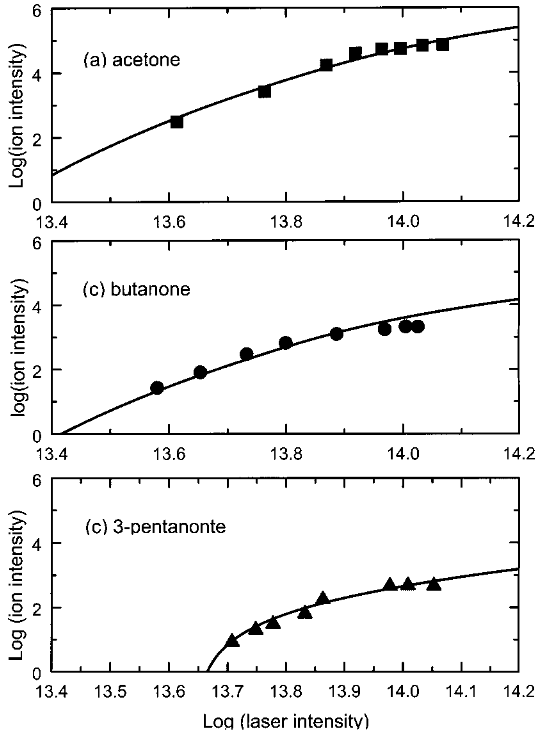

Figure 2. The logarithm of total ion yield versus the logarithm of laser intensity. The solid lines represent the theoretical curves calculated by our field ionization model, the dots represent experimental data.

The electrostatic potential $V(r)$ for the nonbonding P_x electron attracted by the molecular ion along x axis is obtained by an ab initio calculation with Gaussian 94 program at the B3LYP level of the theory using the 6−311 g(d,p) basis set.[29] During the calculation, the geometry of the parent ion is assumed to be the same as the optimized geometry of the neutral molecule.[14] The dot lines in Figure 3 show the ab initio electrostatic potentials $V(r)$ of acetone, butanone and 3-pentanone. When the laser field V_{E} applies on the molecule, the electrostatic potential will be distorted. The external potential can be written as $V_{\mathrm{E}} = -\mathrm{e}\,(\mathrm{r}-\mathrm{r}_0)\,\mathrm{F}$, where F is the laser field strength and r_0 is the origin of the external field. We set the midpoint of the electrostatic potential as the origin of the external field. This is based on the principle that the total energy of the molecule does not change in the external field. The values of r_0 are 0, 0.215, and 0 angstrom for acetone, butanone and 3-pentanone, respectively. The dashed lines in Figure 3 show the external potentials V_{E} at the field intensity of 1.6×10^8 V/cm.

The superposition of the ab initio electrostatic potential $V(r)$ and the external potential V_{E} causes the really distorted potential $V_{\mathrm{D}}(r) = V(r) + V_{\mathrm{E}}(r)$ of the molecule in an intense laser field. The solid lines in Figure 3 show the V_{D} of acetone, butanone, and 3-pentanone. It can be seen that a potential barrier is formed on the right side of each distorted potential.

The electron in HOMO may penetrate the barrier. The tunneling efficiency of the electron through the barrier is the ionization probability. The accurate tunneling probability through a rectangular potential barrier can be accurately obtained by solving Schrodinger equation. Thus, we can approximate the potential barrier with serials of rectangular potential barriers. Because a wave function and its first order derivative are continuous at boundary, the tunneling probability can be numerically calculated. This method is called transfer matrix method.[24] Using this method, we calculate the ionization probabilities of molecules at different laser intensities. The results are shown in Figure 4. It can be seen that the field

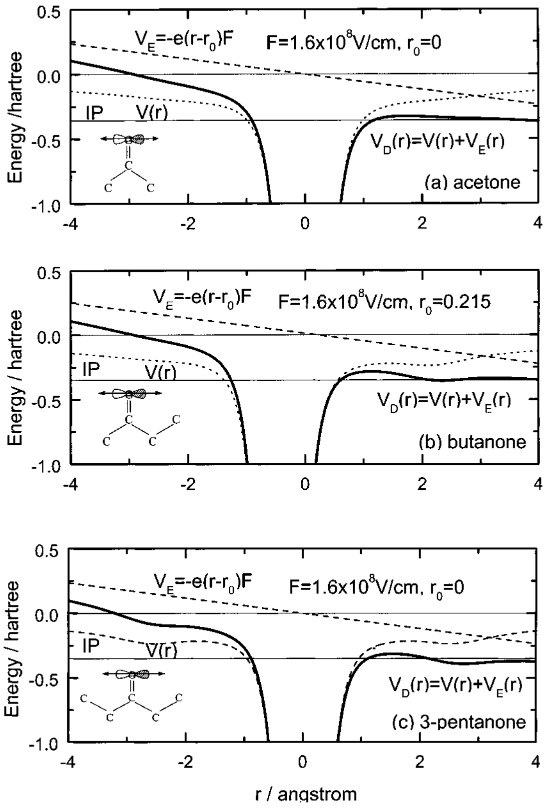

Figure 3. One-dimensional electrostatic potentials of the nonbonding P_x electron in oxygen atom along x orientation for (a) acetone, (b) butanone, and (c) 3-pentanone.

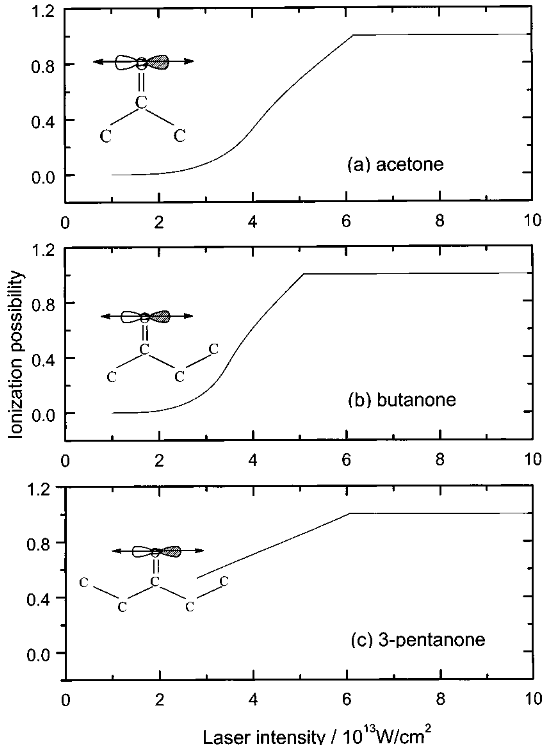

Figure 4. The laser intensity dependence of the ionization probability P for the nonbonding P_x electron in the oxygen atom for (a) acetone, (b) butanone, and (c) 3-pentanone.

ionization begins at laser intensity of 3 × 10^{13}W/cm^2 and increases with the increasing of the laser intensity. In the case of BSI, the trapped electron almost freely escapes from the molecule. The calculated BSI threshold intensities are (6.2, 5.1, and 6.0) × 10^{13}W/cm^2 for acetone, butanone, and 3-pentanone, respectively. In Figure 4, the flat section of the curves reflects the saturation of the ionization. The ion yield continues to increase when the laser intensity further increases. This is due to the increase of the excitation volume.

3. In a focused laser beam, the local field intensity varies with the time t in the pulse duration and the spatial position (r,z) in the beam. Supposing that the temporal distribution of laser intensity is Lorentzian and the spatial distribution is Gaussian, the laser intensity $I(r,z,t)$ can be written as

$$I(r,z,t) = \frac{4E}{\pi^2 T}\cdot\frac{1}{w^2[1 + (z/z_R)^2]}\exp\left(-\frac{2r^2}{w^2[1+(z/z_R)^2]}\right) \quad (1)$$

where E is the energy per pulse, T is the laser pulse width, $2w$ is the diameter of the focal waist, and $z_R = \pi w^2/\lambda$ is the Rayleigh range.

The ion produced in the intense laser field is directly proportional to the integration of probability over the time and space of the laser pulse. The total ion yield in a laser pulse is

$$S = \int_{\text{time}}\int_{\text{space}} P(I)\,\mathrm{d}v\,\mathrm{d}t \quad (2)$$

where $\mathrm{d}v$ is the volume between the isointensity shells of the intensity I and $I + \mathrm{d}I$.

The calculated ion yields at different laser intensities are shown by the solid lines in Figure 2. It can be seen that the theoretical curves fit the experimental data very well. The fact indicates that field ionization dominates under our experimental condition.

In conclusion, both the theoretical calculation and experimental measurement indicate that the field ionization of acetone, butanone, and 3-pentanone takes place at the laser intensities of a few 10^{13}W/cm^2. The laser field distorts the electrostatic potential in the molecule and forms a potential barrier. The field ionization is mainly attributed to the tunneling effect of the electron in HOMO, the nonbonding P_x orbit of the oxygen atom. The P_x electron penetrates through the potential barrier in its longitudinal direction, along the vector of the densest charge distribution. The tunneling probability is calculated by the transfer matrix method. For a specific laser intensity, the total ion yield is obtained by calculating the tunneling probability with the temporal and spatial modifications. The calculated laser power dependence of the ion yield fits the observed relationship in our experiment.

The present study shows that the orbital-based model treats the field ionization of the ketones very well. As the geometry of the ketone molecules is of low symmetry, the orbital-based model may apply to the polyatomic molecules with arbitrary geometry.

The molecular orbital-model is valid in fairly strong laser field (10^{13}–10^{15}W/cm^2), where the external field intensity (10^8–10^9V/cm) is comparable to field felt by the valence electrons. In this case, the electron in HOMO is most feasibly ionized. When the laser intensity further increases, the electrons in the inner shell may be drawn out. Besides, a multiple charged ion is also possibly formed, followed by a Coulomb explosion of the molecular ion.

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