Ionization and Fragmentation of Alkylphenols by 0.8−1.5 μm Femtosecond Laser Pulses

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Ionization and fragmentation were studied on alkylphenols with long alkyl chains (p-(C_6H_4)(OH)(C_nH_{2n+1}), $n = 1,3,5,8,9$) and, for reference, on alkylbenzenes ((C_6H_5)(C_nH_{2n+1}), $n = 1,3,5,7,9$) by intense femtosecond laser pulses, typically with 43 fs duration at 0.8 μm and 140 fs at 1.3 μm in an intensity range of 10^{14} W cm^{-2}. The major products were the corresponding molecular and C_7 fragment ions from the alkylphenols and alkylbenzenes. The molecular ion yields decreased from nearly 1 ($n = 1$) to 0.3−0.5 ($n = 9$) when the carbon number in the alkyl chain increased for both excitation wavelengths. Higher yields of the molecular ions were observed at a longer wavelength of 1.3 μm. The long wavelengths in the range of 1.3−1.5 μm were used to determine whether or not −OH absorption had any increase in fragment ions. No effect was observed by vibrational overtone excitation of the −OH group in this wavelength range. Direct dissociation by cation absorption is the most plausible explanation of the present fragmentation results. Other possible mechanisms were discussed, including a statistical model, an effect of electron rescattering, a multiactive electron model, and dissociation from the superexcited state. In the case of cyclohexane, nonresonant wavelength excitation with a pulse of 1.3 μm (150 fs) effectively suppressed fragmentation more than excitation by a resonant but short-duration pulse (0.8 μm, 15 fs).

Introduction

The formation of intact molecular ions is a distinctive feature in femtosecond ionization. This was demonstrated by DeWitt and Levis in 1995 for some organic molecules with 170 fs, 800 nm pulses having an intensity range of 10^{13} Wcm^{-2}.[1] Ionization by a femtosecond laser pulse is more effective than that by a nanosecond laser pulse.[2−4] This feature is crucial for femtosecond laser mass spectrometry (FLMS).[5,6] However, because some molecules are strongly fragmented, the fragmentation mechanism has been investigated extensively by various parameters of laser pulses: wavelengths,[7−13] pulse durations down to a few cycles,[14−17] and polarization.[12,18−21] Selective bond dissociation or fragmentation has been shown with optimally tailored femtosecond pulses.[22] Since then, the possibilities of controlling bond dissociation have been of high interest.[23,24] Comprehensive feedback loop experiments[25] have been applied to search for fragmentation mechanisms. Selective bond dissociation of biological systems by femtosecond pulse shaping can be crucial for analytical tools in mass spectrometry.[26] Although controls over bond dissociation by tailored pulses have been successful, the mechanisms underlying certain molecular systems remain unclear, including those of benzene derivatives with long alkyl chains. The femtosecond ionization properties of alkylphenols have to be studied, because some of these molecules have been known to be endocrine disruptors.[27]

Several important findings with sub-10 fs-picosecond durations in the range of $10^{12.5-14.5}$ W cm^{-2} infrared pulses are as follows.

(i) When the excitation laser wavelength is resonant with the electronic transition of the cation, fragmentation is violent.[6,7,10−12,28−32] Typical examples are shown using an isomer pair of C_6H_8: 1,3-cyclohexadiene and 1,4-cyclohexadiene.[28] Enhancement of fragmentation by one-photon resonance has been demonstrated at an appropriate delay time using pump−probe femtosecond pulses.[30] Nonadiabatic multiphoton processes in quasi-continuum electronic levels have been proposed.[33]

(ii) Shorter-duration pulses are better for producing an intact molecular ion. Ionization has been studied down to sub-10 fs for cyclohexane, C_{60}, CH_4, etc.[14−16]

(iii) Electron rescattering has various influences on fragmentation.[12,17−20] The enhancement of benzene fragmentation[18] and that of C_nH_{2n+2} ($n = 1,2,3$)[17] have been explained in terms of this mechanism; however, typical organic molecules, such as naphthalene and anthracene, have been reported to make minor contributions.[12,20]

(iv) Excitation pulse durations change fragment patterns significantly, but the chirp directions do not change them significantly. These conclusions have been shown for ethanol[32] and 16 various compounds.[25]

(v) A multiactive electron (MAE) model has been observed at the saturation intensity I_{sat}, which is defined as the intensity leading to 90% ionization of irradiated molecules. I_{sat} is higher for longer-wavelength and/or shorter-duration pulses for the case of decatetraene[8] and C_{60}.[15] Fragmentation of the polyenes was explained in terms of the MAE model.[8]

vi) Raman processes[34] and the effects of white-light laser[35] on fragmentation have been discussed. Superexcited state formation has been found in a high-intensity laser field.[36] The dissociative autoionization process from the superexcited states could control fragment patterns.

Alkylbenzene series of ((C_6H_5)(C_nH_{2n+1}), $n = 1, 2, 3$) were ionized for the first time by 170 fs pulses.[37] In that study, the longer the molecular chain was, the stronger the fragmentation. Those results were tentatively explained in terms of a larger number of dissociation channels to fragments in more complex molecules. We have studied the ionization and fragmentation of alkylphenols with long alkyl chains (p-(C_6H_4)(OH)(C_nH_{2n+1}),

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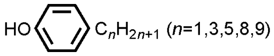
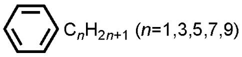
$n = 1,3,5,8,9$; structure1) and, for reference, alkylbenzenes ($(C_6H_5)(C_nH_{2n+1})$, $n = 1,3,5,7,9$, structure 2).



(1)



(2)

In fact, the longer alkyl-chain-substituted molecules show stronger fragmentation for molecules of both series. Finally we found that the fragmentation ratios per total ions seem to converge from 1 to 0.3 or 0.5 around the carbon number of 7−9. Rejecting the initial explanation, we have concluded that the fragmentation for these molecules is mechanism i among the mechanisms outlined above, that is, direct excitation of the cation to a dissociative potential. Other mechanisms, iii-vi, are discussed in relation to EI (electron impact) spectra, statistical rate constants of energized molecules, and so on.

Two experiments were added to support our conclusions. Alkylphenol has overtone absorption due to the −OH group in the wavelength range of 1.3−1.5 μm. We have found that the overtone has no influence on fragmentation. Cyclohexane shows strong fragmentation by femtosecond ionization at a wavelength of 0.8 μm.[38−41] Fragmentation can be considerably suppressed by using a femtosecond pulse with a nonresonant wavelength.

Experimental Section

The details of the femtosecond laser system and time-of-flight mass spectrometry (TOF-MS) have been described elsewhere.[12,20] A Ti:sapphire laser system (Alpha 100/XS, Thales Laser) with a central wavelength of 0.8 μm, a transform-limited pulse of 43 fs, and a repetition rate of 100 Hz was used. The output pulse widths were measured with a single-shot autocorrelator after the pulse passed through equivalent optics composed of neutral density filters, a lens, and a TOF chamber window. The energy was reduced to <500 μJ/pulse. The laser energy was varied using neutral density filters (SIGMA-KOKI). The polarization of the laser pulse was parallel to the TOF axis. Negatively chirped pulses of 100 fs by the Ti:sapphire laser were used to pump an optical parametric generator/amplifier (Quantronix, TOPAS) in order to obtain infrared pulses of 1.3−1.5 μm. Their pulse durations were found to be 140 or 150 fs as measured by a scanning autocorrelator (APE, Pulse Check) after the pulse passed through equivalent optics. Typical energy was 150 μJ/pulse. The polarization of these infrared pulses was orthogonal to the TOF axis. The laser intensity at each wavelength was estimated by measuring the saturation intensity I_{sat} of Xe, the details of which have been described elsewhere.[41−43] The saturation intensity I_{sat} of a molecule was evaluated by plotting the total ion yields, which include the molecular ion, fragment ions, and multiply charged ions, as a function of the logarithm of the laser intensity. I_{sat} is defined as the intersection of the logarithmic laser intensity and the straight line of total ion yield extrapolated back from the high intensity. The errors in these vales are discussed in Results D.

All of the TOF data and spectra were obtained by accumulating 1000 laser shots. Molecular ion intensities were evaluated by a ratio of molecular ion intensity M^+ divided by the total ion (M^+ + fragment ions + multiply charged ions) based on the TOF spectra, and the ratio is denoted as ratio[M^+/total ion]. The error in ratio for *p*-pentylphenol was estimated to be 0.02 or 3% as a standard deviation, assuming that the molecule shows a constant ratio at excitation wavelengths between 1.3−1.5 μm. Errors in the ratios for other molecules can be regarded as being in the same order of magnitude; therefore, they are about the size of the symbols in Figures 2, 4, and 5.

The produced ions were analyzed with a linear TOF mass spectrometer (KNTOF-1800, TOYAMA), which had a total drift length of 1.3 m and a mass resolution of 1000 at $m/z = 132$. Each laser beam was focused into the TOF chamber through a quartz window with a lens ($f = 200$ mm). The lens position was adjusted to produce the highest charge state of the Xe ion. A slit 0.5 mm wide × 10 mm long was located on the extraction electrode to collect the ions produced at the most tightly focused region of the laser beam. The output signals of produced ions from a microchannel plate (MCP) were averaged by a digital oscilloscope (Wave Runner 6100, 1 GHz, LeCroy) typically over 1000 shots. The base pressures of the interaction and the TOF chamber were below 5.0×10^{-7} Pa.

The following were used without further purification: commercial samples of alkylbenzenes, including toluene (Aldrich, anhydrous, 99.8%), propylbenzene (Tokyo Kasei, 99%), pentylbenzene (Aldrich, 99%), heptylbenzene (Tokyo Kasei, 97%), and nonylbenzene (Tokyo Kasei, 97%); and alkylphenols, including *p*-cresol (Tokyo Kasei, 99%), *p*-propylphenol (Tokyo Kasei, 98%), *p*-pentylphenol (Wako Pure Chemical, 99.5%), *p*-octylphenol (Aldrich, 99%), and *p*-nonylphenol (Wako Pure Chemical, 99.3%). The alkylbenzenes and alkylphenols, except for *p*-octylphenol and *p*-nonylphenol, were measured at room temperature. *p*-Octylphenol and *p*-nonylphenol were vaporized by heating at 323 and 343 K, respectively. All samples were introduced to the interaction chamber of the TOF through a needle valve, and the pressure was kept constant at approximately 2.0×10^{-5} Pa in order to avoid a space-charge effect.

Results

A. The Longer the Alkyl Chain Is, The Stronger Is the Fragmentation of Alkylbenzenes at 0.8 μm. Alkylbenzenes ($(C_6H_5)(C_nH_{2n+1})$: $n = 1, 3, 5, 7, 9$) were irradiated with pulses having a duration of 43 fs at a central wavelength of 0.8 μm and at an intensity of 5×10^{13} W cm^{-2}. The dominant ions in the TOF spectra are the intact molecular ions and $C_7H_7^+$ ($m/z = 91$) due to β C−C bond dissociation in all alkylbenzenes, as shown in Figure 1. In the case of $n = 3$, the signal intensity of the molecular ion is higher than that of $C_7H_7^+$, while the signal intensities of $C_7H_7^+$ are higher than those of the molecular ions in $n \geq 5$. The ratios were determined by molecular ion yields divided by total ion yields and are shown in Figure 2. The ratio of molecular ions decreases as the number of carbons in the alkyl chain increases, converging around 0.2. This tendency is in line with that observed in alkylbenzenes $n = 1-3$ by a pulse duration of 170 fs at 0.8 μm[37] and in diphenylalkanes $(C_6H_5)(CH_2)_n(C_6H_5)$: $n = 1-2$ by a pulse duration of 125 fs at 0.8 μm.[44]

B. Alkylphenols at 0.8 and 1.3 μm. Figure 3 shows the TOF mass spectra of alkylphenols (p-$(C_6H_4)(OH)(C_nH_{2n+1})$, $n = 1,3,5,8,9$) irradiated with 140 fs pulses at a central wavelength of 1.3 μm, except for propylphenol, for which 1.38-μm pulses were used. The intact molecular ions and $C_7H_7O^+$ ($m/z = 107$), which is formed by β C−C bond dissociation, are dominantly observed. This tendency is consistent with the alkylbenzene series, that is, fragment yields increase with an increase in the number of carbons in the alkyl chain. The ratios of molecular ion yield to the total ion yield of alkylphenols are shown in Figure 4 for two wavelengths: 0.8 and 1.3 μm. The long-wavelength excitation with 1.3 μm effectively suppresses

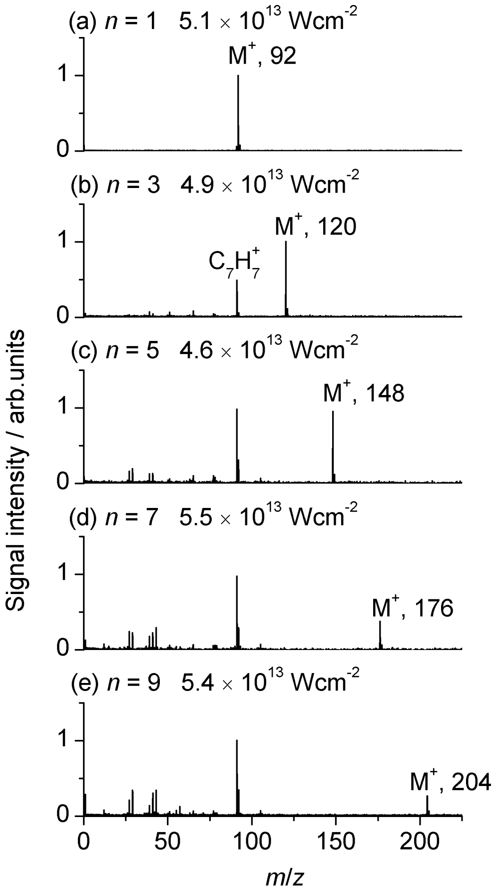


Figure 1. TOF mass spectra of alkylbenzenes irradiated with a 43 fs pulse at 0.8 μm with the intensities indicated in the figures. Shown are (a) $n = 1$, toluene, (b) $n = 3$, propylbenzene, (c) $n = 5$, pentylbenzene, (d) $n = 7$, heptylbenzene, and (e) $n = 9$, nonylbenzene. M^+ is the intact molecular ion and $C_7H_7^+$($m/z = 91$) is the radical ion formed by β C−C bond dissociation.

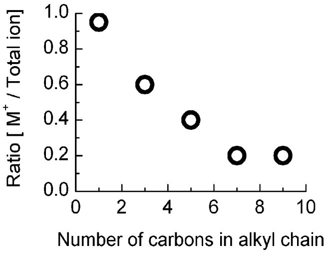


Figure 2. The ratios of molecular ion yield M^+ divided by the total ion yield are plotted vs the number of carbons in the alkyl chain in alkylbenzenes irradiated with a 43 fs pulse at 0.8 μm with an intensity of 5×10^{13} W cm^{-2}.

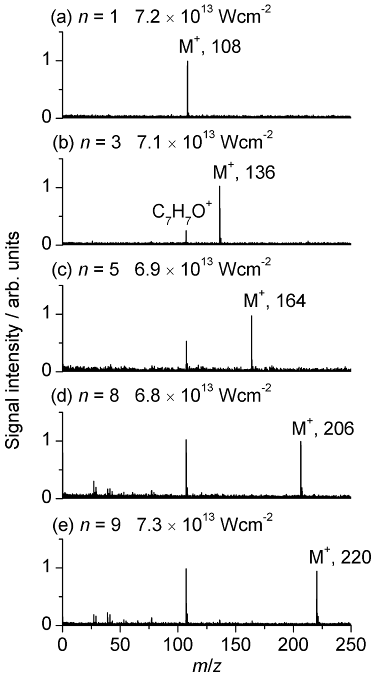


Figure 3. TOF mass spectra of (a) $n = 1$, *p*-cresol, (b) $n = 3$, *p*-propylphenol, (c) $n = 5$, *p*-pentylphenol, (d) $n = 8$, *p*-octylphenol, and (e) $n = 9$, *p*-nonylphenol are shown on irradiation with 140 fs laser pulses at a central wavelength of 1.3 μm, except for *p*-propylphenol of 1.38 μm, with the indicated intensity. M^+ is the intact molecular ion and $C_7H_7O^+$($m/z = 107$) is the radical ion formed by β C−C bond dissociation.

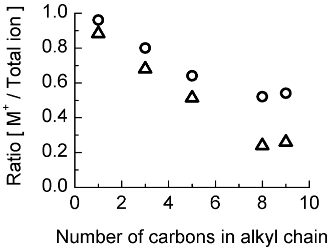


Figure 4. The ratios of molecular ion yield M^+ divided by total ion yield are plotted vs the number of carbons in the alkyl chain in alkylphenols at 1.3 μm (140 fs, 7×10^{13}), denoted by open circles (○) and 0.8 μm (43 fs and an intensity of 4×10^{13}), denoted by triangles (Δ).

fragmentation more than that with 0.8 μm. The ratios at 1.3 μm are twice those at 0.8 μm for *p*-octylphenol and *p*-nonylphenol.

C. No Influence on Fragmentation by IR Absorption. A molecule has weak IR absorptions by the overtones of a neutral molecule. The peak at 1.43 μm in the absorption spectra of *p*-pentylphenol in benzene solution can be assigned to the overtone of the −OH group, because this peak disappears in *n*-pentylbenzene. *p*-Pentylphenol was ionized with pulses in a wavelength range of 1.3−1.5 μm. The ratio of molecular ion yield to total ion yield at I_{sat} was constant, as shown in Figure 5. The absorption spectra of −OH in *p*-pentylphenol are not the same as those in the gas phase and/or of the cation. However, the wavelength widths of the excitation laser pulses of 45 nm would cover the overtone somewhere in the range of 1.3−1.5 μm.

D. MAE Behavior in Wavelength and Chain-Length Dependence on I_{sat}. I_{sat} is defined as the intensity at which 90% of irradiated molecules become ionized.[41] The I_{sat} values of alkylphenols at 0.8 μm (pulse duration of 43 fs) and 1.3 μm (140 fs) are shown in Figure 6a. As shown in Figure 6b−e for example, the I_{sat} values including Xe were evaluated by plotting the total ion yields, which include the molecular ions, fragment ions, and multiply charged ions, as a function of the logarithm of the laser intensity. I_{sat} is defined as the intersection of the logarithmic laser intensity and the straight line of the total ion yield extrapolated back from the high intensity.[41] Because the slopes of the straight lines include some arbitrariness, the errors in I_{sat} values in Figure 6a would be ∓10% of the central values. The present results for the I_{sat} values at 0.8 μm can be reasonably put on the correlation curves with organic polyatomic molecules.[42,43] The ionization potentials are known to be 8.17 eV (*p*-methylphenol), 8.14 eV (*p*-ethylphenol), and 8.09 eV (*p*-propylphenol).[45]

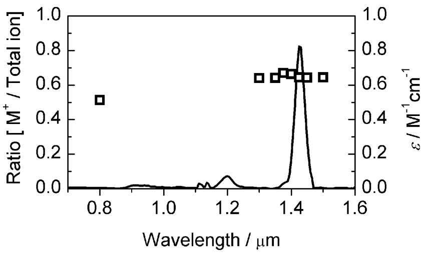


Figure 5. The ratios of molecular ion yield divided by total ion yield of *p*-pentylphenol in the wavelength region of 1.3−1.5 μm, where the −OH overtone absorption is expected. The open squares (□) indicate the central wavelengths of the excitation pulses. The excitation laser intensities were kept at I_{sat} values (at 0.8 μm 4×10^{13} W cm^{-2}, 1.3−1.5 μm 9×10^{13} W cm^{-2}). The solid line is the absorption spectrum of *p*-pentylphenol in benzene with a molar extinction scale on the right vertical axis.

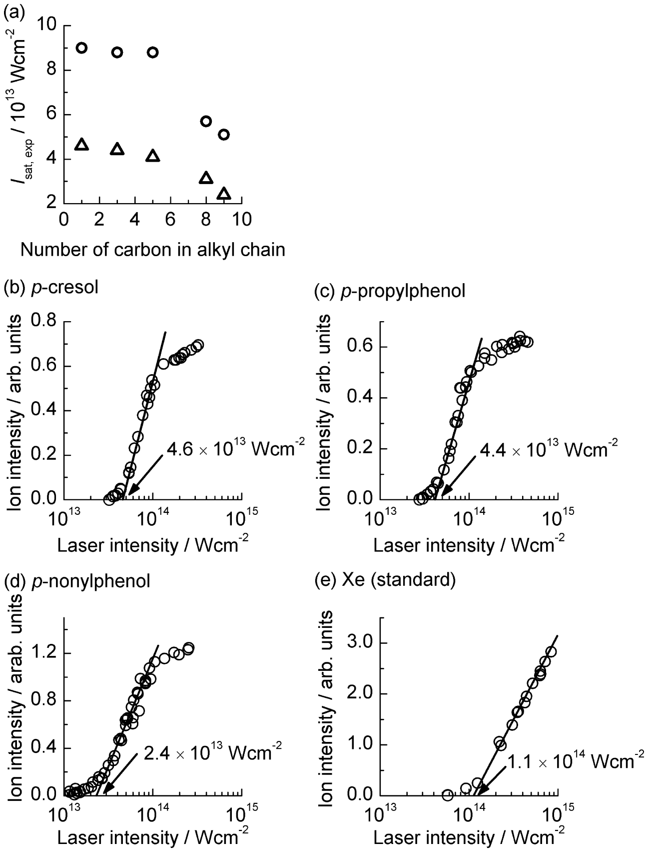


Figure 6. (a) I_{sat} values are plotted vs the number of carbons in the alkyl chain in alkylphenols. Open circles (○) are for 1.3 μm (140 fs) and triangles (Δ) are for 0.8 μm (43 fs). (b−e) Ion intensities for 0.8 μm excitation are plotted vs laser intensities on a log scale. (b) I_{sat} of 4.6×10^{13} W cm^{-2} for *p*-cresol (number of carbons in alkyl chain, $n = 1$), (c) 4.4×10^{13} W cm^{-2} for *p*-propylphenol ($n = 3$), (d) 2.4×10^{13} W cm^{-2} for *p*-nonylphenol ($n = 9$), and (e) 1.1×10^{14} W cm^{-2} for Xe, which is used as the standard value.

I_{sat} values at 0.8 μm are about half of those at 1.3 μm. This indicates that alkylphenols are easier to ionize at 0.8 μm than at 1.3 μm. At either of these irradiation wavelengths, I_{sat} values decrease as the length of the alkyl chain increases. The dependence of I_{sat} on wavelength would reflect MAE behavior, which has been proposed and studied in detail for polyenes and discussed in relation to the fragmentation.[8]

Discussion

We have demonstrated that molecular ions with shorter alkyl chains have higher yields for both alkylbenzenes and alkylphenols. For alkylphenols, fragmentation at 1.3 μm was weaker than that at 0.8 μm and was almost the same in the wavelength region of 1.3−1.5 μm for *p*-pentylphenol. We here discuss the energy acquisition processes leading to dissociation. Among the possible processes, the most likely ones would be cation formation by field ionization followed by absorption of femtosecond pulse energy through the cation electronic levels. A plausible mechanism to explain the present results is direct dissociation by electronic excitation of cations into repulsive electronic levels.

A. Cation Absorption Followed by Dissociation. The cation-absorption mechanism followed by dissociation has successfully been applied to many systems: benzene,[7] cyclohexadiene isomers,[28] 2,3-dimethyl-1,3-butadiene,[11] dibenzofuran,[6] anthracene,[11] naphthalene,[12] metal carbonyl compounds $M(CO)_5$,[10] and cycloketones.[29] The cation absorption at an excitation laser wavelength gives rise to strong fragmentation. On the other hand, nonresonance with the cation electronic levels leaves an intact molecular ion except for halogenated compounds.[6] Pearson et al. have shown that molecular fragmentation is driven by ultrafast dynamic ionic resonances using pump−probe femtosecond pulses.[30] In some halomethanes, the ionic potentials in the bound state after initial strong-field ionization are transferred to the dissociative state, leading to bond dissociation effectively by one-photon resonance at an appropriate delay time.

The cation electronic levels of organic molecules have been discussed based on the absorption spectra in a low-temperature matrix, photoelectron spectra, and laser-induced fluorescence studies.[46−48] Alkylbenzene cations presumably have electronic states in the visible region, corresponding to the C ← X transition of the benzene cation. The transitions appear in the energy range of 1.5−3 eV above the ionization potential and shift to lower energy as the alkyl substitution grows.[49,50] As a result, the threshold wavelengths in photodissociation spectrometry of alkylbenzene cations shift from 620 nm for toluene to 750 nm for *n*-butylbenzene, and beyond 1 μm for cyclohexyl benzene.[50] The toluene cation absorbs wavelengths far from the excitation pulse wavelength of 0.8 μm, so the molecular ion is dominant. For $(C_6H_5)(C_nH_{2n+1})$, $n \geq 5$ fs excitation wavelength (fwhm 30 nm) would have an overlap with the cation photodissociation spectra. This trend could be the same for alkylphenol. The fragmentation results suggest that the longer the alkyl chain is, the stronger is the resonance between the laser wavelength and the electronic levels of the cations. The electronic states would be merged in a quasi-continuum in a strong laser field, as suggested by a "doorway transition" mechanism proposed by Markevitch et al.[33] The present results suggest that the same resonance behavior remains in the continuum states.

The photodissociation spectra of alkylbenzene cations,[50] and recent experiments by ultrafast dynamic ionic resonances using pump−probe femtosecond pulses,[30] have shown that one-photon resonance from the cations leads to the dissociation. The energy acquisition processes leading to fragmentation are not necessarily one-photon absorption, and naturally include nonlinear processes. Multiphoton absorption and stimulated Raman excitation could create electronically and vibrationally excited states of the cations, because the laser intensities of $4-9 \times 10^{13}$ W cm^{-2} were high enough to induce these nonlinear excitation processes, though we do not have clear evidence.

B. Dominant Fragments of $C_7H_7^+$ ($m/z = 91$) and $C_7H_7O^+$ (107), and the Statistical Model. The strongest signals among the fragments in the present femtosecond ionization were $C_7H_7^+$

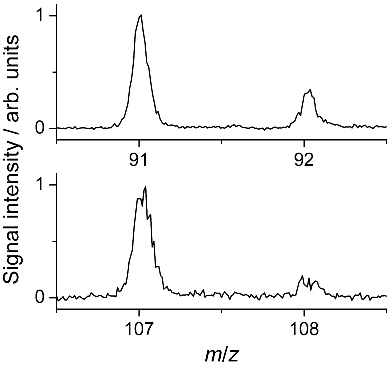


Figure 7. $C_7H_7^+$ (m/z = 91), $C_7H_8^+$ (92) for *n*-nonylbenzene in the upper spectrum and $C_7H_7O^+$ (107) and $C_7H_8O^+$ (108) for *n*-nonylphenol in the lower spectrum are shown by the expanded scales of Figure 1e and Figure 3e, respectively.

(m/z = 91), as shown in Figure 7, which are produced by the β C−C bond dissociation. These results coincide with the photodissociation of ionized alkylbenzenes with medium-sized alkyl chains[50] and are different from the electron impact (EI) spectra. The EI spectra sometimes accompany strong signals of $C_7H_8^+$ (m/z = 92) fragments produced by the McLafferty rearrangement.[51] The ratio of $C_7H_7^+$ (91)/$C_7H_8^+$ (92) has been used as a sensitive probe for internal (excess) energy transferred to an ion by a given excitation technique, where the internal energies are thought to be vibrational. As the number n in $(C_6H_5)(C_nH_{2n+1})$ increases, $C_7H_8^+$ (92) signals grow, exceeding those of $C_7H_7^+$ (91) at n = 9 in the 70 eV EI spectra.[52] The femtosecond results are different from the EI spectra results. It is clear that $C_7H_7^+$(91) at n = 9 is much higher than the ion with a mass number of 92 in Figure 7. This trend would be the same for the alkylphenols, although photodissociation of the cations and reference EI data are limited. The $C_7H_7^+$ (91)/$C_7H_8^+$ (92) ratio for the alkylbenzenes corresponds to that of $C_7H_7O^+$ (107)/$C_7H_8{}^+O$ (108) for the alkylphenols. In fact, the products of $C_7H_7O^+$ (107) due to β C−C bond dissociation, which is a typical photocleavage, always give an intensity higher than that of $C_7H_8{}^+O$ (108). For an example, the mass spectrum of nonylphenol is shown in Figure 7.

C_2 dissociation from C_{60} in nanosecond duration pulse excitation has been explained in terms of a statistical model.[53] The statistical model can explain recent CH_4 ionization and dissociation in femtosecond fields.[54] Vibrational energy in the cation is accumulated by linear or nonlinear processes; concurrently vibrational energy is redistributed and the cation finally reaches a highly vibrationally excited state. The dissociation rate constant k of the ion can be expressed by the RRKM formulation:

$$k = \sigma \frac{W}{h\rho} \tag{3}$$

where k is the cation's fragmentation rate after an intense laser field, W is the number of channels open to dissociation, h is the Planck constant, ρ is the density of the state, and σ is the reaction degeneracy.[54] With a larger ion, the molecular ion ratio should be higher by virtue of the slower rate of fragmentation according to the statistical reaction rate theory. In our observation of fragmentation, the tendency was clearly reversed. Molecular ions likely dissociate before distributing absorbed enegy into the many vibrational modes, indicating direct dissociation in the case of the present femtosecond experiments.

C. Electron Rescattering Does Not Explain the Present Results. Electron rescattering has been known to produce fragments and nonsequentially doubly charged ions in benzene,[18] C_{60},[19] alcohols,[21] alkanes,[17] and naphthalene.[12] In the case of anthracene, electron rescattering induced much less fragmentation than that induced by resonant excitation of the cation transition.[20] The present femtosecond fragmentation cannot be explained in terms of rescattering. We compared the results between the two wavelengths. The maximum rescattering energy RE_{max} is known to be 3.17 times the ponderomotive potential. RE_{max} is 9.5 eV in the case of alkylbenzenes at 0.8 μm with an intensity of 5×10^{13} W cm^{-2}, while RE_{max} = 35 eV for alkylphenols at 1.3 μm with an intensity of 7×10^{13} W cm^{-2}. As we have seen in Figure 4, molecular ion yields were higher for the cases of 1.3 μm femtosecond pulse excitation, although the recollision energy at 1.3 μm is 3.7 times higher than that at 0.8 μm. At 1.3 μm excitation, the ratio of the molecular ion of alkylphenol was 0.5 at n = 8, 9, while it was 0.2 for alkylphenol at 0.8 μm. The fact that molecular ion yields are higher at higher electron recollision energy cannot be reconciled with the model of dominant fragmentation induced by electron recollision.

The laser intensities chosen were those at which almost the same intensities of the total ions were detected experimentally for both wavelengths. The typical intensities were 5×10^{13} W cm^{-2} at 0.8 μm and 7×10^{13} W cm^{-2} at 1.3 μm. Keldysh parameters are 1.16 at 0.8 μm with 5×10^{13} W cm^{-2} and 0.60 at 1.3 μm with 7×10^{13} W cm^{-2} assuming IP of 8.0 eV. These values indicate that the present experiments were done around the borders of tunneling or multiphoton ionizations. A lower value of γ at the long wavelength of 1.3 μm indicates that ions are produced with higher probability by tunneling ionization. We do not know whether the ionic species are produced via tunneling or multiphoton processes.

D. MAE Behavior Exists and the Cation Resonance Leading to Dissociation Is Still Effective. MAE behavior can be seen in the I_{sat} values. I_{sat} is known to be lower for shorter-wavelength and/or shorter-duration pulses for the case of decatetraene[8] and for that of C_{60}.[15] Similar tendencies can be seen in the saturation intensities I_{sat}: the 0.8 μm (43 fs duration pulse) values are about 50% of the 1.3 μm (140 fs) results. MAE behavior in molecules with nonconjugated but saturated hydrocarbon chains could be due to the π electrons in the benzene ring. In fact, the ratios of I_{sat} at 0.8 μm/I_{sat} at 1.3 μm are about 0.5 and do not depend on the alkyl chain lengths. The stronger fragmentation of molecules with longer alkyl chain cannot be explained in terms of MAE behavior.

Femtosecond fragmentation of polyene series (hexatriene, decatetraene, cyclooctatetraene, and β-carotene) was explained in terms of MAE behavior.[8] It is notable that the resonance effect between the excitation wavelength and the cation electronic levels can also explain the results of fragmentation for large polyenes.[10,55] The dominant ions of hexatriene and decatetraene at 1.45 μm (40 fs) are intact molecular ions, whereas β-carotene shows strong fragmentation. Hexatriene and decatetraene cations have no electronic level at 1.45 μm,[46] but β-carotene has actually the first electronic transition around this wavelength region[56] and has transitions in the visible region.[57] Decatetraene has an electronic level at 0.7 μm[46] and shows strong fragmentation. On the other hand, cyclooctatetraene has a slight absorption in the low-temperature matrix,[46,47] which could correspond to no absorption in the gas phase at 0.7 μm and thus would show molecular ion formation. The resonance between laser wavelength and cation electronic level in the polyene series can still be a good indicator that fragmentation has occurred.

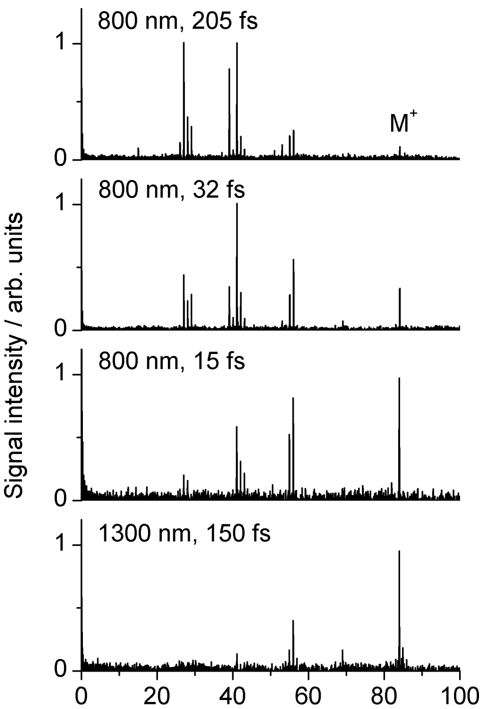


Figure 8. TOF mass spectra of cyclohexane at an intensity of 4.0 × 10^{13} W cm^{-2} are shown. Shorter-duration pulses show less fragmentation at 0.8 μm. Excitation by a pulse with a duration of 150 fs at 1.3 μm produces the intact molecular ion (M^+) more efficiently than those by the short wavelength of 0.8 μm.

E. Superexcited States Could Be Involved. Another possibility is fragmentation from superexcited states, though our observations present no evidence to either support or dismiss the involvement of superexcited states. Recently, methane fragmentation to CH in a femtosecond intense laser field was interpreted in terms of superexcited states.[36] Among this state's many decay channels, two channels related to the present experiments are picked up in the next scheme.[58]

$$A^{**} \rightarrow A^+ + e^- \quad (4)$$

$$\rightarrow B^+ + C + e^- \quad (5)$$

A** is a superexcited state reached by a femtosecond pulse. The channel 4 is called autoionization and forms an intact molecular ion A^+. The 5 channel is called a dissociative photoionization channel or dissociative auto ionization, producing fragment ions B^+ and C. The ratio of 4/(4 + 5) could be in agreement with our observations.

F. Comments on Nonresonance Condition vs Short Pulse. There are two clear influences on the suppression of fragmentation: excitations by short-duration pulses with several cycles and by nonresonant wavelengths with 50−200 fs duration. The two parameters were compared in the same laboratory using cyclohexane ionization, as shown in Figure 8. Cyclohexane has been studied extensively,[14,38−41] and its molecular ion intensity is stronger at the shorter-duration pulse down to 15 fs at 0.8 μm.[14] The cyclohexane cation in the low-temperature matrix has an absorption around 0.5 μm, extending to an excitation wavelength of 0.8 μm, and has no absorption at a wavelength of 1.3 μm.[59] The TOF spectra at a nonresonant wavelength of 1.3 μm with a duration of 150 fs suppressed the degree of fragmentation better than it did with short-duration pulses at 0.8 μm.

Conclusions

We have demonstrated higher yields of molecular ions with shorter alkyl chains for both alkylbenzenes and alkylphenols. Less fragmentation was observed with longer-wavelength excitation for alkylphenols. The fragmentation would be induced by the absorption of femtosecond pulse energy through the electronic levels of the cations into repulsive electronic levels.

Many other fragmentation mechanisms have been proposed. We adopted the mechanism of cation resonance leading to dissociation. Effects on fragmentation by the electron rescattering were not clearly observed; furthermore, the fragment distributions are different from EI spectra. Dissociation of an energized ion based on the statistical model does not reproduce the present results from the standpoint of the alkyl chain-length effect. MAE behavior was observed in the saturated intensities, but MAE may not be necessary to explain fragmentation. Formation of superexcited states followed by dissociative autoionization could be another candidate to explain the alkyl chain effect.

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