Ionization and Fragmentation of Some Chlorinated Compounds and Dibenzo-*p*-dioxin with an Intense Femtosecond Laser Pulse at 800 nm

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We detected parent and fragment ions from 14 chlorinated and a few fluorinated compounds as well as dibenzo-*p*-dioxin (dioxin) in intense laser fields. The irradiation pulse had an intensity from 1×10^{13} to 1×10^{15} W cm^{-2}, with a 130-fs pulse duration at a central wavelength of 800 nm. Irradiation at this intensity led to a singly ionized species and a small amount of atomic ions, indicating the onset of Coulomb explosions. We have previously reported finding a key factor in determining the parent and/or fragment ion formations of organic hydrocarbons with an intense femtosecond laser pulse [Harada, H.; et al. *Chem. Phys. Lett.* **2001**, *342*, 563−570]. This key factor is a requirement for parent ion predominance if the excitation laser wavelength and the absorption spectra of the target cation are in nonresonance, and vice versa. Use of this factor has been found to be effective for molecules other than hexachlorobutadiene. The threshold intensities I_{sat} at the infinity ionization rate were determined and are reasonably comparable to those of previously reported hydrocarbons.

Introduction

Parent ion formation with little fragmentation has been observed in response to intense laser pulse excitation for some aromatic molecules; in other words, many molecules behave like atoms, bypassing fragmentation pathways.[1] These characteristic features should be of great advantage, allowing femtosecond laser mass spectrometry (FLMS) to be used as a means of carrying out sensitive analytical mass spectrometry.[2] Comparative studies of femto- and nanosecond pulses have shown the advantages of femtosecond ionization.[3−5] Ledingham and co-workers have studied a number of polyaromatic hydrocarbons (PAHs) and nitro-PAHs to develop FLMS.[6−12] FLMS and related trials have been carried out with various molecules, including metal carbonyls and biomolecules.[13,14] Many persistent organic pollutants are chlorinated compounds. It is therefore important to examine whether chloro compounds produce parent ions. Pentachlorobenzene cation has been preliminarily detected by femtosecond pulse excitation.[15] Dissociative ionization of halogenated ethylenes has recently been studied.[16] In this paper we extended the study of ionization and fragmentation to 14 chlorinated compounds, three fluorinated benzenes, two fluorochlorobenzenes, and dibenzo-*p*-dioxin (dioxin) in a high-intensity femtosecond laser field.

With regard to analytical applications, a method of resonance-enhanced multiphoton ionization (REMPI) with a tunable laser pulse has been effective for the detection of trace quantities of organic compounds. Isomers of polychlorodioxins and polychlorobenzenes have been separately detected by REMPI; however, the number of chlorine atoms in these molecules has been limited thus far to less than four.[17,18] It is important, however, to detect molecules containing 4−6 chlorine atoms because some of them are highly toxic. Pentachlorobenzene levels have been known to correlate with the concentrations of toxic equivalent dioxin in the stack gas of a hazardous waste incinerator.[17] It is therefore important to determine whether FLMS can be useful in the detection of polychlorinated compounds.

In our previous study, we concluded that the resonance between the laser wavelength and the electronic energy levels of parent cations is a key factor in the formation of fragment ions during femtosecond laser excitation. If a molecular cation has no resonance at the laser wavelength, both the parent ion and multiply charged ions are observed.[19] Parent ion formation, however, has recently been reported in the case of some polyaromatic hydrocarbons of anthracene, tetracene, pentacene, etc., even though the cation absorptions are resonant with the excitation wavelength.[10] These findings indicate that we should examine the fragmentation of other molecules and discuss in detail the related mechanisms of fragmentation.

The intensity dependencies of excitation laser pulses against ion intensities give I_{sat}, with an ionization probability of 1.0 being expected at the irradiation volume. The I_{sat} was defined by Hankin et al.,[20,21] who have studied in detail the ionization mechanisms of organic molecules. The I_{sat} values in this study showed a good correlation with previously reported values, indicating that the ionization mechanism is not significantly different from that for rare gases.

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Experimental Section

The apparatus and experimental method used in the present study have been described elsewhere.[22,23] An outline is provided below. The maximum output energy from a Ti:sapphire laser system was 500 mJ per pulse of 130-fs duration, with a central wavelength of 800 nm and a repetition rate of 10 Hz. The laser intensity was reduced, and the pulse energy in this experiment was lower than 4 mJ per pulse. Pulse widths were monitored with a rapid-scanning autocorrelator. The energy fluctuation was typically ±15% in 1σ. The laser beam was focused with a 200-mm lens. The ion species were recorded using a reflectron time-of-flight (TOF) mass spectrometer (Jordan D-850) with the stated resolution of 4000 under cold beam conditions. The spectrometer was placed parallel to the electric field of the linearly polarized laser beam, and the aperture diameter of the entrance was 12 mm. The vacuum chamber was evacuated down to 2×10^{-6} Pa, and the sample was introduced through a pulse valve (General Valve Co., Ltd.). The pressure in the chamber was kept to a level of 4×10^{-5} Pa. The TOF data were recorded by a digital oscilloscope (LeCroy LT344).

The detection efficiency would be down to 80% for the heaviest mass in this paper, 272, on the basis of the detailed study on the sensitivity.[24] The ions were accelerated to 4 kV, and the voltage applied to the MCP was 2.1 kV. This discrimination would change I_{sat}, but it was not discernible according to our replots, taking into account the supposed sensitivity.

Aperture size and position are important, as pointed out by Ledingham and co-workers[10,25] and by research groups studying atoms and simple molecules.[26] We were aware that atomic ion intensities increased with decreases in the aperture diameter.[27] The atomic ions probably came from Coulomb explosion and would have kinetic energy of about 15 eV, which was reported for the case of C^+ at Coulomb explosion of benzene.[22] The atomic ions' intensities were not large, and the values of I_{sat} were the same within experimental error for the cases of 12- and 1-mm apertures.

The irradiation intensity was estimated on the basis of the detection of Xe^{n+}, the formation of which has been used as an intensity reference.[21] Hankin et al. proposed a clear definition of the irradiation intensity, defining I_{sat} as an intensity that is the threshold of the barrier suppression ionization.[21] From the plots of Xe ion intensity vs log I (laser intensity), I_{sat} can be derived as the crossing point with the log I axis. The I_{sat} of Xe has been reported to be 1.12×10^{14} W cm^{-2}. Our preceding estimation[19] was 1.6 times higher than that; in other words, it should be divided by 1.6 to allow direct comparison with the present results. All intensities in this study were newly normalized on the basis of the I_{sat} of Xe. The spot size was measured by a CCD camera to be 60 μm in diameter at an intensity of $1/e^2$ and at a 0.1-mJ pulse. This reduction may be due in part to nonlinear absorption losses in the transmission of the lens and window. The laser system was designed so that the B integral was smaller than 1.5, and it was supported by interferometer measurement of the wave front of the output beam. The contrast ratio between the femtosecond pulse and amplified spontaneous emission was in the range of 10^{-8}. The pulses that occurred in a time range greater than 1 ns before or after were less than 10^{-7} of the main pulse.[23]

The absorption spectra of some cations were newly measured in n-butyl chloride at 77 K by γ-ray radiolysis.[28] The absorption spectra of the 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorophenol cations were newly recorded. The chemicals were used as received from Aldrich, Nacalai, Wako, and Tokyo Kasei.

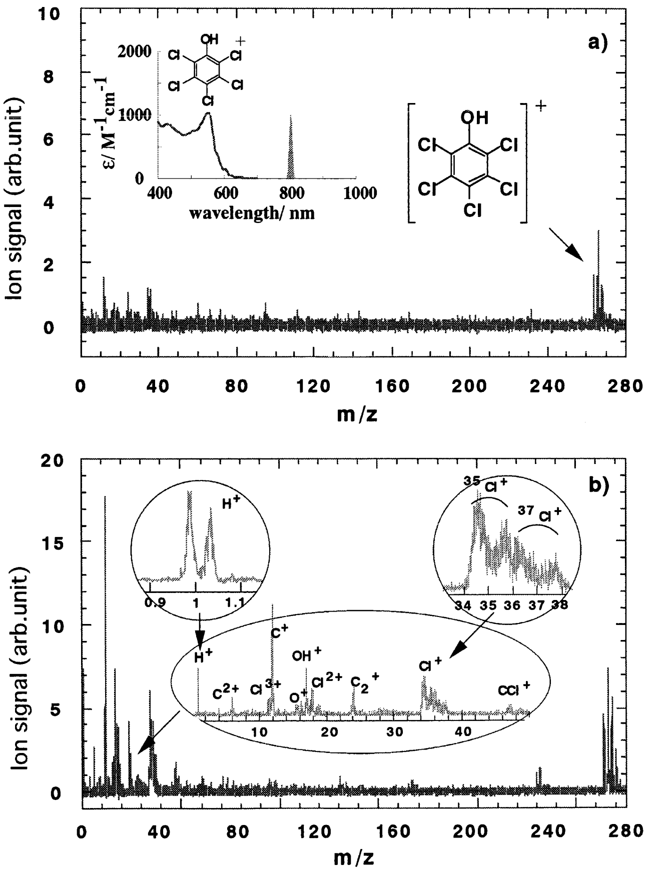


Figure 1. TOF mass spectra of pentachlorophenol at 800 nm with a 130-fs pulse at irradiation intensities of (a) 0.35×10^{14} and (b) 0.75×10^{14} W cm^{-2}. The absorption of the cation in a low-temperature matrix and the laser spectrum of the excitation pulse are indicated in the upper part (a). The pentachlorophenol cation is not in resonance with the laser wavelength, resulting in a high yield of parent ion formation. (b) Expanded mass spectra in the region of mass numbers less than 40. Coulomb explosions are indicated from the split signals of H^+ and Cl^+.

Results

A. Pentachlorophenol as a Typical Example of Femtosecond Ionization of Chloro Compounds. The TOF mass spectra of pentachlorophenol at irradiation intensities of 0.35 $\times 10^{14}$ and 0.75×10^{14} W cm^{-2} are shown in Figure 1, along with the absorption spectrum of the cation. The absorption spectra of the cation radical were measured by γ-radiolysis. The pentachlorophenol cation has no absorption resonance with an excitation wavelength of 800 nm; therefore, the parent dominant spectra were expected, on the basis of our finding that a parent ion will be dominant if the excitation wavelength has no resonance with the cation absorption.[19]

It should be noted that the signals around 266 mass number correspond to the parent ion in Figure 1. Figure 2 shows the spectra on an expanded scale, and it can clearly be seen that these mass peaks represent the natural isotope distribution of chlorine. The atomic ion signals of C^+, C^{2+}, Cl^+, and Cl^{2+} can be seen in the high-intensity spectra in Figure 1b. These atomic and doubly charged ions suggest that the laser intensity has already reached a level where Coulomb explosions have set in. Actually, the peaks of Cl^+, Cl^{2+}, H^+, and O^+ have split into double peaks, two of which can be seen in Figure 1b. Even in the low-intensity spectra at an average power of 0.35×10^{14}

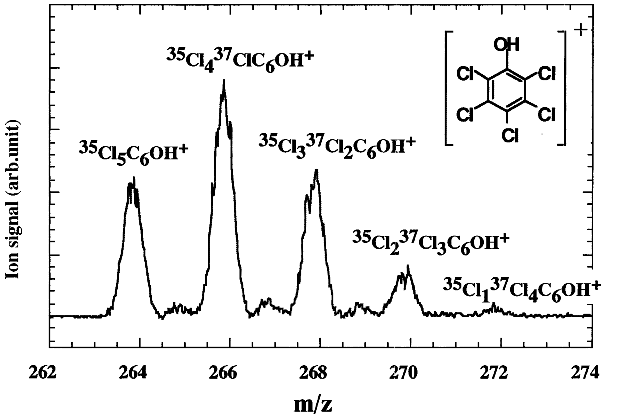


Figure 2. Isotopically separated spectrum in the region of the parent mass of pentachlorophenol ion observed at 1.4 × 10^{14} W cm^{-2}.

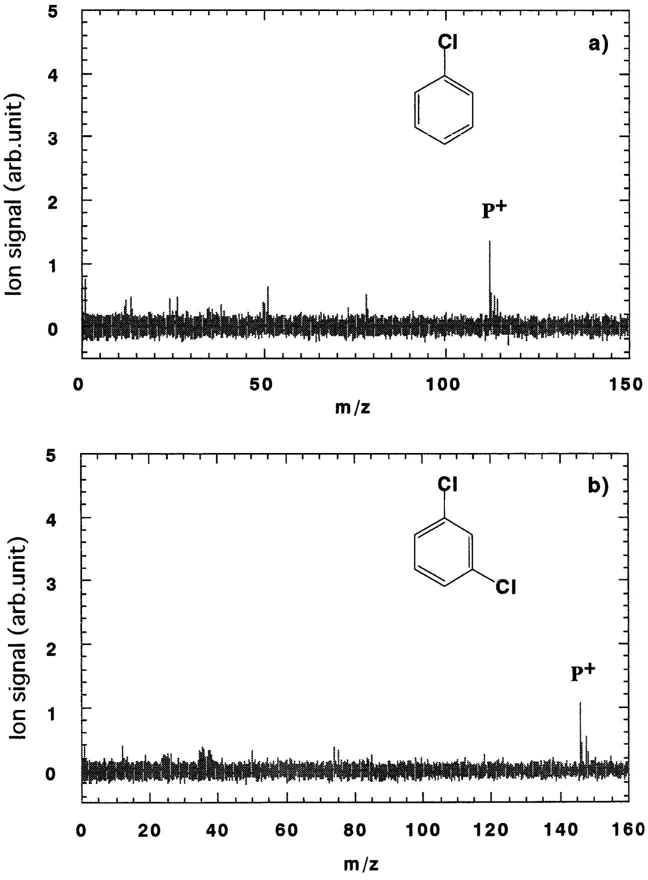


Figure 3. TOF mass spectra of (a) chlorobenzene and (b) 1,3-dichlorobenzene at 800 nm with a 130-fs pulse at irradiation intensities of 0.32 × 10^{14} W cm^{-2}.

W cm^{-2}, split Cl^+ ion peaks can be seen in Figure 1a. These results indicate that the threshold intensities of ionization and Coulomb explosion are close.

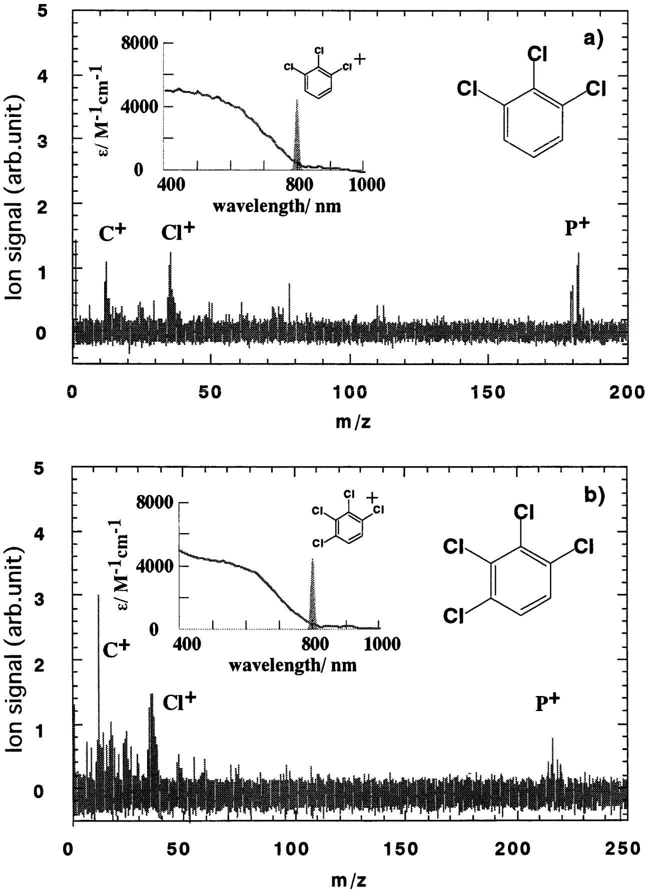


Figure 4. TOF mass spectra of (a) 1,2,3-trichlorobenzene and (b) 1,2,3,4-tetrachlorobenzene at 800 nm with a 130-fs pulse at irradiation intensities of 0.36 × 10^{14} W cm^{-2}, with the absorption spectra of the cation in a low-temperature matrix and the excitation laser spectrum. With increases in the number of chlorine atoms, the degree of parent ion dominance decreases.

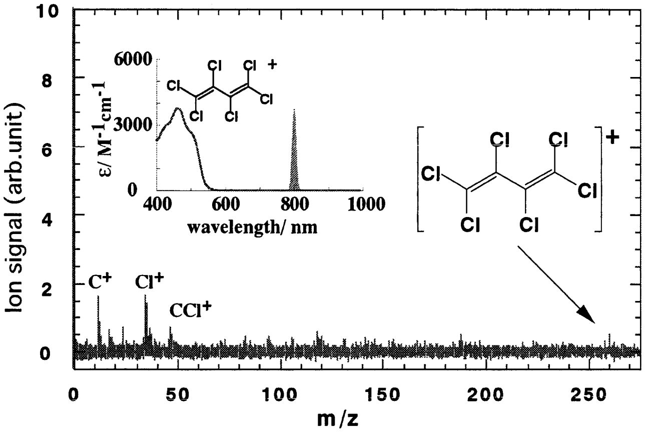


Figure 5. TOF mass spectra of hexachlorobutadiene at 800 nm with a 130-fs pulse at an irradiation intensity of 0.39 × 10^{14} W cm^{-2}, with the absorption spectrum of the cation. Although there is no overlap with the laser wavelength, no parent ion was detected.

B. Halogenated Compounds and Dibenzo-*p*-dioxin. Some of the results are shown in Figures 3−6 and are summarized in Table 1. The structured parent ion peaks represent the natural isotope distribution of the chlorine atom. Cation spectra of some chlorinated compounds were examined to determine whether the excitation laser wavelength of 800 nm, with a spectral width of about 10 nm, is in resonance. The $\tilde{B}^+ \leftarrow \tilde{X}^+$ electronic transition develops in the UV and visible range up to the longest wavelength of the 0−0 transition. The 0−0 transition of chlorobenzene is at 548.9 nm in the gas phase.[29] The 0−0 transition of 1,3-dichlorobenzene in the gas phase is at 532.8 nm,[30] and that of 1,3,5-trichlorobenzene is at 649.4 nm.[31] Photoelectron spectra of some chlorobenzenes are available[32] with a low-energy resolution, but the whole $\tilde{B}^+ \leftarrow \tilde{X}^+$ transition can be estimated.

Absorption spectra can be obtained by the methods of γ-ray radiolysis and VUV photolysis, although there are matrix shifts. The red shifts are several tens of nanometers; the 0−0 transition is from 649.4 nm for 1,3,5-trichlorobenzene in the gas phase to 690 nm in solid Ar[33] and beyond 700 nm in halogenated

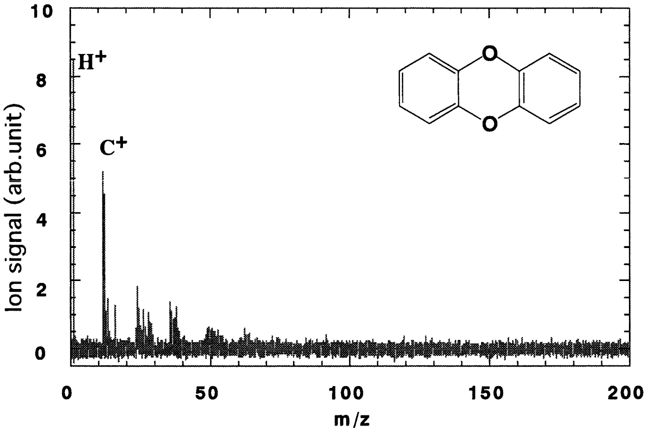


Figure 6. TOF mass spectra of dioxin at 800 nm with a 130-fs pulse at an irradiation intensity of 0.33 × 10^{14} W cm^{-2}. Complete fragmentation with no parent ion suggests that this cation has an absorption at the laser wavelength.

TABLE 1: I_{sat}, Ionization Potential, and Fragmentation Degree

molecule	IP (eV)[a]	I_{sat} ($\times 10^{14}$ W cm^{-2}) this work	I_{sat} ($\times 10^{14}$ W cm^{-2}) ref 19	P/F[c]
dibenzo-*p*-dioxin	7.598	>1.0		F
1,3-cyclohexadiene[b]	8.25	>0.53	0.66	P
1,4-cyclohexadiene[b]	8.82	>0.81	0.81	F
chlorobenzene	9.07	1.2		P
1,4-dichlorobenzene	8.92	1.1		F
1,2-dichlorobenzene	9.06	1.2		I
1,3-dichlorobenzene	9.10	>0.80		P
1,2,4-trichlorobenzene	9.04	1.2		F
1,2,3-trichlorobenzene	9.18	1.4		I
1,2,4,5-tetrachlorobenzene	9.0	>0.62		I
1,2,3,4-tetrachlorobenzene	8.9			F
1,2,3,5-tetrachlorobenzene	9.02	>0.93		I
pentachlorobenzene	8.8	1.1		I
pentachlorophenol		0.81		P
1,4-difluorobenzene	9.16	1.7		P
pentafluorobenzene	9.63	1.6		P
hexafluorobenzene	9.90	>1.2		P
o-chlorofluorobenzene	9.18	1.2		I
chloropentafluorobenzene	9.72	1.6		I
1,3-dichlorotetrafluorobenzene		>1.6		P
hexachloro-1,3-butadiene		1.4		F
tetrachloromethane	11.47	>1.0		F
xenon	12.13	1.12	1.12	

[a] NIST Standard Reference Database No. 69- July 2001 Release, WebBook http://webbook.nist.gov/chemistry/ [b] Obtained from Figure 3 in Harada's paper,[19] and the laser intensity in the paper was divided by 1.6. [c] P, parent dominance (parent ion >40% of the total ion intensities); F, fragments dominance (<5%) at 0.35 × 10^{14} W cm^{-2}; and I, intermediate between P and F.

solvents.[34] The cation spectra of 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorophenol were measured by the method of γ-ray irradiation in the work described in this paper. They are shown with mass spectra in Figures 1 and 4. We can conclude that they are not in resonance with the laser wavelength, taking into account the matrix shifts. The key factor for the parent ion dominance works for chlorobenzenes.

The TOF patterns of fluorinated benzenes (1,4-difluorobenzene and hexafluorobenzene) are simple, and the peaks are assignable to the parents. The ion spectra[35] are far from the resonance. Some chlorofluorobenzenes' cation spectra have been studied[36] and also show nonresonance.

On the basis of comparison of their TOF spectra with those of hydrocarbons and fluorinated benzenes, the chlorinated molecules are more easily fragmented. One reason for this phenomenon would be that the cation has a low-lying dissociative potential above the ground electronic level of the cation.[27] Hexachloro-1,3-butadiene showed a small intensity for the parent ion, as shown in Figure 5, though the absorption spectrum of the cation has no overlap with the laser wavelength. Mass spectra of dibenzo-*p*-dioxin showed heavy fragmentation, as shown in Figure 6, suggesting that this cation has an absorption at the laser wavelength. We may need to change the irradiation wavelengths to apply FLMS to the detection of dioxins.

The fragmentation degrees of TOF mass spectra on these halogenated compounds are classified in Table 1, where P indicates parent dominance (parent ion >40% of the total ion intensities), F indicates fragment dominance (<5%) at 0.35 × 10^{14} W cm^{-2}, and I indicates intermediate between P and F.

C. Laser-Power Dependence of Parent and Fragment Ion Intensities. The parent ion has a slope of 5−7 for a log−log plot of the ion yield vs laser intensity, as can be seen in Figure 7 for pentachlorophenol, when a molecule shows parent dominance. The slope is reduced to 1.5−2.0 around 10^{14} W cm^{-2}. In the case of molecules showing heavy fragmentation, atomic ions have a slope of 5−7, as shown in Figure 8, while the parent ions have a slope of 2. In the high-energy range above 10^{14} W cm^{-2}, the slopes for both systems are reduced to 1.5−2.0. These two typical characteristics are commonly observed.[19]

The ionization potential of pentachlorobenzene is 9.2 eV, and the ponderomotive potential at 0.5× 10^{14} W cm^{-2} is 3.0 eV; therefore, the expected slope of the ionization is 8 at 1.55 eV (800 nm) if the mechanism is nonresonance multiphoton ionization. The observed value of the slope of 6−7 was a little smaller than expected, probably because fragmentation processes are included. If the fragmentation is included in the ion signal, the slope could be reduced to a small value, as shown for the case of hexachlorobutadiene in Figure 8. The degree of resonance with the cation absorption is so high that the cation is efficiently consumed. The rate-determining step for atomic ion formation is not cation formation. In the high-intensity range with a slope of 1.5−2.0, different ionization processes are taking place. The most probable phenomenon is the Coulomb explosion; in fact, the split signals of atomic ions appear, as shown Figure 2b. A volume effect has been known by use of a large aperture. If a large aperture compared with the Rayleigh range is used, ionization products occurring via different mechanisms can be included, and the slop would become small.[25,26]

D. I_{sat} and the Ionization Mechanism. Hankin et al. have demonstrated a new procedure for evaluating well-defined saturation intensities, I_{sat}, applicable to organic molecules.[21] The saturation intensity is defined as the irradiation intensity at which the ionization rate suddenly becomes infinity. The I_{sat} corresponds to the threshold intensity of the barrier suppression ionization (BSI) model in an optical electric field. Figure 7 shows plots to determine I_{sat} of 0.81 × 10^{14} W cm^{-2} by summing up signals of species of P^+, Cl^+, and C^+. We followed Hankin's method, in which the C_n^+ signals are summed while those of H^+ are not used. Similarly, we did not take into account minor O^+ and H^+ signals. In fact, these signals were small, and the possibility of contamination from water in the chamber could be excluded. The detection efficiency for the heaviest mass would be down to 80% on the basis of the sensitivity given in the literature[24] and the present conditions. This discrimination effect on the value I_{sat} was small; therefore, these values are listed in Table 1 without any sensitivity corrections. They are close to those reported by Hankin et al., indicating that the ionization mechanism is similar to that of other organic molecules. I_{sat} values of 1,3- and 1,4-cyclohexadienes have been

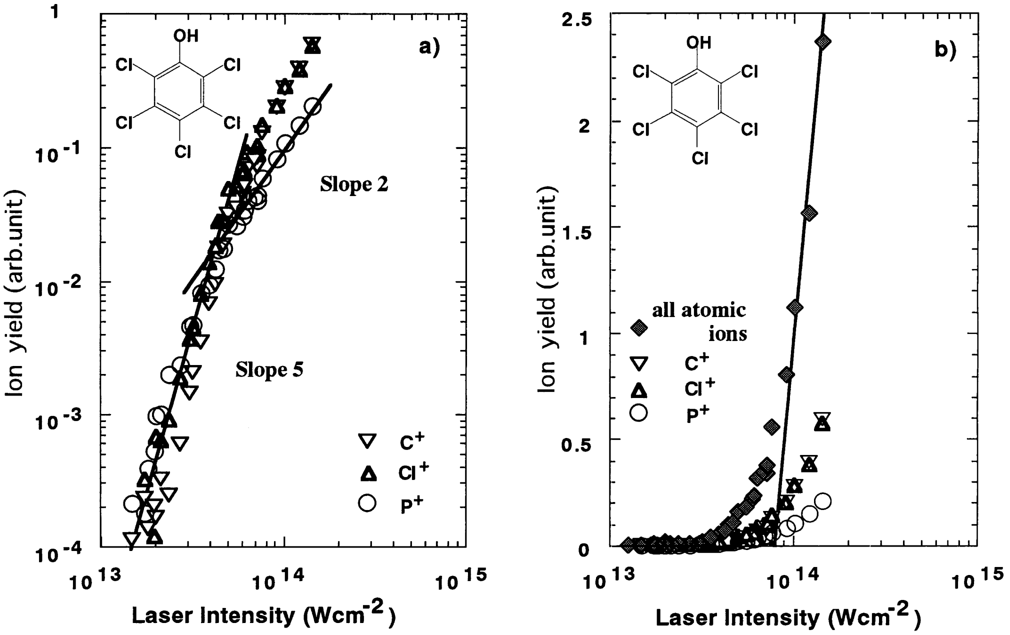


Figure 7. Intensity dependence of ion signals from major fragments in the femtosecond ionization mass spectra of pentachlorophenol. (a) log−log plot for the parent ion (P^+), singly charged chloride ion (Cl^+), and singly charged carbon ion (C^+). (b) Hankin's plots (see text) obtained by summing the three species P^+, Cl^+, and C^+ vs the laser intensity. An I_{sat} of 0.81 × 10^{14} W cm^{-2} was determined as the crossing point of the asymptote line with the horizontal axis.

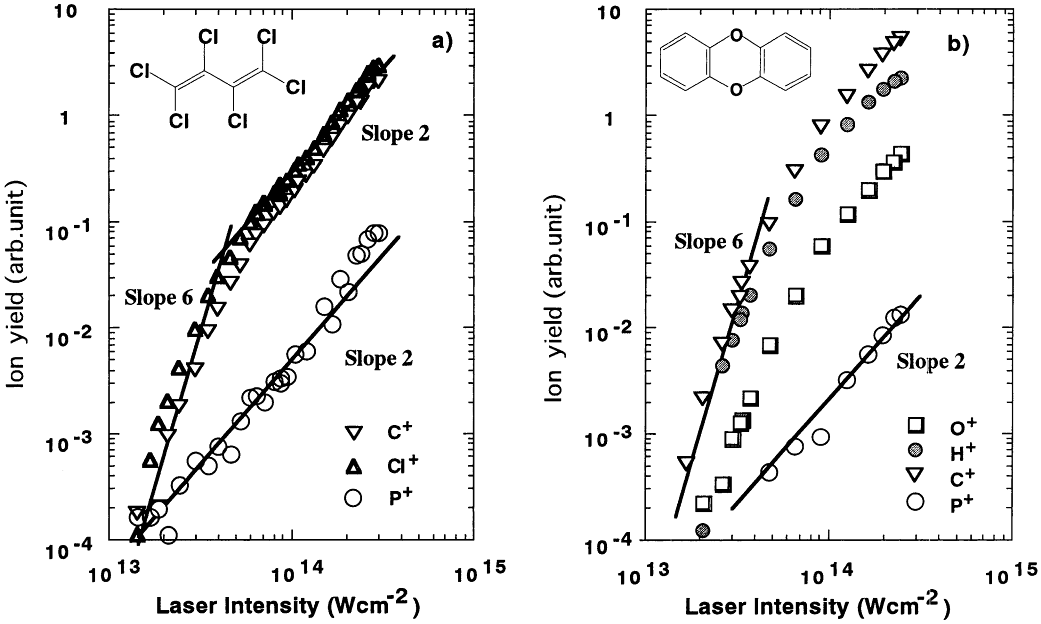


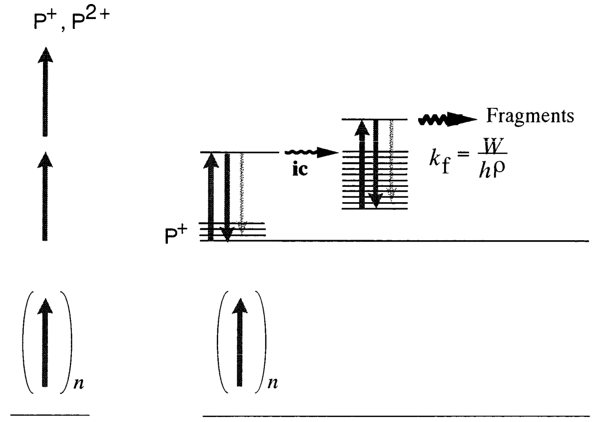
Figure 8. Intensity dependence of ion signals of major fragments in the femtosecond ionization mass spectra of (a) hexachlorobutadiene and (b) dioxin.

reported by Hankin et al.,[21] and the present values were deduced from those in our previous report.[19] They are in agreement with those of Hankin et al. We conclude that halogenated compounds are not very different from hydrocarbons on the basis of the I_{sat} values. The onset intensity of the Coulomb explosion, I_{Coul}, was estimated to be not much higher than I_{sat}, as atomic ions that have shown split signals can be seen around the I_{sat}.

The I_{sat} values in this paper are reasonably scattered around the hydrocarbon data measured by Hankin et al. These results indicate that the ionization mechanism of the halogenated compounds treated here is the same as that for hydrocarbons. The ionization mechanism is explained in terms of the multiphoton ionization in the intensity region lower than I_{sat}, and ADK theory, which is applied to rare gases, is effective just above I_{sat}.

Discussion

A. Validating the Key Factor of Nonresonance. The key factor which has been applied to hydrocarbons was found to be valid for the halogenated compounds examined in the present study, as well. It was found, however, that halogenated compounds are more easily fragmented than hydrocarbons. Figure 9 explains the mechanisms of ionization and fragmentation in intense laser fields. Under nonresonant conditions, in Figure 9a, parent ion formation will be dominant if there is nonresonance between the laser wavelength and the electronic energy levels of the parent cations. At a high excitation intensity, a multiply charged cation is produced, finally inducing a Coulomb explosion. In the case of Figure 9b, fragmentation is dominant if the electronic energy levels of the parent cations



(a) No-resonance Parent Ion (b) Resonance Fragmentation

Figure 9. Mechanisms of ionization and parent ion formation by nonresonant multiphoton ionization. (a) Parent ion formation will be dominant, giving a multiply charged cation and finally leading to the Coulomb explosion, if the excitation on, iwavelength is off-resonant with the electronic absorption of parent cations. (b) Fragmentation will be dominant if the excitation wavelength is resonant with the electronic absorption of parent cations. Induced absorption and emissions take place simultaneously in an intensity region of $10^{13}-10^{14}$ W cm^{-2}. Laser energy will accumulate in the molecule via induced processes. An efficient nonradiative transition to the electronic ground state of the cation also occurs. Intramolecular redistribution occurs, and a vibrationally excited ion (hot ion) forms. The laser light can be resonant with the electronic level of the hot cation. The internal energy eventually increases to far above the dissociation energy. The vibrationally excited ion undergoes dissociation at a statistical rate. If there is a low-lying dissociation channel, the ions dissociate immediately.

are resonant with the laser wavelength. Induced absorption and emissions take place simultaneously in an intensity region of $10^{13}-10^{14}$ W cm^{-2}. The potential surfaces of the coupled states can be deformed through induced absorption and emissions; in other words, there is a formation of light-dressed states. This deformation would enhance nonradiative transitions to the ground electronic state of the cation. Ordinarily, aromatic cations exhibit very fast nonradiative decay. Intramolecular redistribution occurs within a few vibration periods, and a hot ion forms. The vibrationally excited ion will show similar absorption spectra but a broadened shape. The spectrum shape of a hot molecule formed by internal conversion has been well-explained for the case of polyatomic neutral molecules such as benzene.[37] The laser light can resonate with the absorption spectra of the hot cation after internal conversion. Within the femtosecond pulse, these processes repeatedly occur, and excitation energy is accumulated in the hot ion, eventually resulting in the internal energy being far higher than the dissociation energy. The extremely vibrationally excited ion undergoes dissociation at a statistical rate. A cation undergoes a prompt dissociation if it has a low-lying dissociation channel just above the electronic ground state of the cations. Discussions based on resonance between the cation absorption and excitation wavelengths in intense laser fields have appeared in the literature of this group,[19,27] for the case of benzene,[38] and for the case of aniline decomposition to $C_5H_6^+$ + HNC and its suppression of decomposition by forming hydrogen-bonded clusters.[39] Ionization of hexatriene[40] and the metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ can occur by laser pulses 110 and 50 fs in length at wavelengths of 0.8 and 1.35 μm.[41]

We should note the similarity to and difference from the multiphoton ionization scheme which has been established for the case of nanosecond laser excitation.[42] The fragmentation mechanism has been called a "ladder-switching model". A difference is the occurrence of efficient induced absorption and emissions under an intensity region of $10^{13}-10^{14}$ W cm^{-2}. Although the processes enhance accumulation of the internal energy, femtosecond excitation reduces the accumulation.

B. Comments on Polyaromatic Hydrocarbons (PAHs): a Larger Ion Size Corresponds to a Slower Fragmentation Rate. In fact, Markevich et al. have observed very weak parent signals from anthracene and tetracene.[43] According to the present authors' criterion, the PAHs should be fragmented because the absorption coefficients of the cations at the excitation laser wavelengths are high enough to induce fragmentation. Important and different results were published by Robson et al., who found that a parent ion forms from PAHs in intense laser fields for very similar laser and detection systems.[10,11] Parent ion formation has an essential advantage for FLMS; this difference, however, must be explained. Robson et al. suggested that this difference would be due to differences in excitation beam qualities as well as in the magnitude of the ion-extraction volume of the mass spectrometer.[10] The beam qualities could be related to differences of *B* integrals, pre-pulse, amplified spontaneous emission, and pulse shape and length.

Multiply ionized fullerene ions $C_{60}{}^{q+}$ ($q = 1-6$) have been observed in response to intense femtosecond pulse irradiation.[44-47] We should recall that the cation absorption of C_{60} has a large molar extinction coefficient of 2700 M^{-1} cm^{-1} at an excitation wavelength of 800 nm.[48] C_{60} is fragmentated to C_{60-2n} through nC_2-loss reactions in response to nanosecond pulse excitation.[49] The C_{60} cation has a strong absorption at the representative excitation wavelength of 532 nm, with a molar extinction coefficient of 5400 M^{-1} cm^{-1},[40] and the fragmentation mechanism can be categorized as corresponding to the so-called ladder-switching model.[42] Wurz and Lykke have estimated the dissociation rate constant of $C_{60}{}^+$ using eq 1, described below.[49] The rate of unimolecular decay of C_{60} has been calculated to be on the order of 10^6 s^{-1} using activation energies of 4.6−5.6 eV. The internal energy is approximately 4000 kJ mol^{-1}. A strong reason for the parent ion formation by femtosecond laser excitation would be a dissociation rate much slower than 10^6 s^{-1}. The formation of $C_{60}{}^{q+}$ implies that the internal energy in the femtosecond pulses is far below 4000 kJ mol^{-1}.

According to a statistical reaction rate theory, a larger ion size slows the fragmentation rate. We can estimate the order of the typical bond-breaking rate by a statistical theory. The dissociation rate can be evaluated by using the following equation:

$$k_f = W/h\rho \qquad (1)$$

where k_f is the fragmentation rate of the cation in an intense laser field, W is the number of channels open to dissociation, h is the Planck constant, and ρ is the state.[50]

The decay rate of benzene cation has been investigated in great detail.[51] The internal energy of benzene cation is sharply defined in the two laser pump−pump experiments. The actual decay reactions are composed of the H loss and C loss channels. The rate is 10^6 s^{-1} at 510 kJ mol^{-1}. The acceleration time in the TOF was approximately 1 μs for benzene in the present system. We know that the benzene ion is heavily fragmented at the resonance condition at 375 or 400 nm.[2,38,52] At these wavelengths, the molar extinction coefficient of the benzene cation is 950 M^{-1} cm^{-1}.[53] Because the benzene cation is completely fragmented under resonance conditions in a femtosecond laser field, the accumulated energy can be estimated to be much larger than 510 kJ mol^{-1} at 400-nm excitation. Benzene fragmentation requires an internal energy of more than

510 kJ mol^{-1}; on the other hand, this energy can be said to be far below 4000 kJ/mol in the case of C_{60} parent ion formation.

PAHs can be intermediate cases between benzene and C_{60}. Larger PAHs will have a slower dissociation rate, and eventually a PAH cation can survive. The efficiency of the accumulated internal energy in the PAH cation would increase with a long excitation pulse width, a high level of pre- and/or postpulses, and a higher B integral.

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