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**Studies on Chlorinated Benzene Derivative Ions by
Resonance Enhanced Multiphoton Ionization and
Electron Attachment Measurements**

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I. Introduction

1. Preface

Some of chlorinated benzene derivatives are known for their toxicity as carcinogenic substances or endocrine disruptors¹ though they had been used for herbicides and insecticides, and also known as by-products in the chemical industry in the past. Recently, chlorinated phenols are likely to be a precursor of polychlorinated dibenzo-p-dioxins (PCDD) in the incinerators through the dimerization reaction. Because those phenols should be regarded as an index of PCDD, it is necessary to develop an effective analytical system for chlorinated phenols. Therefore, the sufficient knowledge about physical and chemical properties of the material should be required for chemical analysis. In this thesis, two kinds of experimental approaches, the resonance enhanced multiphoton ionization (REMPI) technique and negative chemical ionization (NCI) method, were used to study the character of chlorinated benzene derivatives. In addition to these methods, mass spectrometry was used for the detection. The fragmentation mechanism and the analytical efficiency of these methods were also discussed.

2. REMPI-TOF spectrum measurement

The schematic energy diagram for the RE2PI measurement is drawn in Fig. I-1. When the photon energy is resonant to the energy difference between the ground (S_0) and the excited (S_1) states of the molecule, the molecule absorbs the photon to produce the S_1 state. The excited molecule should relax through fluorescence, intersystem crossing to the triplet manifolds, and internal conversion to the vibrational excited states in the S_0 state. If the excited molecule absorbs second photon during its lifetime and total photon energy is larger than the ionization potential of the molecule, the molecule should be ionized. When the two-photon excitation energy is larger than the ionization potential of the molecule, the photon can be used for both excitation and ionization (one-color two-photon ionization).

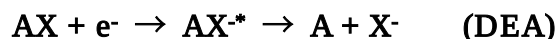
The produced ions are extracted to the flight tube of the TOF mass spectrometer and reflected by the reflectron before arriving at a microchannel plate (MCP). If ions have the same kinetic energy (E), the velocity (v) of each ion is described as $(2E/m)^{1/2}$ (m = mass number of the ion). When the ion travels the flight tube with the length L , the arriving time to the MCP (t) is expressed by,

$$t = L/v = L(m/2E)^{1/2}.$$

The arriving time of the ion is proportional to the square root of the mass number and we can estimate the mass number of the unknown ion by the delay time between the departure of the pulsed laser and the ion signal observed. The delay time of each ion is dependent upon the flight length and its mass number and the time in the present study was ranged in the order of tens of μ sec.

3. Electron attachment measurement

There are two processes for electron attachment: dissociative electron attachment (DEA) and nondissociative electron attachment (NDEA).



The schematic diagram for electron attachment is shown in Fig. I-2.

Through an electron attachment process, vertical transition takes place between two potential curves, obeying the Frank-Condon principle. In case of Fig. I-2a, the vibrationally excited parent anion (AX^*) has a repulsive potential and thus AX^* can easily be dissociated to produce A and X^- (DEA).

When the potential of AX^* has a minimum, the relative position of the anionic and the neutral potentials, and the depth of the anionic potential should affect the reaction process. If the Frank-Condon state pumped by a vertical transition is higher than the dissociation limit of the anionic potential (Fig. I-2b), the DEA process should take place. In case that the anionic dissociation limit is higher than the Frank-Condon state (Fig. I-2c), the DEA process does not occur. The produced anion should be vibrationally excited. In consequence, the excited anions are thermalized

by collisions with other molecules. If the excited anions are not thermalized within their lifetimes, the detachment of electron should take place.

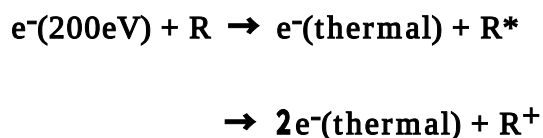
Ionization method with thermal electrons is useful for the study of the production mechanism of anions. The energy level of the Frank-Condon state could be controlled by the temperature of the attachment region. For the case of Fig. I-2b, the kind of anions produced and their relative abundances may be varied with temperature. This effect was observed for C_6F_5X ($X = Cl, Br, I$), and also depended on the number and the kind of the substituent.² If the energy level of the Frank-Condon state at higher temperature was still lower than the anionic dissociation limit as in the case of Fig. I-2c, only parent anions should be produced. When the electron affinity of the molecule was not so large and the detachment activation energy of anions was in the order of the kinetic energy of the attaching electrons, the intensity of parent anions decreased with increasing temperature due to electron detachment, like hexafluorobenzene.³ The amount of the parent anions were found to be independent of temperature when the electron affinity of the molecule was large and the detachment

activation energy was much larger than the kinetic energy of the electrons, like fluorobenzene derivatives.⁴ For the case of Fig. I-2a, only fragment ions should be observed, like halogenated alkanes and alkenes.⁵ The ion signal intensities and their temperature effect depend on the kind and the number of the halogen substituent.

Negative chemical ionization (NCI) process is known to undertake the two steps as shown in Scheme I-1.

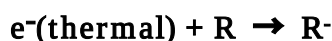
Scheme I-1

1. Thermalization of electrons

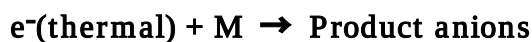


2. Anion formation

2.1 Electron transfer from the anion of the reagent gas



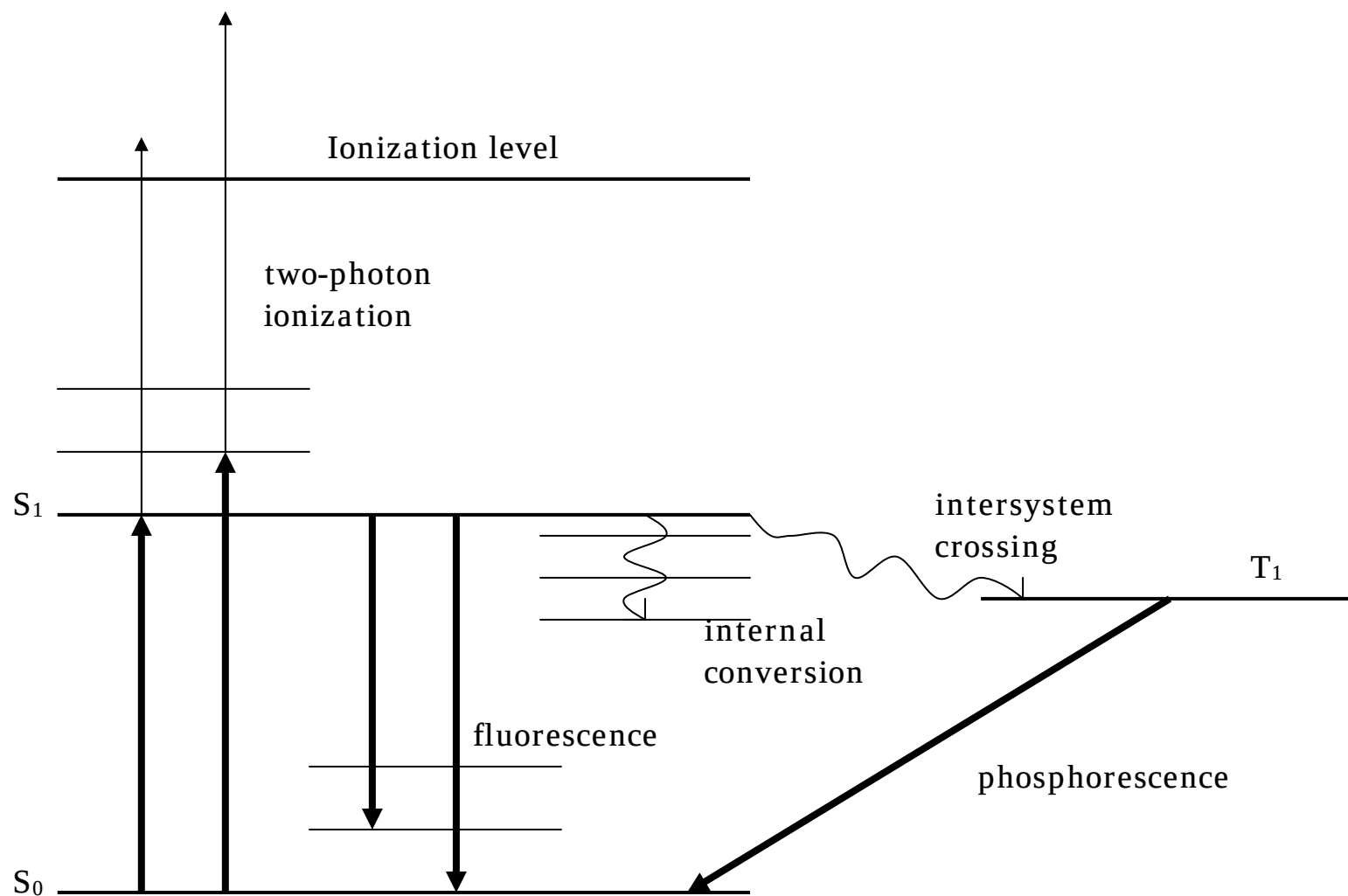
2.2 Electron attachment to the sample molecule



where R means the reagent gas and M means the sample molecule.

In the first step, electrons provided by a filament are thermalized by collisions with the reagent gas. The second step has two cases. First case: thermalized electrons are captured by the reagent gas to form anions of the

reagent. The produced anions should react with the sample gas. When the electron affinity of the sample gas is higher than that of the reagent gas, electron transfer to the sample molecule should take place. Second case: thermalized electrons are directly captured by the sample gas if the concentration of the sample gas is larger and its electron affinity is higher than the reagent. In this study, isobutane which has a high ability to thermalize electrons and its electron affinity is low, was used as a reagent gas. Therefore, the latter case should become main process in this study.



(8)

Fig. I-1 The schematic diagram for absorption, ionization, and intramolecular relaxation processes.

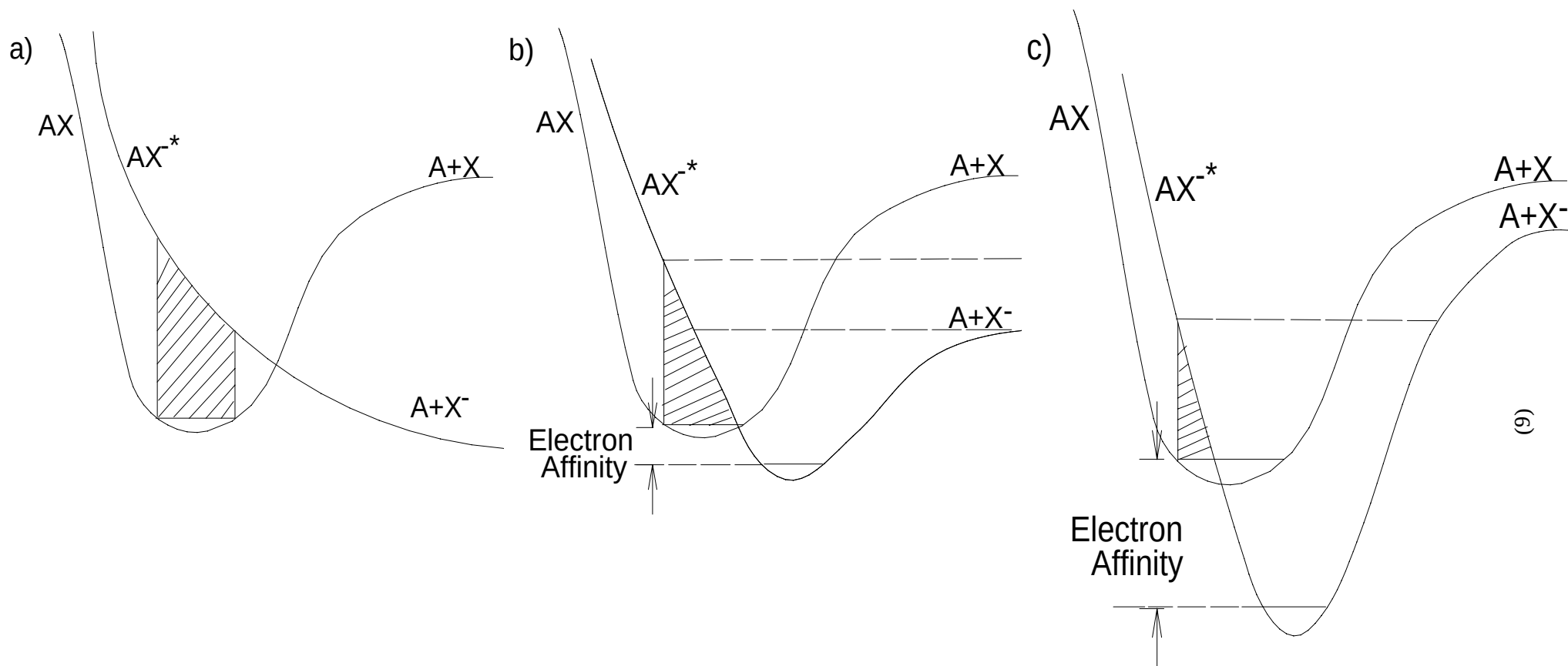


Fig.I-2 The schematic energy diagram for electron attachment. For the case of a) and b), dissociative electron attachment (DEA) and for the case of c), non-dissociative electron attachment (NDEA) takes place, respectively.

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II. REMPI-TOF spectrum of 3-chlorophenol

1. Introduction

When molecules are jetted out with high pressure into vacuum, the temperature of vibration and rotation of them is cooled down because of the insulate expansion. Under the jet condition, many molecules are populated in the lowest vibrational level of the ground (S_0) state. Consequently, the excitation spectra for the jet-cooled molecules become sharp and clear. Therefore, spectroscopy in a supersonic jet is one of the powerful techniques to study the excited state dynamics and analyze characteristic properties of large molecules. In combination with time-of-flight (TOF) mass spectrum measurements, the jet spectroscopy also gives useful information on the molecular structure.

There have been some studies of excitation spectra of chlorinated phenols in a supersonic jet.¹⁻⁵ Ito's group¹⁻³ reported the phosphorescence and fluorescence excitation spectra of jet-cooled chlorinated phenols. Two intense peaks appeared for 3-chlorophenol (3-ClP). They also studied the fluorescence excitation spectra of 3-ClP-water cluster and assigned the lower energy peak to the cis isomer and the higher energy one to the trans isomer,

arising from the orientation of the hydroxyl group with respect to the Cl atom at the meta position. The vibronic bands for the first excited singlet (S_1) state of the 3-ClP, however, were not assigned.

Cockett et al.⁴ have measured the resonance enhanced multiphoton ionization (REMPI) ion current spectrum and threshold photoelectron spectra of 3-ClP in a supersonic jet. They have tentatively assigned some prominent vibronic bands of the S_1 state and the ionic state (D_0). From the result of threshold photoelectron spectrum measurements, the adiabatic ionization energy for the cis and the trans isomers was found to be 8.655 and 8.682 eV, respectively. These results indicated that the parent ion should be produced by one-color resonant enhanced two-photon ionization (RE2PI). However, the mass selective spectra were not measured.

Uchimura and Imasaka⁵ have studied the REMPI excitation spectra of mono-chlorinated phenols with TOF mass spectrometry for analytical use. They have also analyzed the products in reaction of phenol and $FeCl_3$ in the vessel heated at 873 K and found formation of mono-chlorinated phenols. They have measured the excitation spectrum of 3-ClP⁺, which was one of the products, for the limited wavelength region of the origin band of the cis

isomer. Dimer cation of chlorinated phenols could not be observed by the REMPI-TOF technique. The detection limit of chlorinated phenols has not been reported for application of the REMPI technique in a supersonic jet.

In Chapter II, measurements of the REMPI excitation spectrum of jet-cooled 3-chlorophenol (3-ClP) and the TOF mass spectrum were described. Parent-water cluster formation and the production mechanism of fragment ions and dimer cations will be discussed. The detection limit of the cation of 3-ClP was also estimated for analytical use.

2.Experimental

2-1 Sample preparation

The sample of 3-ClP was purchased from Aldrich. Some water is included in liquid phenol and phenol-water clusters were observed with jet-cooled REMPI technique. As will be described in later section, the intensity of the cation of 3-ClP becomes smaller when the 3-ClP-water clusters are existent. It is necessary to distill off the water from 3-ClP to eliminate this effect. To remove contaminated water, the liquid sample in a U-shaped glass tube at ice-water temperature was distilled under vacuum, and the vapor was trapped by liquid nitrogen. The temperature of the reservoir was varied from 308 to 363 K to control the vapor pressure of 3-ClP, and the pressure dependence of the signal intensity was measured in order to estimate the detection limit. REMPI excitation spectra and TOF mass spectra were obtained at the reservoir temperature of 333-353 K.

2-2 Experimental apparatus

2-2-1. Jet system

Fig. II-1 shows the experimental apparatus for the REMPI-TOF spectrum measurements. Jet-cooled 3-ClP was generated by expanding 3-ClP vapor seeded in Ar (0.4-2.0 atm) into a vacuum chamber through a pulsed nozzle (General Valve Series 9) with a 0.8 mm orifice. The pulsed nozzle was controlled by the nozzle driver (Perker Hannifin IOTA ONE) and the interval time between the opening and the closing of the nozzle was set to obtain the suitable intensity of the signal. The free jet was skimmed through a skimmer, with a 1.0 mm diameter at 12 mm downstream from the orifice. The pressure of the vacuum chamber was about 3×10^{-6} and 1×10^{-7} Torr with and without the nozzle valve driven. To keep the high vacuum condition of the vacuum chamber and the flight tube, mechanical rotary pumps (ULVAC, D-950DK, 900 L/min for the vacuum chamber and Alcatel, 2015SD, 180 L/min for the flight tube) and turbo molecular pumps (Pfeiffer, TMU-1601P, 1500 L/sec for the vacuum chamber and Pfeiffer, TMU-260, 150 L/sec for the flight tube) were used.

2-2-2. Laser system

To excite the samples from the S_0 to the S_1 states and simultaneously ionize from the S_1 state, a dye laser (Lambda Physik, Scanmate IIE, spectral resolution: 0.02cm^{-1}) operated with Coumarine 153 (Lambda Physik, methanol solution) pumped by the third harmonic (355nm) of a Nd:³⁺YAG laser (Continuum, Surelite II-10 or Powerlite 8010) was used. The output of the dye laser was frequency doubled by BBO crystal and the angle of the crystal was controlled by Auto Tracker (Inrad, AT-III). To cut off the visible light, UV filter (Toshiba, UVD-33S) was used. The laser was focused with a convex lens and introduced into the vacuum chamber perpendicularly to the jet. The timing between the laser pulse and the nozzle was controlled by the pulse generator (Stanford Research System, DG535).

2-2-3. Detection system

Ions, which were generated by photo-ionization process, were mass-selected by a Wiley-McLaren style time-of-flight (TOF) mass spectrometer and the reflectron, and detected by a microchannel plate (MCP), (R.M.Jordan Co., 40mm Z-gap MCP). The apparatus of the reflectron TOF mass spectrometer is shown in Fig. II-2. The produced ions were collected by the electric field presented between the divider Vd (-2.8kV) and the repeller VA1 (1.8kV), extracted through VA2 (1.32kV), and polarized by VXY (0.03-0.06kV). After traveling the drift region, ions were reflected by the reflectron provided by VR1 (1.16kV) and VR2 (1.90kV). The signals were fed into a boxcar integrator (Stanford Research System, SR250) and transferred to a personal computer (NEC, PC-9801) through an A/D converter (Union Data, UAD-98KJ). The arriving time of ions to MCP was measured by the trigger signal of the PIN photodiode, which can detect the laser pulse. The laser power was measured by photo diode (Hamamatsu Photonics, S1336-5BQ) and the ion signal intensity was normalized by the laser power. REMPI excitation spectra were measured by ion signals with scanning the wavelength of the laser. TOF mass spectra were recorded

with the digital oscilloscope (Lecroy, Waverunner2) and accumulated by 2000 shots of the laser pulse.

3.Results and Discussion

3-1. TOF mass spectrum

The intense signal was observed in the fluorescence excitation spectra¹⁻³ and photoelectron excitation spectra⁴ when the excitation photon energy was about 35770 cm⁻¹. Therefore, the ion signal of TOF mass spectrum should be observed at the photon energy of 35770 ~ 35780 cm⁻¹.

The TOF signals obtained for 3-ClP without distillation at 35776 cm⁻¹ are shown in Fig. II-3. The most intense ion signal observed at the delay time of 43.5 μsec will be 3-³⁵ClP⁺ (m/e = 128). Because the square root of the mass number of the ion is proportional to the delay time as described in the previous section, the transformed TOF mass spectrum is shown in Fig. II-4. The ion signal at the mass number of 130 should be 3-³⁷ClP⁺. In the higher mass number region than 128 and 130, ions were observed at every 18 mass number. They were the series of 3-ClP-water cluster cations and the signal intensity of 3-ClP-(H₂O)⁺ was about one third of that of 3-ClP⁺. The observed intensity of 3-ClP⁺ was relatively smaller for the sample without distillation and ion signals were not observed when the temperature of the sample reservoir was set under 333 K, revealing that the abundance of

3-ClP molecule should be much lower due to the presence of water clusters.

The mass spectrum obtained for 3-ClP with distillation is shown in Fig. II-5.

After distillation, the ion signal of 3-ClP⁺ could be observable even at room temperature when the backing pressure was 0.4 atm. In due course, the intensity of 3-ClP·(H₂O)⁺ decreased about 1/100 of that of 3-ClP⁺.

3.2 REMPI excitation spectrum

We can obtain the RE2PI excitation spectrum at $m/e = 128$ by scanning wavelength of the laser with monitoring the peak ion intensity observed at 43.5 μ sec of the delay time. The RE2PI excitation spectra at $m/e = 128$ without and with distillation off the water are shown in Figs. II-6 and 7, respectively. The spectrum became simple with distillation. Two intense peaks were observed at $35776 \pm 1 \text{ cm}^{-1}$ and $35894 \pm 1 \text{ cm}^{-1}$ as shown in Fig. II-7. These transition energies well correspond to those of the previous reports.¹⁻⁴ These bands observed at 35776 cm^{-1} and 35894 cm^{-1} were assigned to the origin bands of the cis and the trans isomers, respectively, arising from the orientation of the hydroxyl group with respect to the Cl atom at the meta position. The structure of two rotational isomers is shown in Fig. II-8. The ratio of signal to noise (S/N) was approximately 100 for the peak intensity at 35776 cm^{-1} .

Kleiner mann et al. have studied the REMPI excitation spectra of phenol-(H₂O)_n⁺.⁶ The spectral feature of phenol-(H₂O)₂⁺ was similar with that of phenol-(H₂O)⁺, indicating that some phenol-(H₂O)⁺ should be produced from phenol-(H₂O)₂⁺. In the RE2PI excitation spectrum (Fig. II-6),

the background at the origin band of the cis isomer was about half of the peak intensity and increased with increasing the excitation energy. 3-ClP⁺ is likely to be produced from dehydration of water cluster cations. The dehydration process would take place in a similar fashion to the formation of the phenol-(H₂O)⁺ from the phenol-(H₂O)₂⁺.⁶ The background signals in Fig. II-6 drastically decreased after distillation shown in Fig. II-7, suggesting that the signal intensity should be attributed to the abundance of 3-ClP-water clusters.

The vibronic band frequencies observed for each isomer are shown in Table II-1 together with those values previously reported.⁴ The energy of the vibronic bands in the cis and the trans isomers is almost coincident with each other in this study. Three bands newly appeared above 36350 cm⁻¹ in Fig. II-7, which are also listed in Table II-1. For the assignment, the vibrational frequencies in the ground (S₀) and the excited (S₁) states of 3-ClP were calculated with Gaussian98 program.⁷ CIS and B3LYP density functional methods with the 6-31+G(d) basis set were used for the calculation of vibrational frequencies in the S₁ and the S₀ states, respectively. The calculated results are listed in Table II-2 together with the experimental

ones in the S_0 state obtained by IR and Raman spectrum measurements.⁸ The calculated values in the S_0 state are in good agreement with the experimental ones. The frequencies in the S_1 state correspond with those in the S_0 state, except for the 10b mode.

The 10b mode would have a'' symmetry because the structure of 3-ClP should have C_s symmetry. Therefore, only even number transitions become allowed and observable in the spectrum. The band of the 10b mode appeared at the twice of the frequency in the RE2PI excitation spectrum (Fig. II-7). The frequency of the 10b mode in the S_1 state obtained in Table II-2 is smaller than half of that in the S_0 state. The calculated molecular structures with the 10b mode in the S_1 and the S_0 states are shown in Fig. II-9. The calculation suggests that the structure in the S_1 state should have a character of slight out-of-plane deformation. The structural change would result in much lower frequency of the 10b mode in the S_1 state.

With these calculations mentioned above, the observed vibronic bands including three bands newly observed were assigned and summarized in the last column of Table II-1.

The ratio of the signal intensity between the 3-ClP⁺ ($m/e = 128$) and 3-ClP⁺ ($m/e = 130$) should reflect the natural abundance of the ³⁵Cl and ³⁷Cl

isotopes (3:1). The momentum of inertia and vibrational frequency is different between $3\text{-}^{35}\text{ClP}^+$ and $3\text{-}^{37}\text{ClP}^+$. The difference should be reflected for the intensity ratio of the vibronic level in the excitation spectra. The RE2PI excitation spectral profiles of 3-ClP^+ ($m/e = 128$) and 3-ClP^+ ($m/e = 130$) near the origin bands were compared in Fig. II-10. The signal intensity of 3-ClP^+ ($m/e = 130$) was multiplied by three and that of 3-ClP^+ ($m/e = 128$) was added to 0.3 for clarity in Fig. II-10, indicating that the relative intensity reflects the natural abundance. The feature observed for the two isotopes was similar and no isotope shift in the excitation spectral profile was observed with 0.06cm^{-1} spectral resolution at 35776 cm^{-1} .

3.3 Fragmentation mechanism

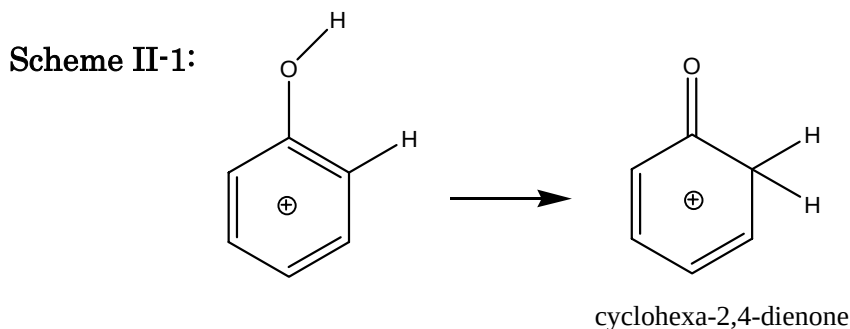
There appeared C_3H_3^+ ($m/e = 39$) and C_5H_5^+ ($m/e = 65$) as lower mass number fragments than 3-ClP^+ in Fig. II-5, though these signal intensities are quite low. The REMPI excitation spectrum of C_3H_3^+ in Fig. II-11 suggests that C_3H_3^+ should be produced through the S_1 state of 3-ClP , since the spectral profile for C_3H_3^+ resembles that for the parent ion (Fig. II-7).

The laser power dependences of the intensities of the parent ion and C_3H_3^+ are shown in Figs. II-12 and 13, respectively, though the intensity of C_5H_5^+ was too low to measure its power dependence. The values of slopes of 2.1 and 3.0 should imply that the parent ion and C_3H_3^+ could be produced from two-photon and three-photon processes, respectively. This is the evidence that the parent cation could be energetically generated by one-color two-photon ionization, since the two-photon energy of 35776 cm^{-1} is 1734 cm^{-1} above the ionization potential⁴ (69818 cm^{-1}).

Fragmentation channel of 3-ClP^+ to form C_3H_3^+ has not been clarified yet. The wavelength dependence of the fragmentation of chlorobenzene cations was studied by resonance enhanced multiphoton dissociation spectrometry (REMPIDS).⁹⁻¹⁰ In these studies, the unimolecular loss of the

Cl atom from the parent ion was observed. The result is reasonable because the C-Cl bond can be easily dissociated compared to the C-H bond.¹¹ Accordingly, the C-Cl bond cleavage may be expected in the REMPI process of 3-ClP.

The breakdown diagram of phenol cations postulated that $C_5H_6^+$ should be produced by the CO elimination with the least excess energy, and thus that formed $C_5H_6^+$ should lead to the formation of $C_3H_3^+$ subsequently.¹² Le et al. have calculated the schematic potential energy curve for the fragmentation process of the CO loss from the phenol cation.¹³ Their results suggested that the cyclohexa-2,4-dienone isomer should be produced for the first place by hydroxylic hydrogen transfer as shown in Scheme II-1, and then, a ring opening reaction yields the open-chain ketene radical cation and in consequence, a cyclization reaction to form the five-membered ring takes place. The similar mechanism will be probable for the fragmentation process in the case of chlorinated phenol s.



The appearance energy of $C_5H_6^+$ from the phenol cation has been studied by time-resolved electron impact,¹⁴ photoionization,¹⁵ and photoelectron photoion coincident (PEPICO)¹⁶ methods. These results well corresponded with the calculated activation energy obtained to be 3.0 eV.¹³ The result of PEPICO measurement suggests that $C_5H_5^+$ should be produced from $C_5H_6^+$ subsequently at the initial excitation energy of 12.7 eV.¹⁶

In the case of 3-ClP, the Cl atom loss from $3-ClP^+$ to produce $C_6H_4OH^+$ will occur before the CO loss, because the bonding energy of the C-Cl is weaker than that of the C-H, as described in the fragmentation of chlorobenzene cation. On the other hand, the signal intensity of $C_6H_4OH^+$ produced by the Cl loss from $3-ClP^+$ was much weaker in the electron impact (EI) mass spectrum.¹⁷ $C_6H_4OH^+$ could not be observed at all in this study.

Because the excess energy provided to the parent ion produced by the EI method was widely distributed, the fragmentation pattern should be variable. The qualitative comparison between mass spectra obtained by the EI and the REMPI methods may give useful information about the fragmentation mechanism of the parent ion. The mass spectrum of 3-ClP obtained by the EI method¹⁷ is shown in Fig. II-14. In the EI mass

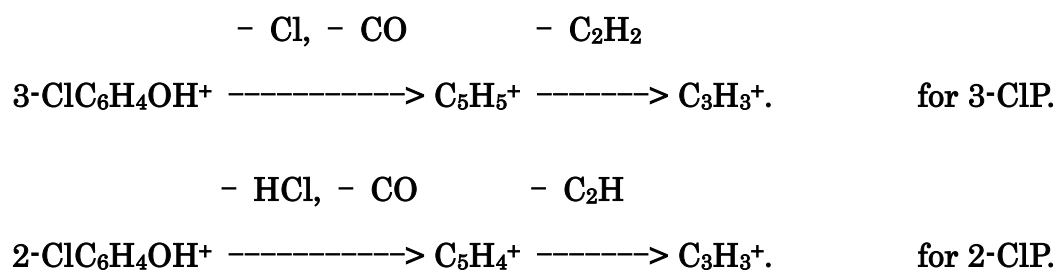
spectrum measurements, the major fragment cation of 3-ClP⁺ was C₅H₅⁺, and certain amounts of C₃H₃⁺ and C₅H₅Cl⁺ generated by the CO loss from 3-ClP⁺ were also observed. Because neither C₆H₄OH⁺ nor C₅H₅Cl⁺ were observed in this study, I cannot decide which fragmentation takes place for the first process, the Cl loss or the CO loss from 3-ClP⁺. Instead of C₅H₅Cl⁺, C₅H₅⁺ which would be the fragment of C₆H₄OH⁺ or C₅H₅Cl⁺ and the presumable precursor of C₃H₃⁺, appeared in the TOF mass spectrum (Fig. II-5). The weak signal intensity of C₅H₅⁺ suggests that almost all of C₅H₅⁺ formed by the Cl and the CO elimination from 3-ClP⁺ would yield C₃H₃⁺ in one-colour REMPI process. The total energy of three-photon in this study is approximately 13 eV, which is high enough to give rise to both the Cl loss and the CO loss processes, subsequent formation of C₃H₃⁺. The excess energy of the cation can be precisely decided as the photon energy in the case of MPI process. Wider energy distribution in the case of EI method might have enabled observation of various cations described above.

TOF mass spectrum of 2-chlorophenol (2-ClP) was shown in Fig. II-15. The excitation photon energy was 35892 cm⁻¹ which corresponds to the origin band transition of the cis isomer of 2-ClP reported.³ The major fragment

cation was $C_5H_4^+$, and the $C_3H_3^+$ ion was also observed with large intensity. The formation of $C_5H_4^+$ suggests that the HCl elimination should occur instead of the Cl elimination. In analogy to 3-ClP, I cannot decide from which the HCl elimination occurs, $2-ClP^+$ or $C_5H_5Cl^+$, in this study. The CO loss would not take place directly from $2-ClP^+$ due to the presence of double bond. Therefore, the cyclohexa-2,4-dienone type isomer would be produced for the first place by hydroxylic hydrogen transfer to the ortho position before the CO loss reaction proceeds in a similar fashion to the phenol cation (Scheme II-1). On the other hand, the HCl elimination maybe take place before the hydroxylic hydrogen transfer to form the cyclohexa-2,4-dienone type isomer. In the EI spectrum shown in Fig. II-16,¹⁷ the prominent fragment cation of 2-ClP was also $C_5H_4^+$ as the same result as that obtained by the REMPI method (Fig. II-15). $C_6H_4O^+$ ($= (M - HCl)^+$, HCl loss from the parent ion) was also observed with certain signal intensity. Little amount of $C_5H_5Cl^+$ was observed for 2-ClP. These results strongly support that there should be the HCl elimination from $2-ClP^+$. The expected scheme for the fragmentation of $3-ClP^+$ and $2-ClP^+$ is shown in Scheme II-2. In the REMPI process, the signal intensity of $C_5H_4^+$ was larger than that of $C_3H_3^+$

for 2-ClP though $C_3H_3^+$ was the largest for 3-ClP, revealing that $C_5H_4^+$ obtained from 2-ClP⁺ should be much stabilized than $C_5H_5^+$ produced from 3-ClP⁺. In order to further investigate the detailed fragmentation mechanism, measurements by PEPICO and REMPIDS methods may be required.

Scheme II-2:



Formation of $C_6H_5O^+$ ($= (M - Cl)^+$, the Cl loss from the parent ion) was not observed from both 2-ClP and 3-ClP in the EI mass spectra either. Is not the C-Cl bond of chlorinated phenol cation broken? The mass spectra of 2,4-dichlorophenol (2,4-DCP), 3,4-DCP, and 2,4,6-trichlorophenol (2,4,6-TCP), and 2-bromophenol (2-BrP) and 3-BrP measured by EI method¹⁷ are shown in Figs. II-17 and 18, respectively. $(M - HCl)^+$ was observed for 2,4-DCP and 2,4,6-TCP. Except for $(M - HCl)^+$, signal intensities of $C_5H_3Cl^+$ and $C_5H_2Cl_2^+$,

which were produced from the CO loss of $(M - HCl)^+$, were large for 2,4-DCP and 2,4,6-TCP, respectively. For 3,4-DCP, $C_5H_4Cl^+$ was observed instead of $C_5H_3Cl^+$. $(M - HCl)^+$ and $C_5H_3Cl^+$ were produced from chlorinated phenols possessing the ortho-Cl, revealing that the HCl loss of chlorinated phenol cation should occur from the ortho-Cl. $(M - Cl)^+$ should not be the prominent fragment ion for any chlorinated phenols studied by the EI method.

$C_6H_5O^+$ ($= (M - Br)^+$, the Br loss from the parent ion) was observed for 2-BrP and 3-BrP studied by the EI method (Fig. II-18). For 2-BrP, the signal intensities of $C_6H_5O^+$ and $C_5H_5^+$, produced from the CO loss of $C_6H_5O^+$ were larger than those of $C_6H_4O^+$ ($= (M - HBr)^+$, the HBr loss from the parent ion) and $C_5H_4^+$, produced from the CO loss of $C_6H_4O^+$. For 3-BrP, the signal intensity of $C_5H_5Br^+$ ($= (M - CO)^+$, the CO loss from the parent ion) was much weaker than that of $C_6H_5O^+$, suggesting that the cleavage of the C-Br bond should occur for the first place independent of the Br location, and followed by the CO loss.

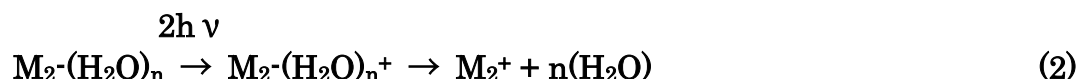
3-4. Dimer cations formation

As shown in the inset of Fig. II-19, dimer cations $((3\text{-ClP})_2^+ = M_2^+, m/e = 256, 258)$ and dimer-water cluster cations were also observed in addition to the parent cation (3-ClP^+) . The chlorine atom has two isotopes (^{35}Cl and ^{37}Cl) and its natural abundance is 3 : 1, which is in good agreement with the intensity ratio of the two 3-ClP^+ peaks in Fig. II-19. The ratio of signal intensity between the mass number of dimer cations at $m/e = 256$ and $m/e = 258$, was found to be about 3 : 2. Because the dimer cation has two Cl atoms, the relative isotopic ratio $^{35}\text{Cl}^{35}\text{Cl} : ^{35}\text{Cl}^{37}\text{Cl} : ^{37}\text{Cl}^{37}\text{Cl}$ in the dimer cation should be derived to be 9 : 6 : 1.

There may be two candidates for the production mechanism of the dimer cation. One is that the direct ionization of the dimer of 3-ClP:



The other is the dehydration of the dimer-water cluster cation:



The signal intensity of the dimer cation was changed little with increasing the temperature of the reservoir up to 403 K, and the backing pressure up to

5 atm, and with scanning the excitation photon energy from 35087 to 36364 cm^{-1} . The signal intensity of the dimer cation was almost the same as that of $\text{M}_2(\text{H}_2\text{O})^+$.

On the other hand, it is known that phenol dimer cations¹⁸ and the phenol-water cluster cations^{6,18} have hydrogen bond structure at the hydroxyl group. It is reported that the one-color two-photon energy ($\sim 72000 \text{ cm}^{-1}$) is about 8000 cm^{-1} larger than the ionization potential ($\sim 64000 \text{ cm}^{-1}$) for both phenol dimer¹⁹ and phenol-water clusters⁶. In those studies, the ionization energy of the dimer and the water clusters decreases in several thousand cm^{-1} than that of the monomer by formation of the hydrogen bond.^{6,18,19} Therefore, the dimer cation produced by one-color two-photon ionization will be decomposed into the monomer cation and the neutral molecule, and the water cluster cation will be dehydrated.

Because the Cl atom substituent of 3-ClP is not adjacent to the hydroxyl group, the hydrogen bonding of the hydroxyl group will not be affected by the Cl atom. Dimer cations of 3-ClP and 3-ClP-water cluster cations would also have the similar hydrogen bond structure as the phenol dimer cation and the phenol-water cluster cations. This assumption and

the experimental results described above suggest that the dimer cations should be produced through the process (2) in this study.

3-5. Detection limit

The vapor pressure dependence of the signal intensity of the 3-ClP⁺ at the origin band of the cis isomer was plotted in Fig. II-20. The backing pressure of Ar was 0.4 atm. and the laser power was 4 μ J/pulse. By extrapolating the signal intensity to 0.0001, where the S/N ratio is assumed to be unity, the lower detection limit of the partial pressure of 3-ClP was roughly estimated to be 1×10^{-2} Torr (4 ppm). The higher the laser power is increased, the higher the detection efficiency becomes. Thus, the detection limit may be improved by increased laser power. Due to the presence of water clusters under the present conditions, the signal intensity of 3-ClP⁺ would become much smaller, especially at lower vapor pressure of the sample. Accordingly, the effect of the water cluster formation will be negligible at higher temperature and we can accomplish much higher detection limit for analytical use.

Here, the detection of other chlorinated phenols is discussed. Because the excitation of the molecule is the first stage of the REMPI process, the signal intensity generated by REMPI process is proportional to the absorption coefficient of the molecule. The absorption coefficients to

their S_1 states of chlorinated phenols are not varied largely. Therefore, the detection limit will not be affected so much by the absorption coefficient among chlorinated phenols.

The excitation energy decreases with increasing the number of the chlorine substituent. On the contrary, the ionization potential energy rather increases. Therefore, the ionization energy in some cases becomes larger than twice of the excitation energy to the origin of the S_1 state. Chlorinated phenols with more than two chlorine atom substituents can be ionized by two-color two-photon ionization and not by one-color two-photon ionization, as far as the origin bands of their S_1 states are concerned.

Because the absorption coefficients of chlorinated phenols are almost the same, the detection limit should be affected by the existence of water cluster. The temperature of the sample reservoir should be higher than 373 K to avoid the effect of water cluster. We must use the two-color two-photon ionization technique and keep the sample temperature higher than 373 K to measure all chlorinated phenols completely.

Table II-1. Vibronic band frequencies observed in the S₁ state of the cis and the trans isomers of 3-ClP and their assignments.

Frequencies/cm ⁻¹				Assignment
cis ^{a)}		trans ^{a)}		
181	(182)	191	(190)	10b ²
241	(241)	241	(238)	9a ¹
366	(367)	-	(379)	10b ⁴
470	(470)	469		6a ¹
486	(486)	480		9a ²
549	(554)	-		10b ⁶
644		-		1 ¹

a) The energy difference from the origin band of each isomer. The values in parenthesis are taken from ref.4

Table II-2. Calculated vibrational frequencies of 3-ClP in the S_0 and the S_1 states.^{a)}

mode	S_0			S_1	
	ref.7	cis	trans	cis	trans
10b	193	183	183	83	79
9a	241	247	248	269	265
7b	411	407	408	395	396
16b	442	450	453	384	362
6a	528	534	535	474	474
4	676	679	673	586	607
1	686	697	695	686	688
11	772	784	771	698	698
6b	859	898	898	951	953
17b	887	889	875	816	776
5	962	980	968	928	920
12	998	1010	1010	1056	1056
18a	1070	1094	1095	1130	1120
18b	1088	1116	1116	1150	1159
9b	1156	1198	1200	1287	1281
13	1249	1284	1282	1407	1394
3	1291	1343	1332	1447	1450
14	1312	1359	1360	1479	1480
19a	1462	1482	1498	1562	1569
19b	1489	1528	1517	1593	1591
8a	1592	1636	1636	1711	1716
8b	1608	1651	1650	1783	1792

CIS and B3LYP methods with 6-31+G(d) basis set were used for the calculation in the S_1 and the S_0 states, respectively. The scale factor was 1.0. All vibrational frequencies are shown in units of cm^{-1} .

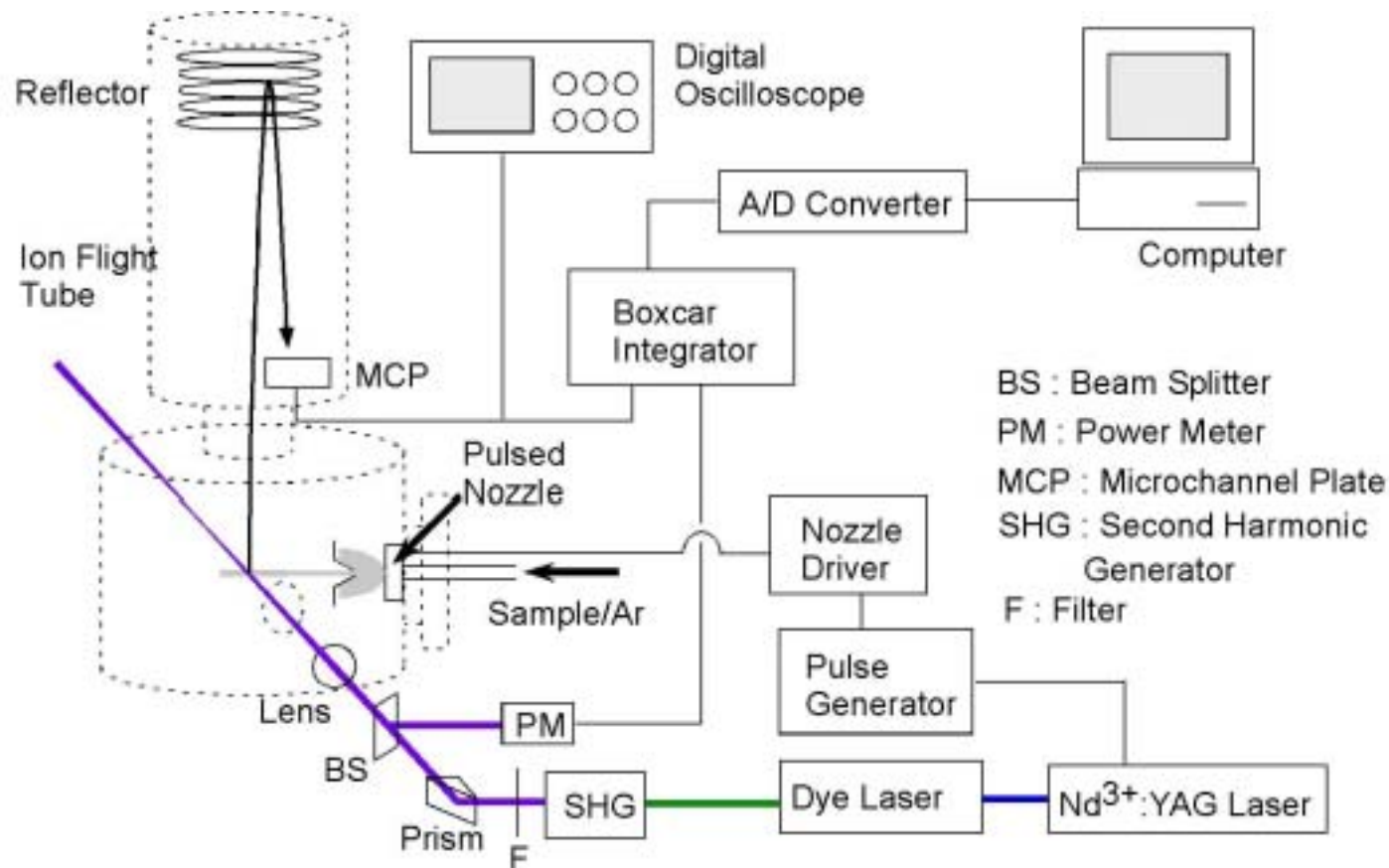


Fig. II-1 The experimental apparatus for the measurements of the REMPI excitation spectrum and the TOF spectrum.

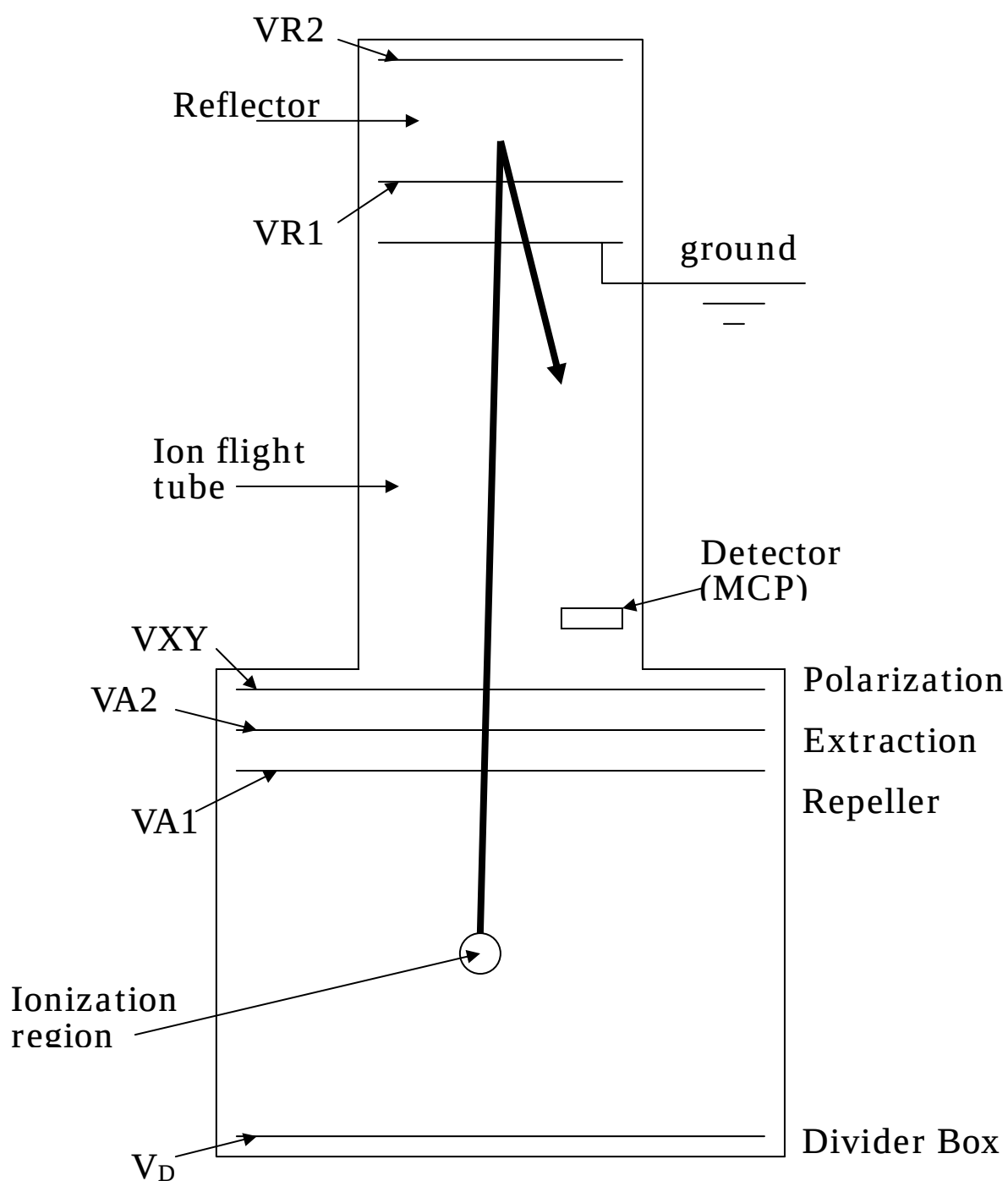
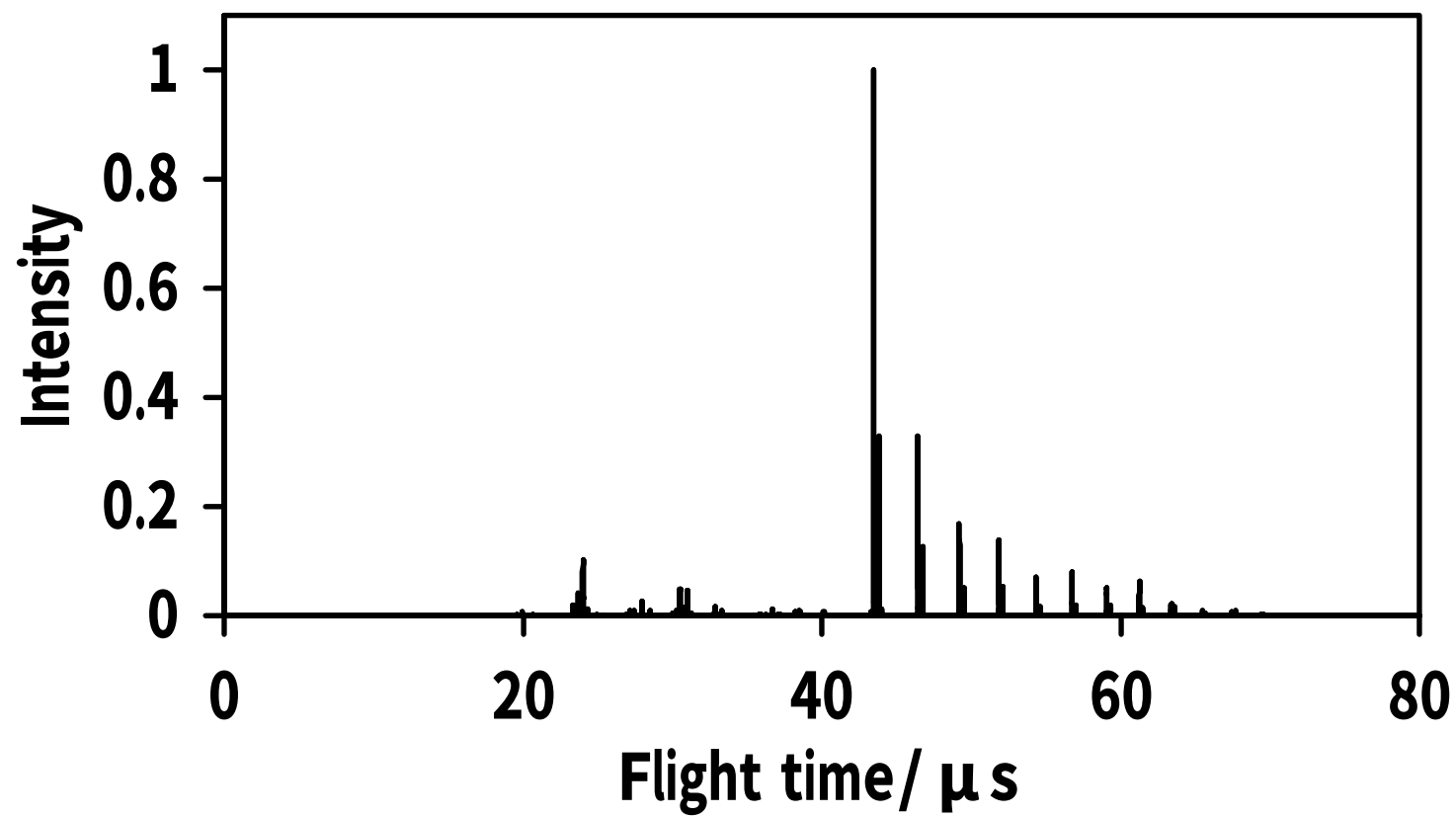
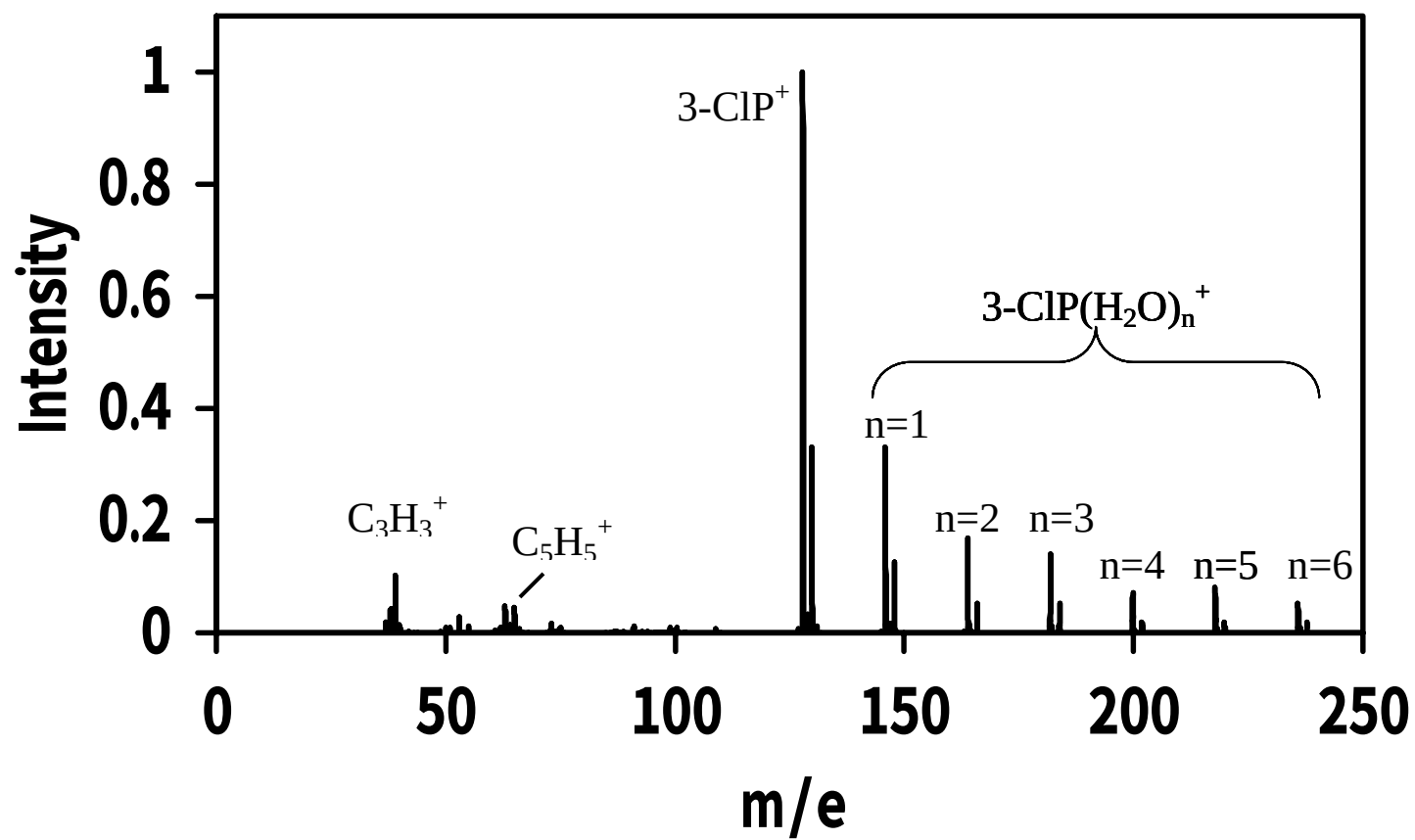


Fig. II-2 The apparatus of TOF mass spectrometer and reflectron.



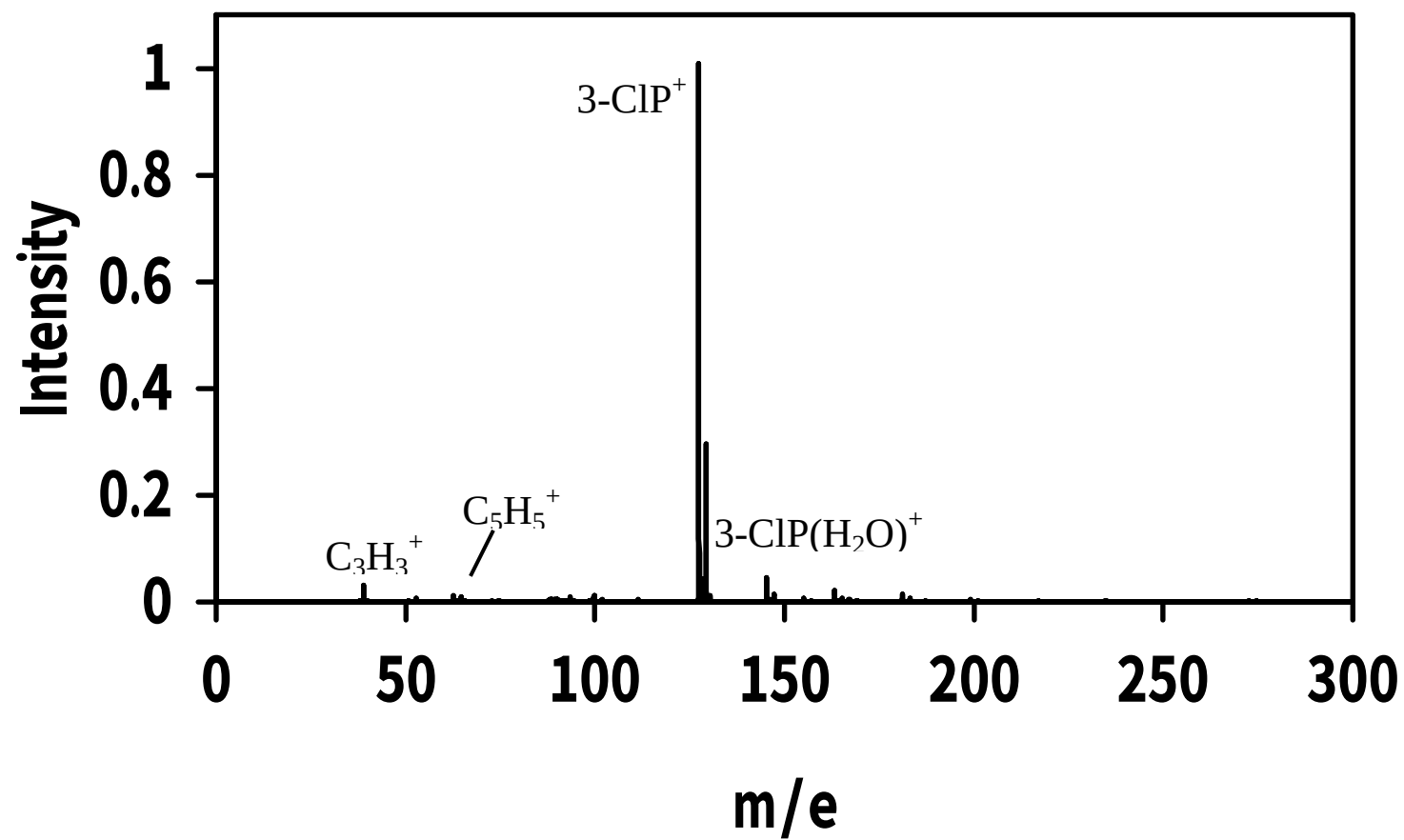
(43)

Fig. II-3 TOF spectrum for 3-ClP without distillation observed by the excitation at 35776 cm^{-1} .



(44)

Fig. II-4 TOF mass spectrum for 3-ClP without distillation observed by the excitation at 35776 cm^{-1} .



(45)

Fig. II-5 TOF mass spectrum for 3-ClP with distillation observed by the excitation at 35776 cm^{-1} .

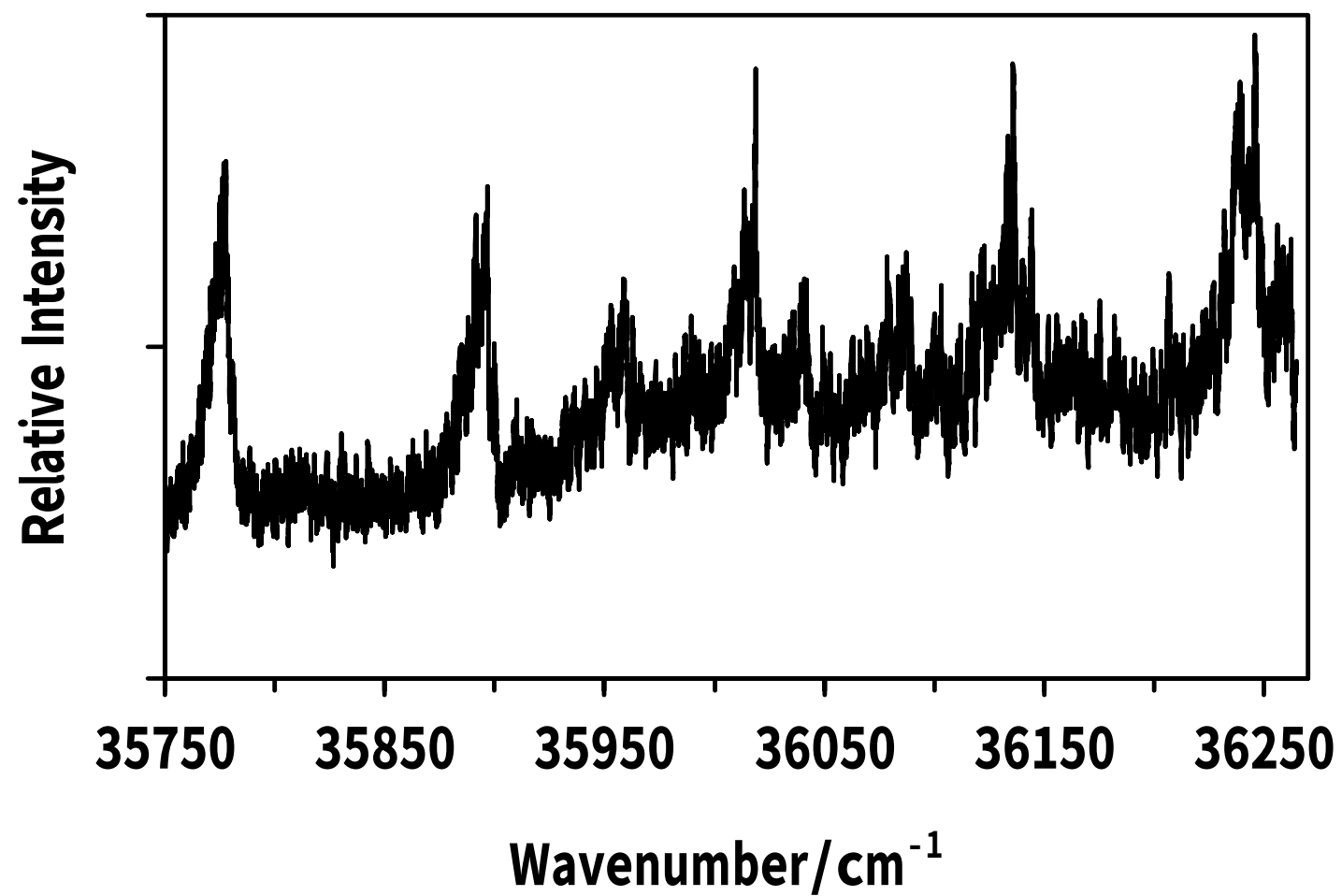


Fig. II-6 The RE2PI excitation spectrum of 3-ClP⁺ (m/e = 128) without distillation.

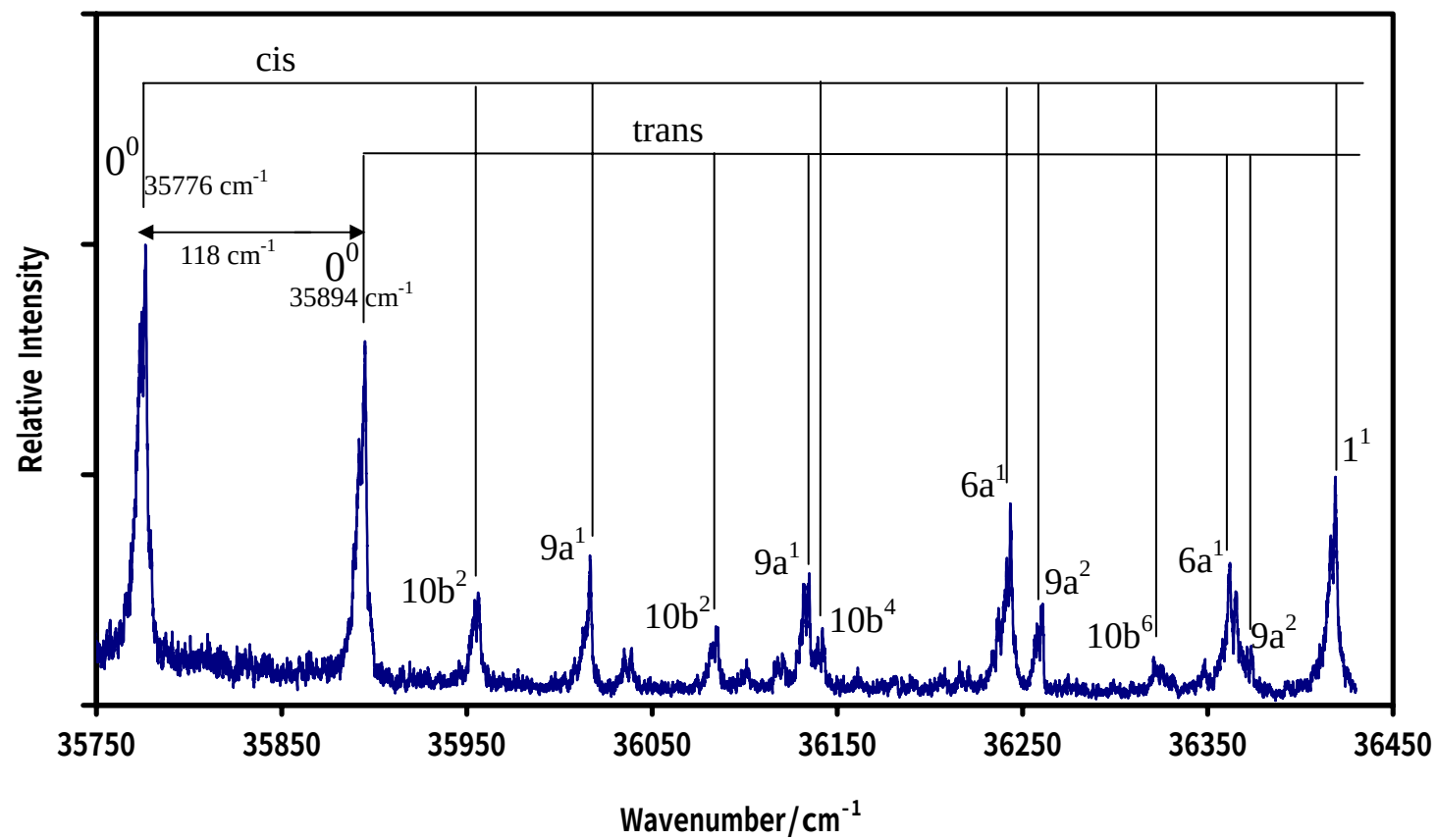
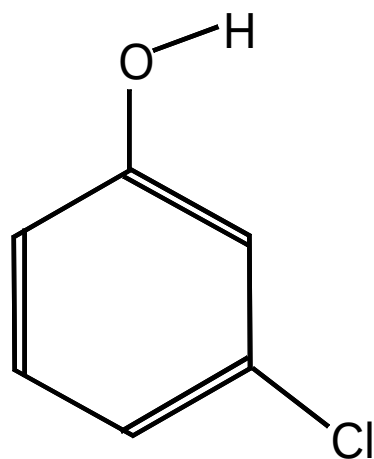
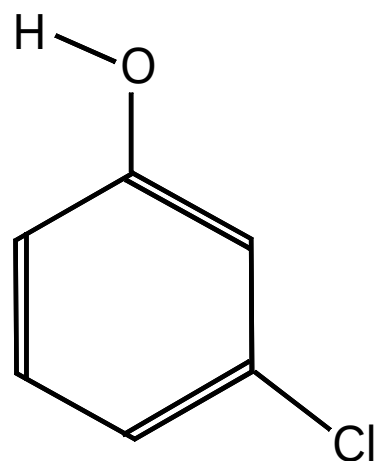


Fig. II-7 The RE2PI excitation spectrum of 3-ClP⁺ (m/e=128) with distillation.



cis



trans

Fig. II-8 The structure of two rotational isomers of 3-ClP.

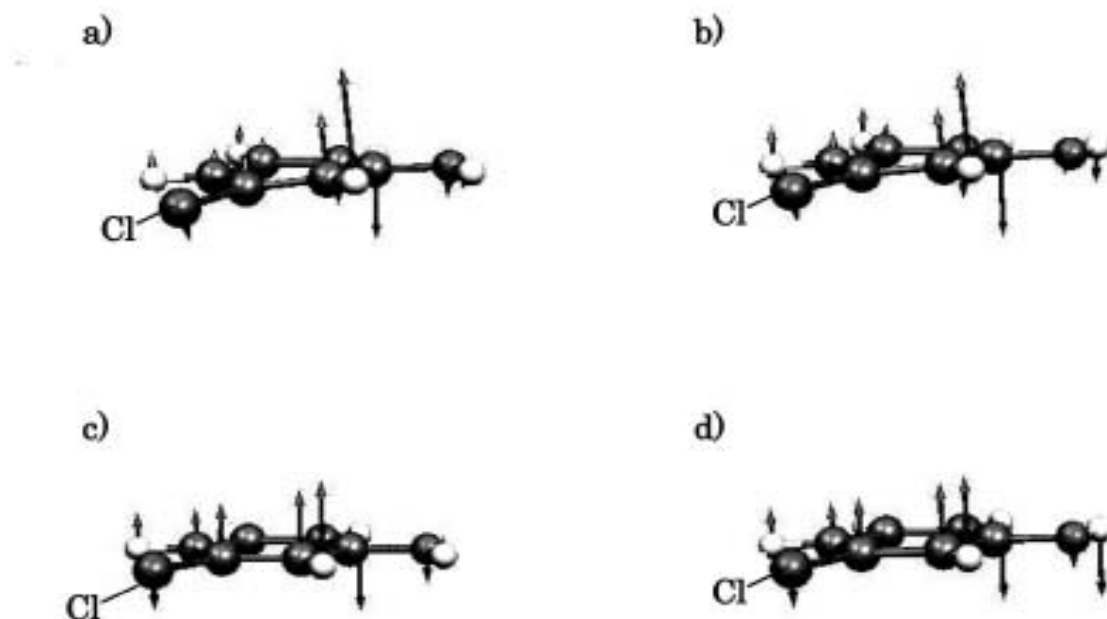


Fig. II-9 The optimized molecular structures of 3-ClP with the 10b mode in the S_1 (a:cis, b:trans) and the S_0 (c:cis, d:trans) states.

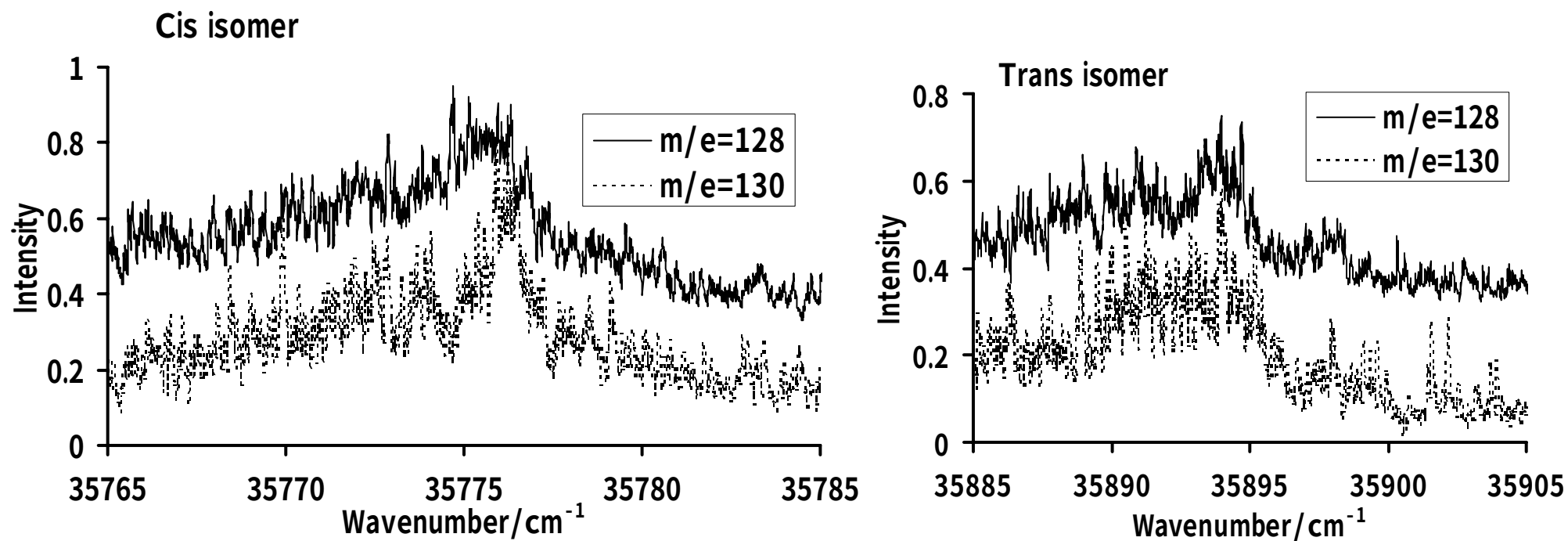


Fig. II-10 The RE2PI excitation spectra of 3-ClP⁺(m/e=128) and 3-ClP⁺(m/e=130) near the origin⁽⁵⁰⁾ bands. The signal intensity of 3-ClP⁺ (m/e = 130) was multiplied by three and that of 3-ClP⁺ (m/e = 128) was added to 0.3.

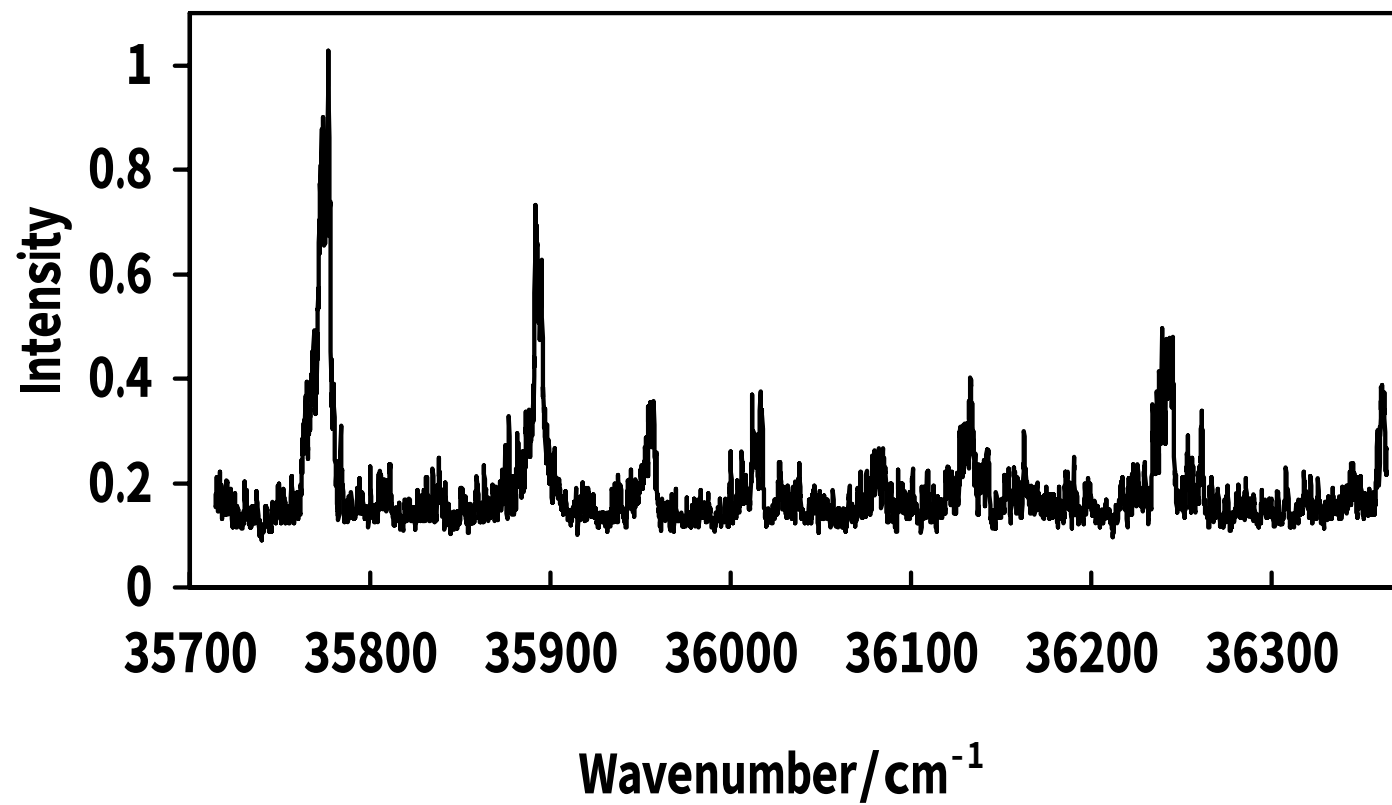


Fig. II-11 The REMPI excitation spectrum of $C_3H_3^+$ ($m/e = 39$).

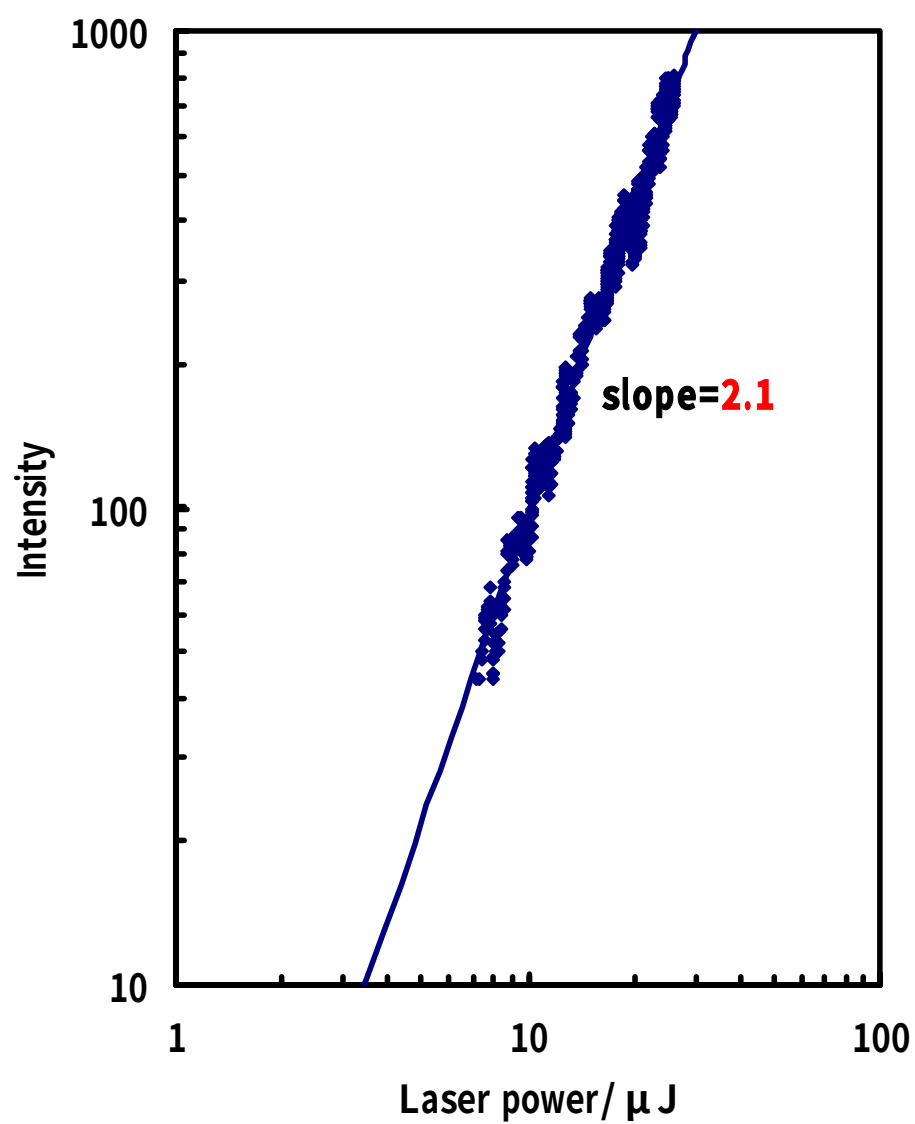


Fig. II-12 Plot of the signal intensity of 3-ClP⁺ against the laser power.

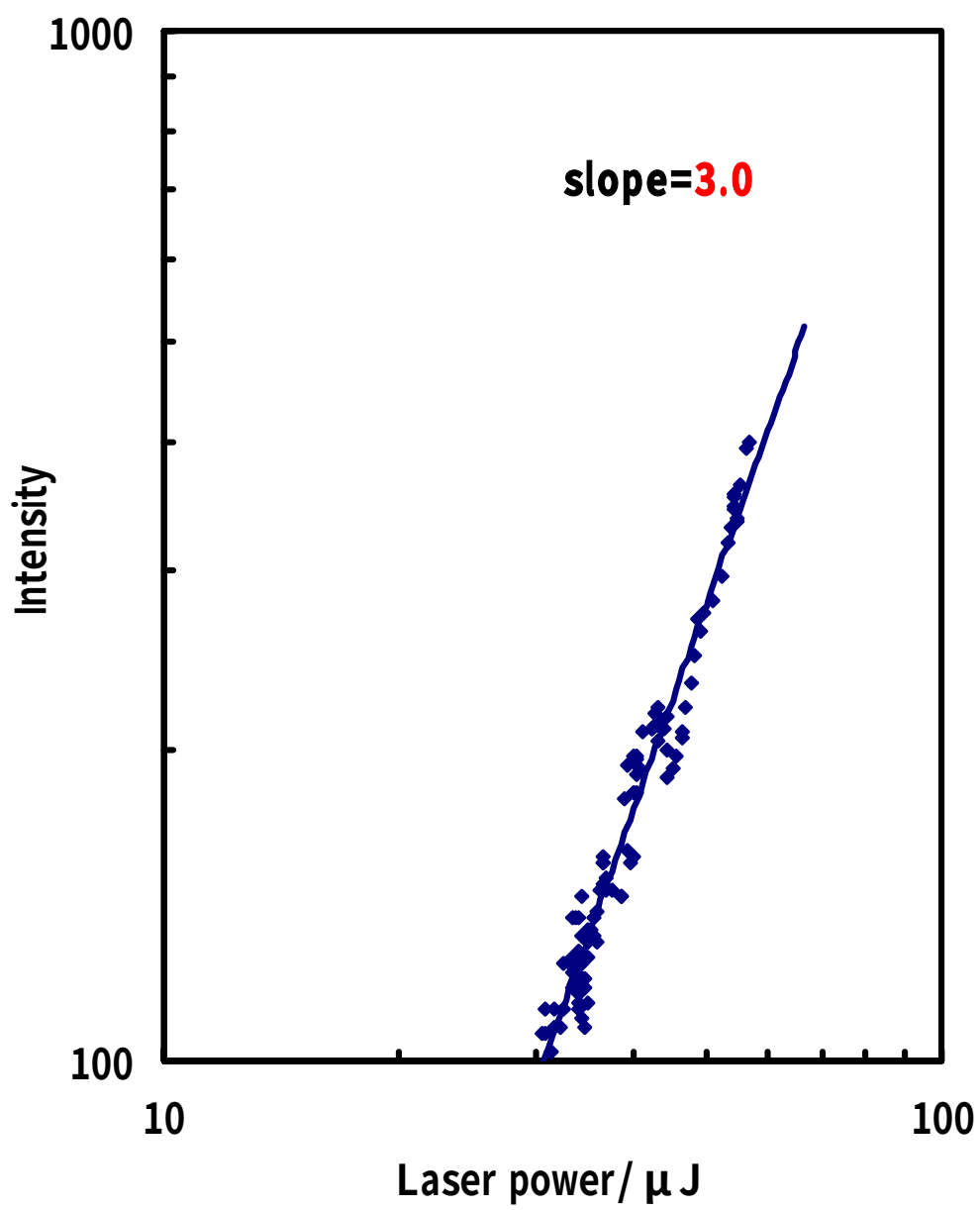
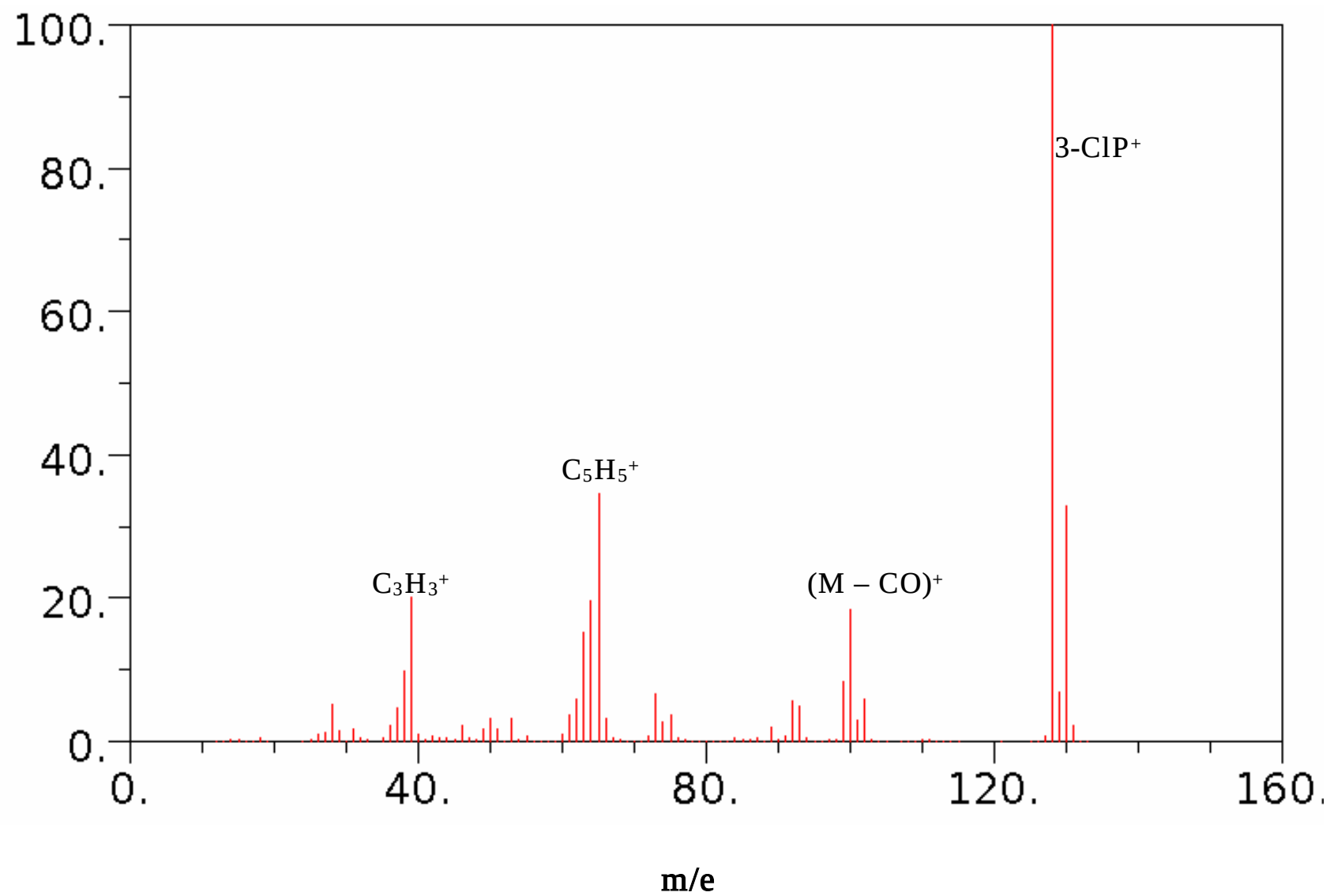


Fig. II-13 Plot of the signal intensity of C_3H_3^+ against the laser power.



(54)

Fig. II-14 The EI mass spectrum of 3-ClP taken from ref.17.

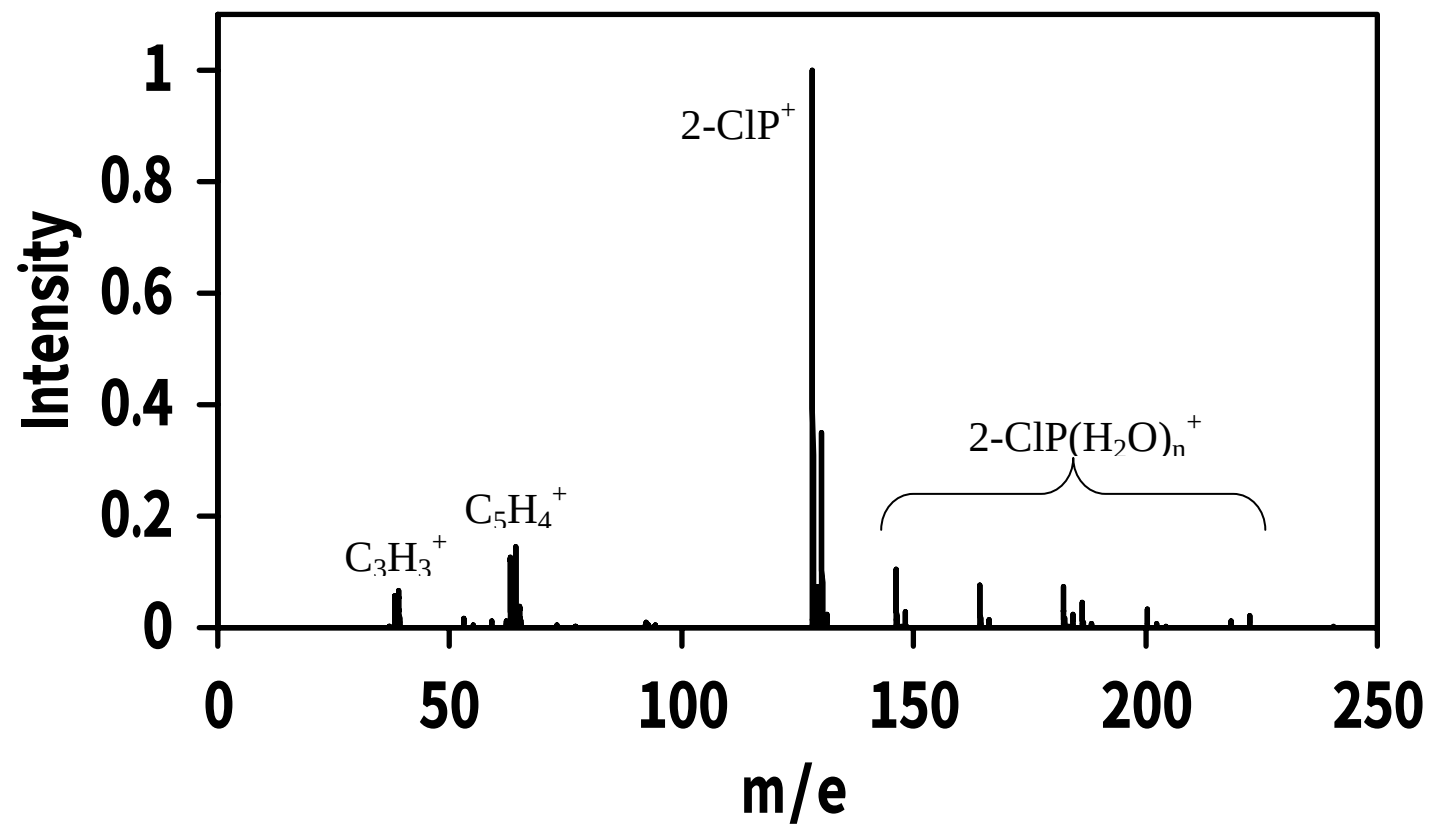


Fig. II-15 TOF mass spectrum for 2-ClP observed by the excitation at 35892 cm^{-1} .

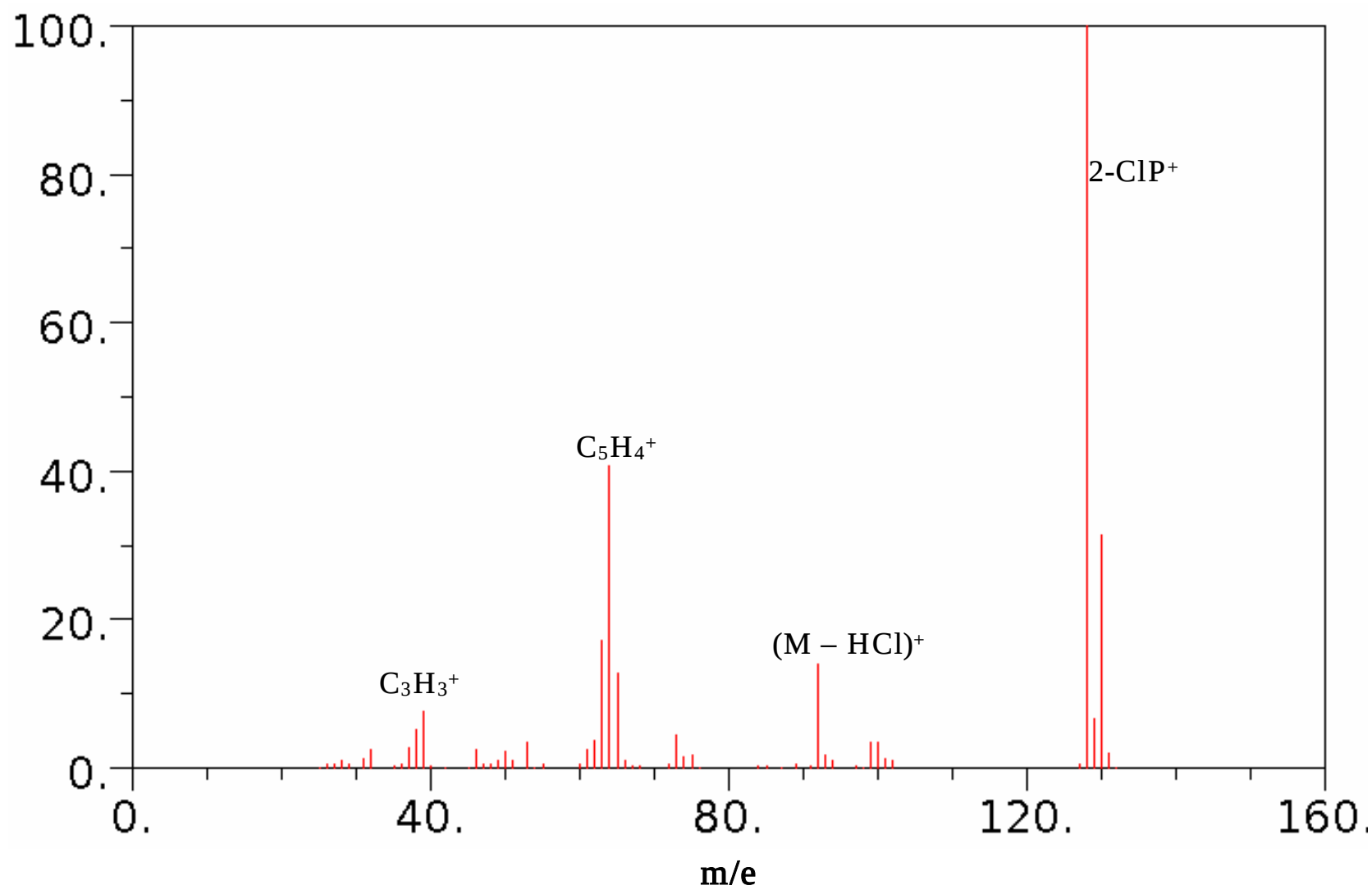


Fig. II-16 The EI mass spectrum of 2-ClP taken from ref.17.

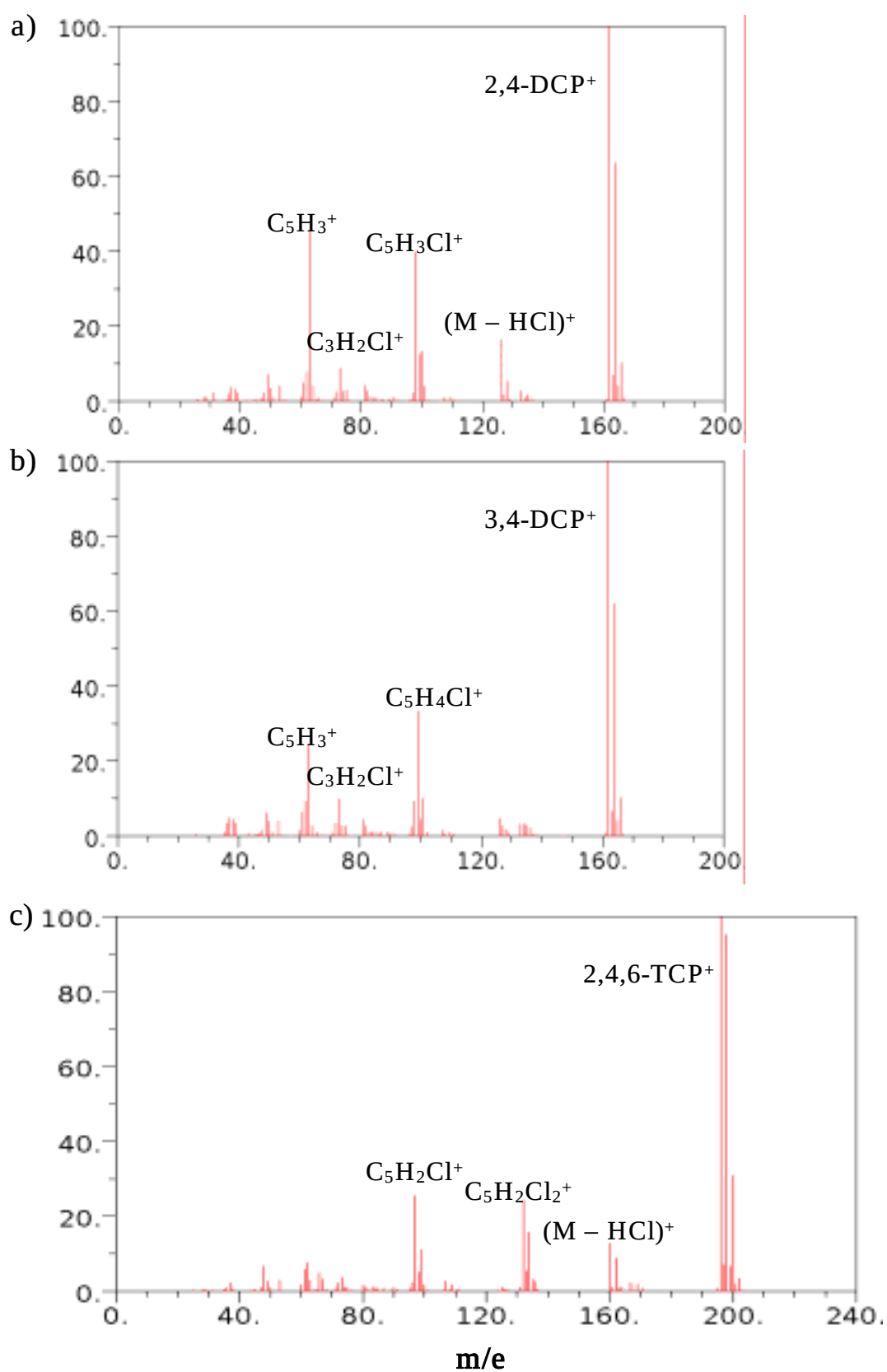


Fig. II-17 The EI mass spectra of a)2,4-DCP, b)3,4-DCP, and c)2,4,6-TCP taken from ref.17.

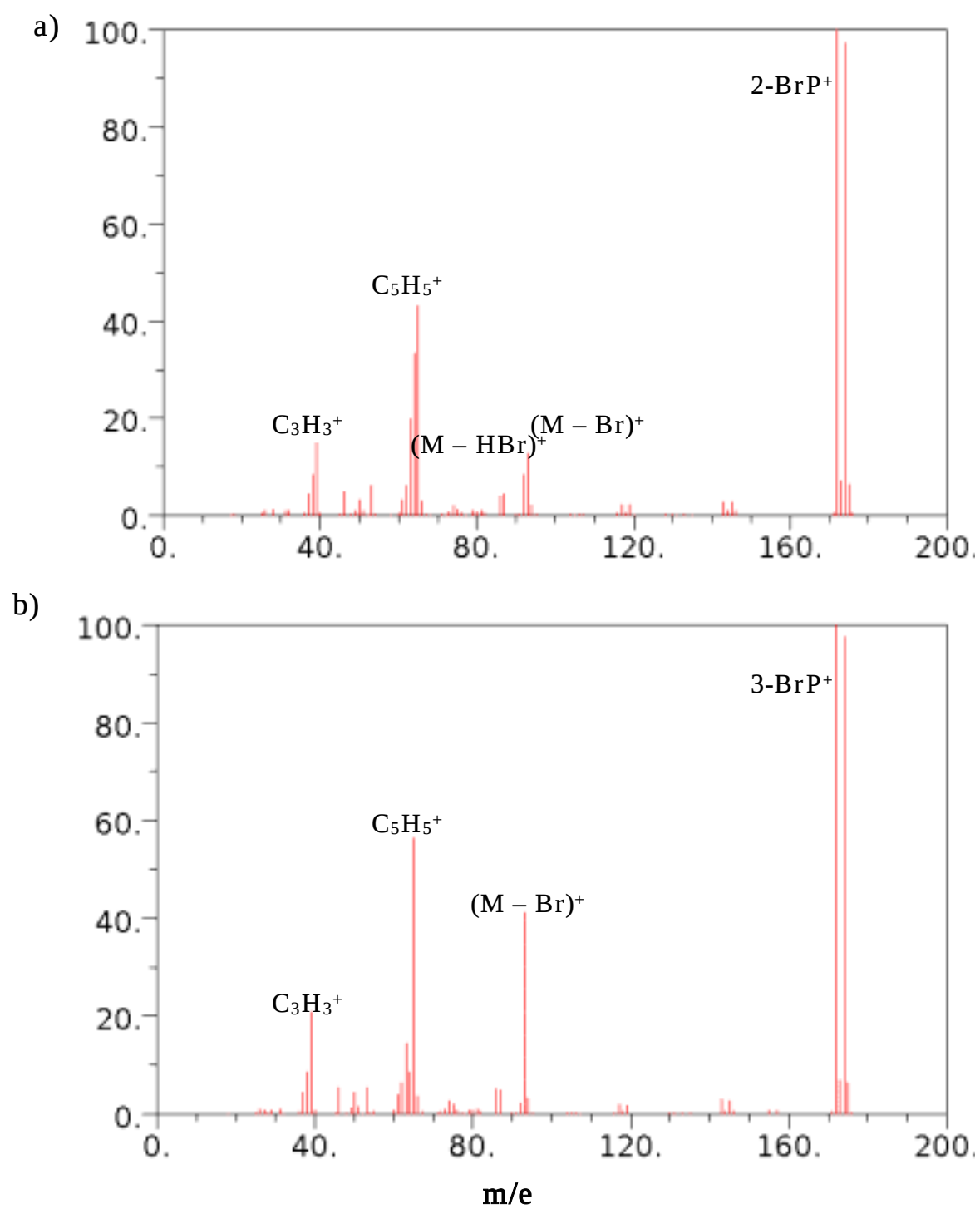


Fig. II-18 The EI mass spectra of a)2-BrP and b)3-BrP taken from ref.17.

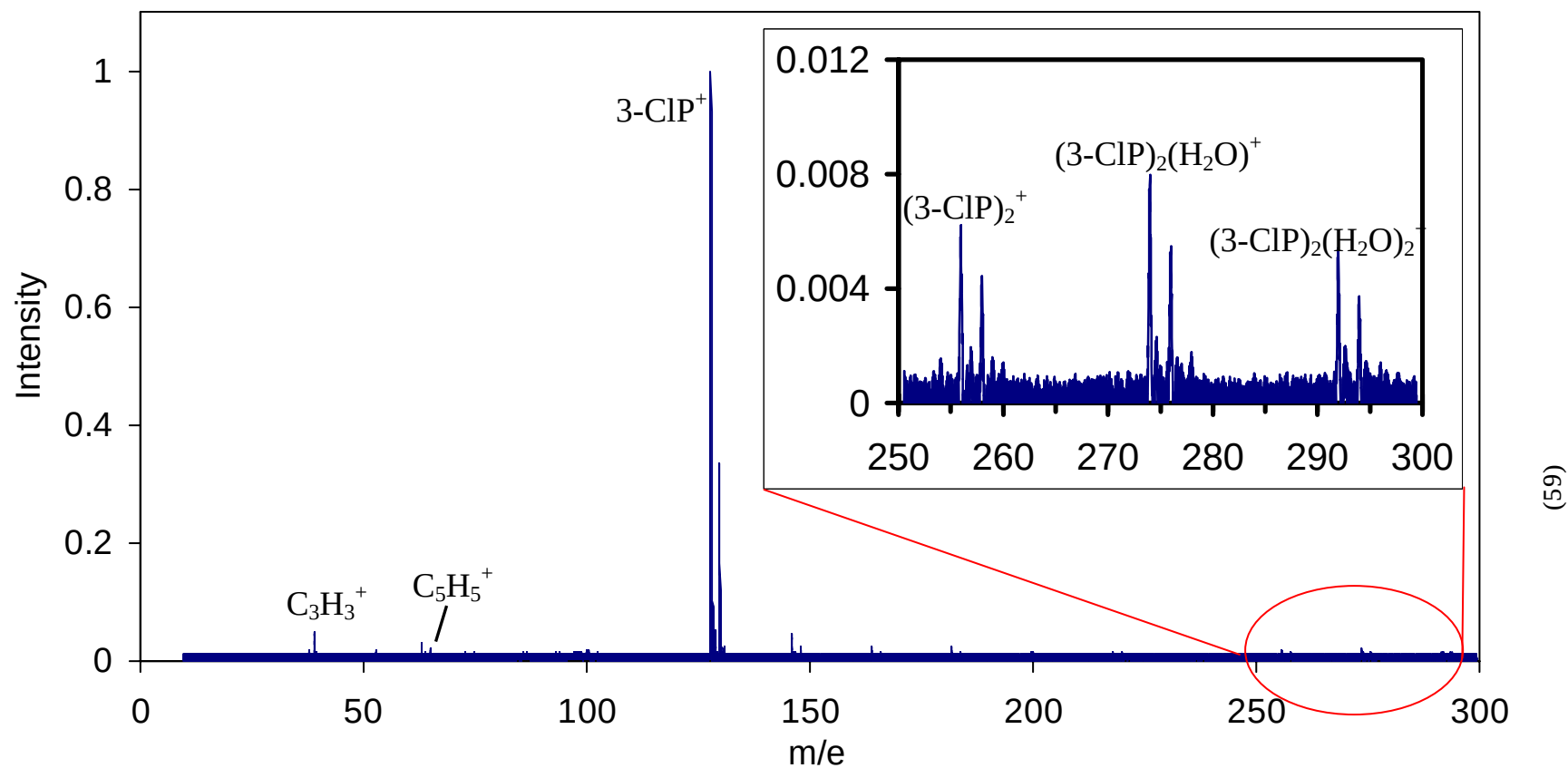
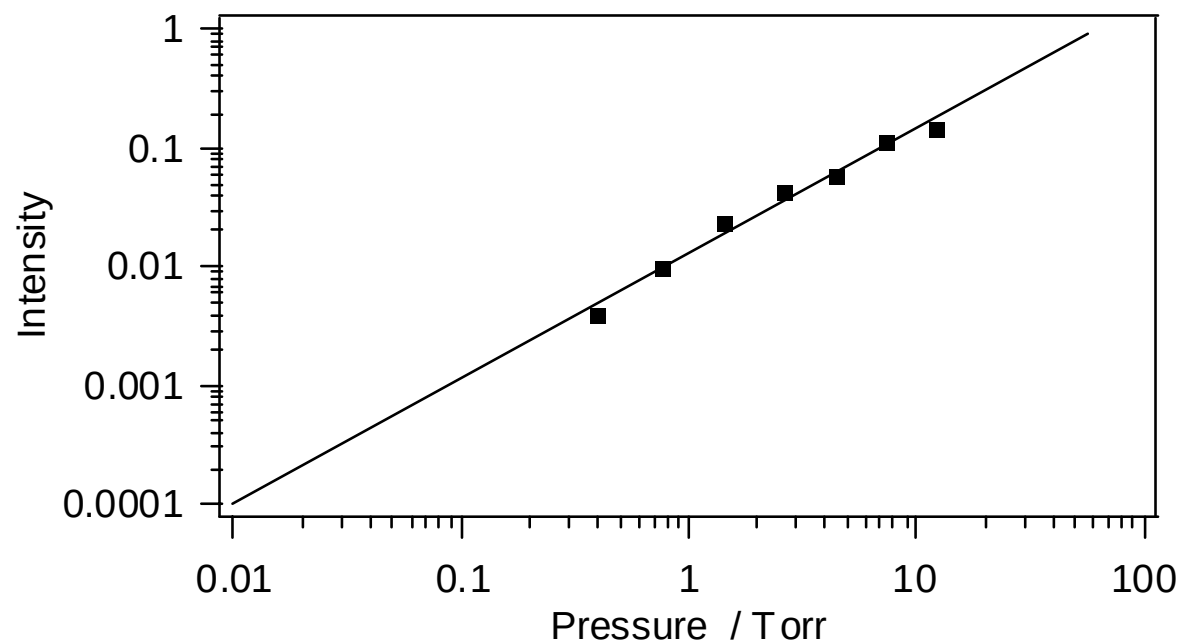


Fig. II-19 TOF mass spectrum for 3-ClP with distillation. The spectrum was observed by the excitation at the origin band of the cis-isomer, where the temperature of the reservoir was at 353 K.



(60)

Fig. II-20 Vapor pressure dependence of the signal intensity for 3-ClP⁺. The signal intensity was observed by the excitation at the origin band of the cis isomer. The backing pressure of Ar was 0.4 atm. and the laser power was 4 μ J/pulse.

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III. Electron attachment to chlorinated phenols

1. Introduction

Electron attachment to halogenated hydrocarbons such as chlorinated phenols is an important and fundamental process in the gas and condensed phases because halogen atoms or halogenated compounds have high electron affinities.¹ In this process, fragment anions and/or parent anions should be produced. There exist some techniques to study electron attachment process, i.e. the flowing afterglow Langmuir probe (FALP) method², the electron swarm (ES) method³, the electron capture detector (ECD) method⁴, the pulse radiolysis microwave cavity (PRMC) method⁵, the electron attachment spectrum (EAS) measurement⁶, and negative chemical ionization (NCI) method⁷. NCI method is a kind of mass spectrometry and it is useful to compare the mass spectrum obtained by NCI method with that by the photon ionization process.

While there are several reports on fluorobenzene derivatives by NCI method, only a few reports about chlorinated phenols are presented. Recently, Deinzer's group have studied the negative ions produced from chlorinated dibenzofurans^{8a} and dibenzodioxins^{8b} with NCI and EAS

techniques. They found that the signal intensity of the fragment ion (Cl^-) increased with increasing the number of chlorine atoms in the molecule. The parent anions were observed for the molecule having more than three chlorine atoms. However, they have not studied on chlorinated phenols yet. Muftakhov et al. have observed the electron attachment spectra of 4-chlorophenol and found fragment ions, Cl^- and $(\text{M} - \text{H})^-$ (M = parent molecule), which were produced when the electrons with energy of 1.0 eV are attached to the molecule.⁹ There is no information on anions produced from electron attachment process for other chlorinated phenols.

In chapter III, the NCI measurement was carried out at the temperature range of 423 K $\sim$ 573 K on various chlorinated phenols (2-ClP, 3-ClP, 3,4-, 3,5-, 2,3-, 2,4-, 2,5-, 2,6-dichlorophenol (DCP), 2,3,4-, 2,4,6-, 2,3,6-, 2,3,5-, 2,4,5-trichlorophenol (TCP)). The reaction mechanism to form fragment anions was also discussed. Furthermore, the optimized structure of the anions was obtained by means of ab initio molecular orbital calculation.

2. Experimental

2-1 Sample preparation

The structure of chlorinated phenols studied in this thesis (2-ClP, 3-ClP, 3,4-, 3,5-, 2,3-, 2,4-, 2,5-, 2,6-dichlorophenol (DCP), 2,3,4-, 2,4,6-, 2,3,6-, 2,3,5-, 2,4,5-trichlorophenol (TCP)) is shown in Fig. III-1. All chlorinated phenols studied in this work and 2-propanol used for the solvent were supplied by Tokyo-Kasei and Wako-Junyaku, respectively, and were used as received. A gas-chromatograph (Shimadzu, GC-14A) was operated in the split mode with a wide-bore capillary column to purify the sample and separate from the solvent. Helium was used for the carrier gas. Samples diluted with 2-propanol were injected 0.4 ~ 1.5 μ l. A single peak from the sample was observed in the chromatogram with no extraneous peaks or interferences.

2-2 Experimental apparatus

2-2-1. Ion source

Fig. III-2 shows the ion-source apparatus for NCI mass spectrometer (Shimadzu, QP-1100EX). Electrons are provided with the filament. The temperature of the ion source is measured with a Pt sensor. Some electrons are collected by the repeller to measure the concentration of electrons and the filament current is controlled to keep the concentration constant. Samples are introduced from the downstream of the filament (× shows the position shown in Fig. III-2) into the ion source chamber through the capillary interface. Electrons, whose energy is 200 eV, are provided and thermalized by collisions with isobutane.

The energy of electrons may be widely distributed. However, to confirm that the energy of the electron is thermalized at the incident temperature, the following experiment was carried out with C_2Cl_4 . It is reported that thermal electron attachment for C_2Cl_4 led to the Cl^- formation.¹⁰ If the intensity of the Cl^- ion from C_2Cl_4 kept constant with changing the flux of isobutane, the electrons should be thermalized. The signal intensities of Cl^- generated from C_2Cl_4 at various fluxes of isobutene

are shown in Fig. III-3. Most electrons should be thermalized at the point indicated by the arrow, where all measurements were performed.

The pressure of the mass analytical tube was monitored by an ion gauge during the measurements. The monitored pressure was kept to be $2.5\text{--}3.0 \times 10^{-5}$ and $1.0\text{--}2.0 \times 10^{-6}$ Torr with and without isobutane, respectively. The main gas in the reaction volume was isobutane and the contribution of nitrogen or oxygen could be neglected. The instrument was tuned using the NCIMS of tris(perfluorobutyl)amine (TPFBA) at 523 K, and the condition was maintained during the measurements.

2-2-2. System control

The temperature of the ion source was controlled by a computer. When the temperature was changed, the ion source chamber was allowed to be equilibrated for 30 $\sim$ 60 minutes. The mass spectra were analyzed by a personal computer. The ion abundance was obtained by summation of all isotopic masses of the ions integrated.

3. Results and Discussion

3.1 NCI mass spectrum

The total ion chromatogram (TIC) and mass spectra at each time were obtained. We can observe ion chromatogram of each ion from TIC. Fig. III-4 shows TIC and mass spectrum at the peak of TIC. Fig. III-5 shows TIC and ion chromatogram of Cl^- ($m/e = 35$), $(\text{M} - \text{HCl})^-$ (the HCl loss from the parent ion, $m/e = 160$), and M^- (= parent ion, $m/e = 196$) obtained for 2,3,4-TCP where the ion source temperature was at 423 K. The longitudinal axes in Fig. III-5 show the ion signal intensity normalized by the most intense peak height. The chlorine atom has two isotopes (^{35}Cl and ^{37}Cl) and its natural abundance is 3 : 1, which is in good agreement with the intensity ratio of the two Cl^- peaks observed in Fig. III-4. Because $(\text{M} - \text{HCl})^-$ and M^- produced from TCP have two and three Cl atoms, the relative isotopic ratio $^{35}\text{Cl}^{35}\text{Cl} : ^{35}\text{Cl}^{37}\text{Cl} : ^{37}\text{Cl}^{37}\text{Cl}$ in the $(\text{M} - \text{HCl})^-$ and $^{35}\text{Cl}^{35}\text{Cl}^{35}\text{Cl} : ^{35}\text{Cl}^{35}\text{Cl}^{37}\text{Cl} : ^{35}\text{Cl}^{37}\text{Cl}^{37}\text{Cl} : ^{37}\text{Cl}^{37}\text{Cl}^{37}\text{Cl}$ in the M^- should be 9 : 6 : 1 and 27 : 27 : 9 : 1, respectively. The relative signal intensities between the isotopes for $(\text{M} - \text{HCl})^-$ and M^- in Fig. III-4 are well coincident with the expected isotopic ratio except for $^{37}\text{Cl}^{37}\text{Cl}$ of $(\text{M} - \text{HCl})^-$ and $^{37}\text{Cl}^{37}\text{Cl}^{37}\text{Cl}$ of M^- , whose signal intensity

was too low to be observed.

Signal intensity of each ion was linearly proportional to the quantity of the sample injected ($0.6 \sim 1.5 \mu\text{l}$) as plotted in Fig. III-6. The intensity of each ion per 10^{-7} mol of the sample was calculated by the least-squares method. Thus, the branching ratio of each ion was obtained as the relative ratio of the ion intensity per 10^{-7} mol of the sample molecule. The temperature of the ion source chamber was changed and the signal intensity of the ions was measured by the same method.

To check whether the temperature of the sample molecule was the same as that of the electrons, the temperature of the capillary interface was changed. The temperature of the interface was kept to be at 100 K lower than that of the ion source. If the sample gas was lead through the interface at a lower temperature and was not heated enough in the ion source chamber, the intensity and the relative ratio of the ions should be influenced. The intensity and the relative ratio of ions did not change, showing that the temperature of the electrons should be almost the same with that of the sample molecules in the reaction chamber.

The mainly observed ion was Cl^- for all compounds studied by NCI

mass spectrometer. The signal intensity of the Cl^- ion increased with increasing the number of the Cl atom involved in the molecule. It is the same result as the case of chlorinated alkanes and alkenes,⁷ halogenated benzenes,¹¹ and chlorinated dibenzofurans^{8a} and dibenzodioxins.^{8b} For chlorinated hydrocarbons, Cl^- should be produced by dissociative electron attachment process shown in Fig. I-2a. The location of the repulsive potential becomes relatively lower with increasing the number of chlorine atoms in the molecules. Therefore, the crossing point of the repulsive potential of the anion and the potential curve of the neutral molecule becomes lower. In consequence, Cl^- was found to be produced by thermal electron attachment, like CCl_4 .

The signal intensity of Cl^- increased in the order of 2,3,4- < 2,4,5- < 2,3,5- < 2,3,6- $\sim$ 2,4,6-TCP, 3,4- $\sim$ 2,5- < 2,4- < 2,6 < 2,3- $\sim$ 3,5-dichlorophenol (DCP), and 3- < 2-chlorophenol (2-ClP). $(\text{M} - \text{HCl})^-$ and $(\text{M} - \text{H})^-$ (the H loss from the parent ion) were also observed for TCP and DCP. The signal intensity of $(\text{M} - \text{H})^-$ was not large and the branching ratio, $[(\text{M} - \text{H})^-]/[\text{Cl}^-]$, was less than 0.05 for all the chlorinated phenols. The signal intensity of $(\text{M} - \text{HCl})^-$ increased in the order of 2,3,4- < 2,3,6- $\sim$ 2,4,6- <

2,3,5- , 2,4,5-TCP and 2,4- < 2,5- $\sim$ 2,6- < 3,4- < 2,3- < 3,5-DCP, though the branching ratio, $[(M - HCl)^-]/[Cl^-]$, was less than 0.05 for 2,4- and 2,6-DCP.

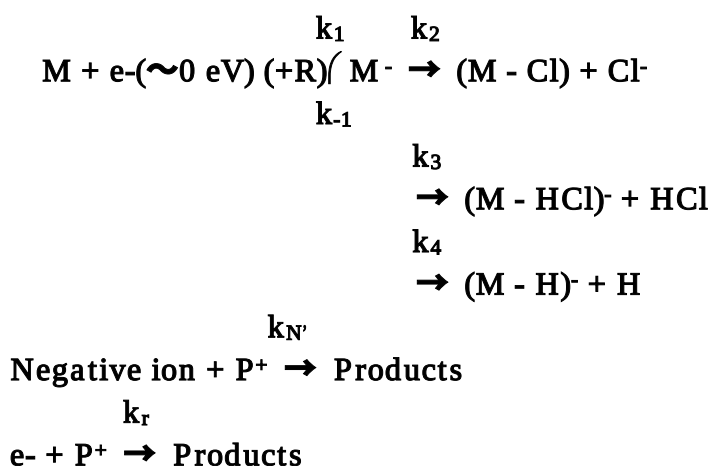
For 2,3,4- and 2,4,5-TCP, M^- was observed at lower temperature than 523 K. The branching ratio of $M^-/[Cl^-(M - HCl)^-]$ became greater than 0.05 at the lower temperature than 473 K. For the other TCPs, M^- was observed at lower than 473 K and no M^- was observed for DCP, 2-ClP and 3-ClP. The result that the parent anions were observed for the molecule having more than three chlorine atoms, is similar to chlorinated dibenzofurans and dibenzodioxins.⁸ The electron affinity of these chlorinated compounds increases with increasing the number of chlorine atoms in the molecule. The signal intensity of the fragment ions, Cl^- and $(M - HCl)^-$, increased with increasing temperature, while that of the parent anion decreased. The decreasing ratio of the parent ions is larger than the increasing ratio of the fragment ions. This result agrees with that of C_6F_5X ($X = Cl, Br, I$).¹¹ Dissociative electron attachment and electron detachment from the parent anion will occur competitively at higher temperature.

Cl^- was the only observed ion for 2-ClP and 3-ClP at the same concentration of the sample as the other chlorinated phenols. $(M - H)^-$ was

also observed at the higher concentration, though the branching ratio of (M - H)⁻/Cl⁻ was smaller than 1/1000. The signal intensity of the Cl⁻ from mono chlorinated phenol was less than 1/100 for TCP and 1/10 for DCP. Muftakhov et al. measured the electron attachment spectra of 4-ClP and reported that the fragment anions, Cl⁻, and (M - H)⁻ were produced from the electron attachment process with energy of around 1.0 eV, which is more than ten times larger than thermal energy (0.05 ~ 0.07 eV in this study).⁸ Thermal electron attachment would not occur for 2-ClP and 3-ClP as the same as 4-ClP.

3.2 Reaction mechanism

Chlorinated phenols would react with electrons as follows,



where P^{+} is a positive ion and R is the reagent gas.

The sample gas should be spread over the ion source chamber ejected from the capillary interface. Electrons were constantly provided from the filament. We can assume a steady state condition of electrons supplied by the ion source just like radiolysis in a cell. When electrons whose energy was 200 eV were thermalized by collisions with isobutane, positive ions of isobutane were produced at high concentration of isobutane. The monitoring pressure at the mass analytical tube did not increase by the introduction of the sample molecules, indicating that the concentration of

the sample should be less than that of isobutane. Therefore, the concentration of electrons and positive ions of isobutene should be much greater than that of the negative ions produced from the sample. The concentration of positive ions and electrons would be kept to be constant during the measurement. These assumptions lead to the results that $k_N[P^+] = k_N = \text{constant}$ and that the rate (k_r) of the electron-ion recombination reaction should be maintained constant during the measurement.

The instrumental constant includes the interaction volume, ion draw-out efficiency, ion lens and mass spectrometer transmission efficiencies and ion detection efficiency of the electron multiplier. If measurements are carried out with the same experimental setup, the ion lens and mass spectrometer transmission efficiencies or ion detection efficiency should be the same for all measurements. However, the absolute value of ion draw-out efficiency would depend on the kind of the sample. When ions with higher translational energy would be produced, they could not be focused as well as the same kind of ions with lower energy.¹² Because I discuss the branching ratio of $[(M - HCl)]/[Cl^-]$ and the production

mechanism of each fragment ion would not largely differ among DCPs and TCPs, the relative difference in the ion draw-out efficiency and the instrumental constants should be regarded as almost the same for all the compounds studied.

The reaction rate constant should be described as $k=A\exp(-E/RT)$, where A is pre-exponential factor and E is apparent activation energy. Therefore, the branching ratio of the fragment ions, $[(M - HCl)^-]/[Cl^-]$, can be expressed as,

$$[(M - HCl)^-]/[Cl^-] \propto A_3/A_2 \exp(-(E_3-E_2)/RT),$$

where A_2 and A_3 are pre-exponential factors, E_2 and E_3 are activation energies for the reaction generating Cl^- and $(M - HCl)^-$, respectively. Figs. III-7 and 8 show the temperature dependence of the branching ratio of $[(M - HCl)^-]/[Cl^-]$ for TCP and DCP, respectively. The slope of the plot should depict the difference between the activation energy of the reaction to produce $(M - HCl)^-$ and that for Cl^- , (E_3-E_2) . The intercept means the ratio of the Arrhenius pre-exponential factor for the formation of $(M - HCl)^-$ and Cl^- , A_3/A_2 . Table III-1 lists the values of (E_3-E_2) and A_3/A_2 obtained from Figs. III-7 and 8. For TCP, the value of (E_3-E_2) is found to be almost the same,

revealing that the activation energy of the reaction intermediate leading to $(M - HCl)^-$ should be almost the same for TCPs. The relative production ratio is related to A_3/A_2 . The A_3/A_2 value becomes larger in the order of $2,3,4- < 2,3,5- \sim 2,4,6- < 2,4,5- \sim 2,3,6-$ -TCP.

Fig. III-9 represents the temperature dependence of the branching ratio of $M^-/[Cl^- + (M - HCl)^-]$ for 2,3,4- and 2,4,5-TCP. Though the branching ratio of 2,4,5-TCP was lower than that of 2,3,4-TCP, the trend in the temperature dependence of the branching ratio between them is almost the same. This means that the parent anions should dissociate into fragment ions with almost the same probability for the two TCPs. $M^-/[Cl^- + (M - HCl)^-]$ extrapolated at 300 K in Fig. III-9 for 2,3,4- and 2,4,5-TCP was estimated to be greater than 20, indicating that the relative intensity of parent anions (M^-) should be 20 times larger than that of fragment ions (Cl^- and $(M - HCl)^-$) and the parent anions should exist relatively stable at room temperature.

3.3 Dynamics of HCl elimination

The A_3/A_2 value in Table III-1 shows that the amount of $(M - HCl)^-$ is several times larger than that of Cl^- at the high-temperature limit. Moreover, the value of A_3/A_2 depends on the molecule. For TCP, the reaction dynamics of the intermediate leading to $(M - HCl)^-$ will be similar, because the value of $E_3 - E_2$ is almost the same. The expected structure of the common intermediate for the HCl elimination from TCPs should be the loss of hydroxylic hydrogen and the ortho-Cl. The H atom loss and the Cl atom loss should not occur separately because the signal intensities of $(M - H)^-$ and $(M - Cl)^-$ were much lower than that of $(M - HCl)^-$. The most appropriate mechanism for the HCl elimination should be the HCl molecular loss of the hydroxylic hydrogen atom and the ortho-Cl atom. It is expected that similar mechanism will take place to produce $(M - HCl)^-$ for 2,3-, 2,5-, and 2,6-DCP, which possesses the ortho-Cl atom. On the other hand, the HCl elimination of the hydroxylic hydrogen and the ortho-Cl cannot occur for 3,4- and 3,5-DCP, of which molecules do not possess the ortho-Cl atom. Otherwise, not only formation of $(M - HCl)^-$ was observed for 3,4- and 3,5-DCP, but also the branching ratio of $[(M - HCl)^-]/[Cl^-]$ became greater

than those of 2,4-, 2,5-, and 2,6-DCP.

To interpret these phenomena, I propose the process in which the hydroxylic hydrogen atom can migrate to the ortho position to produce $C_6Cl_2H_4O^-$, the cyclohexadienone type anion. Subsequently, the elimination of the H atom at the ortho location and the Cl atom at the meta position will take place. The mechanism should be similar for 3,4- and 3,5-DCP, because the value of E_3-E_2 is almost the same. The value of A_3/A_2 for 3,5-DCP is two times larger than that of 3,4-DCP. This means that the probability for the elimination of HCl based on the H atom migration should be twice larger than that for 3,5-DCP. For 3,4-DCP, two rotational isomers (cis and trans) exist and in the trans isomer the subsequent HCl elimination with the hydroxylic H atom migration cannot occur. This is reasonable from the experimental result.

To estimate the reactivity for the production of $(M - HCl)^-$, I have calculated the structure of the intermediates for both reaction processes by the Gaussian98 program.¹³ The structure of the parent anions was also calculated for comparison. B3LYP/D95 method was used to optimize the structures. It was found that the parent anions should have structures of

out-of-plane deformation at the hydroxylic hydrogen atom for all chlorinated phenols.

For the case of the HCl molecular elimination, the ortho-Cl atom is situated nearer to the hydroxylic hydrogen atom than the neutral molecule. I can postulate that the nearer the ortho-Cl is to the H atom, the easier the HCl elimination occurs. The bond length between the ortho-Cl and the hydroxylic hydrogen is listed in the far right column of Table III-1. The value becomes greater in the order of 2,4,5- < 2,3,5- < 2,3,6- < 2,4,6- < 2,3,4- for TCP and 2,5- < 2,6- < 2,3- for DCP. The result almost corresponds to the order of the value A_3/A_2 of TCP and DCP, that is, the branching ratio of $[(M - HCl)]/[Cl]$ is larger and the bond length of H-Cl is the shortest for 2,4,5-TCP and 2,5-DCP among the derivatives. On the other hand, the branching ratio of $[(M - HCl)]/[Cl]$ is the smallest and the bond length of H-Cl is the longest for 2,3,4-TCP and 2,3-DCP among the derivatives. The hydrogen bonding between the hydroxylic hydrogen atom and the ortho-Cl is studied by comparison of the fluorescence excitation spectrum and REMPI excitation spectrum measurements of 2-ClP.¹⁴ As described in the previous section of II-3, HCl elimination from chlorinated phenol cation possessing the ortho-Cl

atom was also observed by EI method. It is reasonable that the HCl elimination from the hydroxylic hydrogen atom and the ortho-Cl atom should take place for chlorinated phenol anions.

For 3,4- and 3,5-DCP, the structure of the intermediate, the cyclohexadienone type anion, was optimized by the molecular orbital calculation. The energy of the intermediate was less than that of the parent anion for both molecules. This suggests that the HCl elimination through the cyclohexadienone type anion should be appropriate for 3,4- and 3,5-DCP. On the contrary, unimolecular HF and HCl loss from fluorinated phenol cation¹⁵ and chlorinated phenol cation¹⁶ was observed by the mass-analyzed ion kinetic energy (MIKE) spectrometry. The ring-walk mechanism of the fluorine and the chlorine atom was proposed. The activation energy of the chlorine atom ring-walk from 3-ClP⁺ was calculated to be approximately 2.1 eV.

However, we cannot optimize the structure obtained by the ring-walk chlorine atom mechanism in the case of chlorinated phenol anions. Moreover, the calculation suggests that the chlorinated phenol anions should have out-of-plane deformed structure of the hydroxylic hydrogen atom, as

described previously. The result reveals that the migration of the hydroxylic hydrogen in the chlorinated phenol anion should take place easily to give rise to the HCl elimination.

Table III-1. The difference between the activation energy of the production of (M-HCl)⁻ and Cl⁻: (E₃-E₂), the ratio of the Arrhenius pre-exponential factor: A₃/A₂, and the bond length between the ortho-Cl and the hydroxylic H atom.

	E ₃ -E ₂ ^{a)} /eV	A ₃ /A ₂ ^{b)}	r(H-Cl) ^{c)} /Å
2,4,5-TCP	0.159±0.004	17.4±0.17	2.029
2,3,5-TCP	0.150±0.007	8.19±1.55	2.041
2,3,6-TCP	0.205±0.013	18.0±4.0	2.048
2,4,6-TCP	0.177±0.017	8.52±2.5	2.052
2,3,4-TCP	0.165±0.013	7.59±2.23	2.056
2,5-DCP	0.215±0.004	11.2±1.72	1.993
2,6-DCP	0.180±0.004	2.99±0.37	2.007
2,3-DCP	0.105±0.003	1.97±0.25	2.034
3,4-DCP	0.060±0.001	0.95±0.20	-
3,5-DCP	0.060±0.001	2.21±0.52	-

a)The difference between the activated energy of the production of (M-HCl)⁻ and Cl⁻

b)The ratio of the Arrhenius parameter for (M-HCl)⁻ formation and for Cl⁻ formation

c)The bond length between the ortho-Cl and the H atom of -OH.

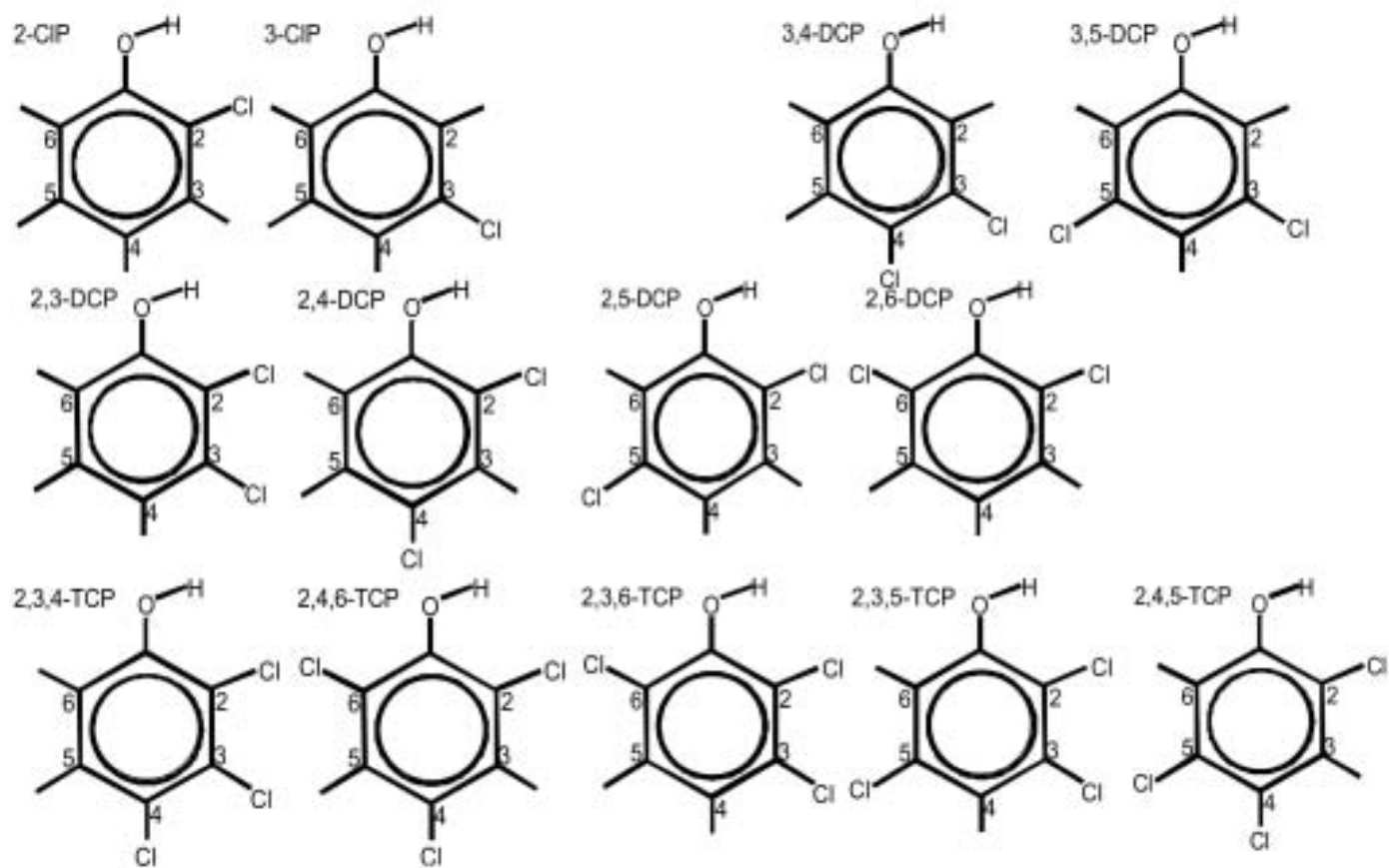


Fig. III-1 Structures of chlorinated phenols studied in this work.

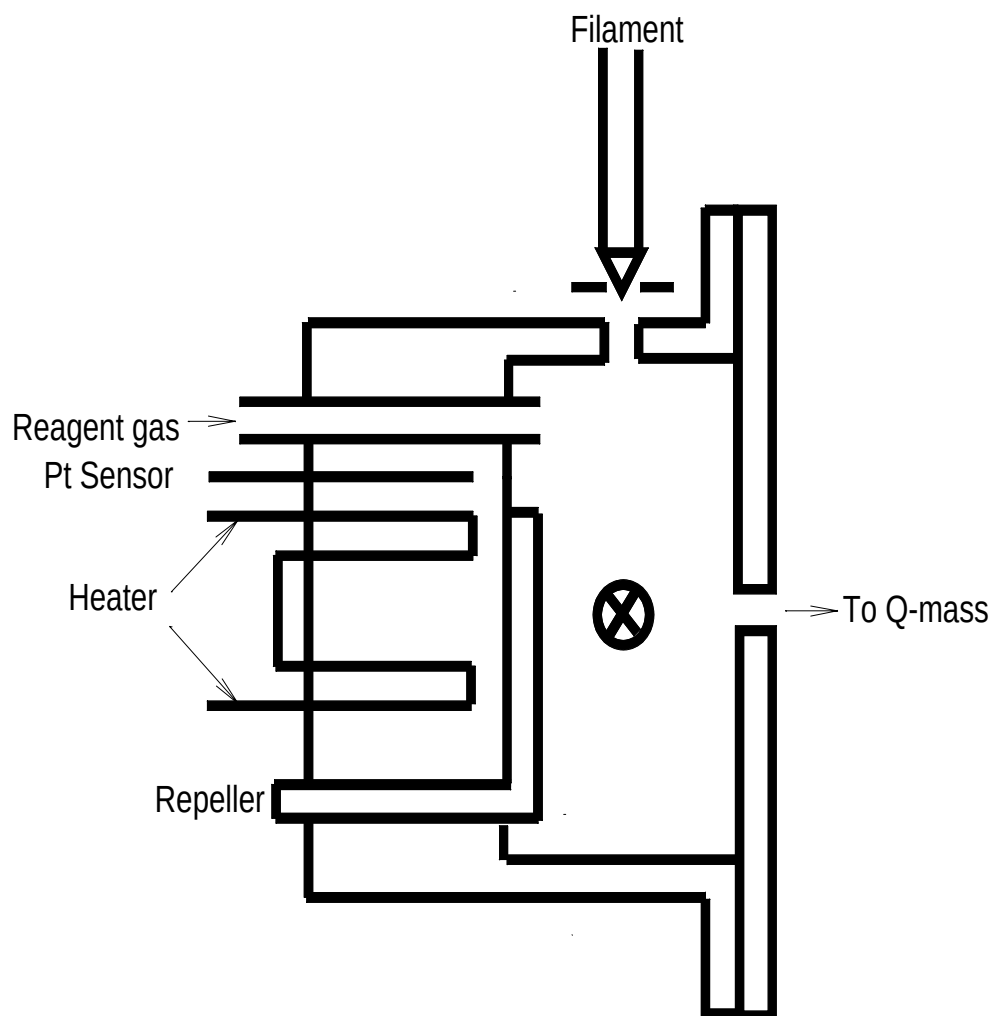


Fig. III-2 The schematic diagram of the ion-source apparatus. Electrons are provided with the filament. The temperature of the ion source is measured with a Pt sensor. Some electrons are collected by the repeller to measure the concentration of electrons and the filament current is controlled to keep the concentration constant.

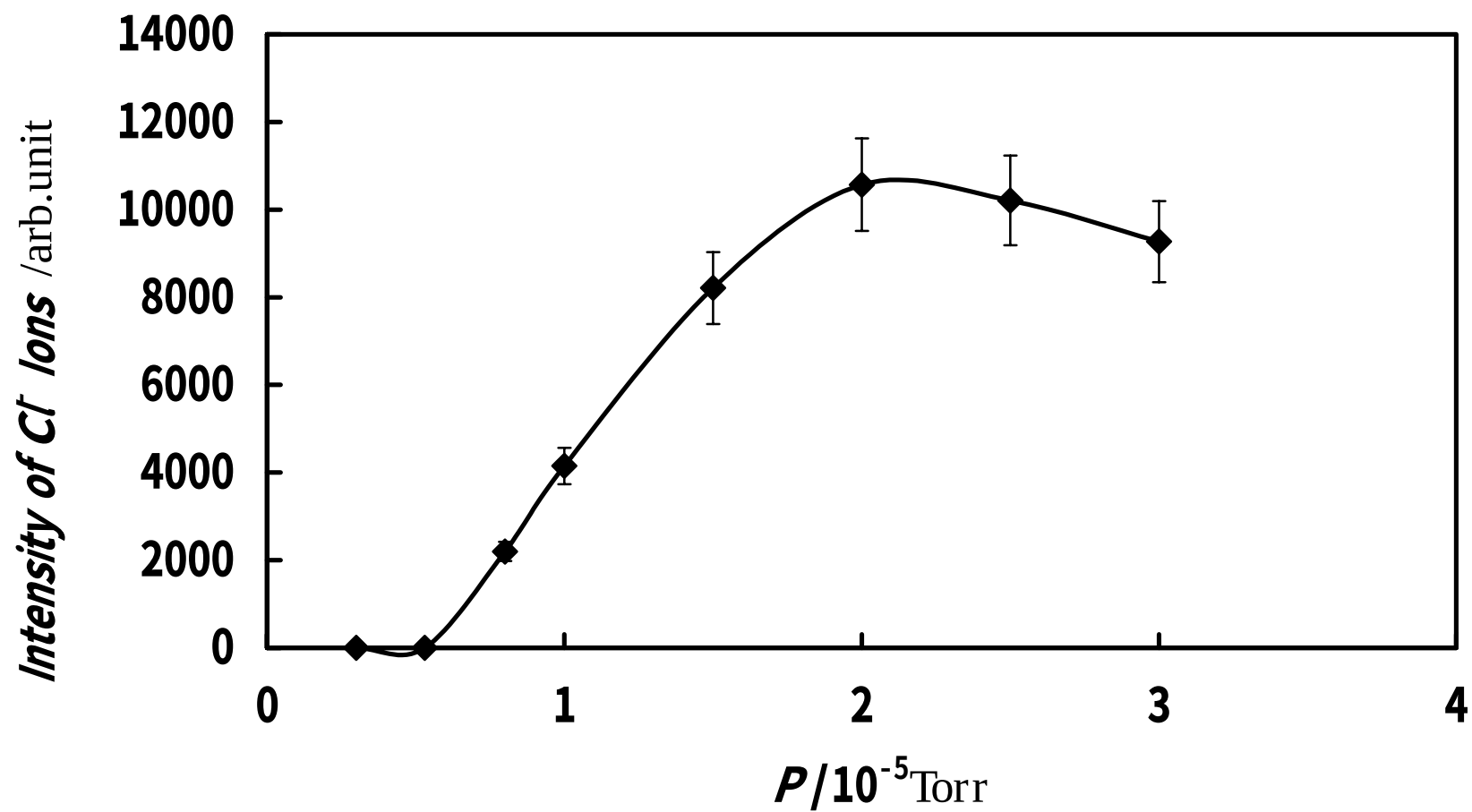


Fig. III-3 Plots of the signal intensity of Cl^- generated from C_2Cl_4 against the pressure of the reagent gas (isobutene).

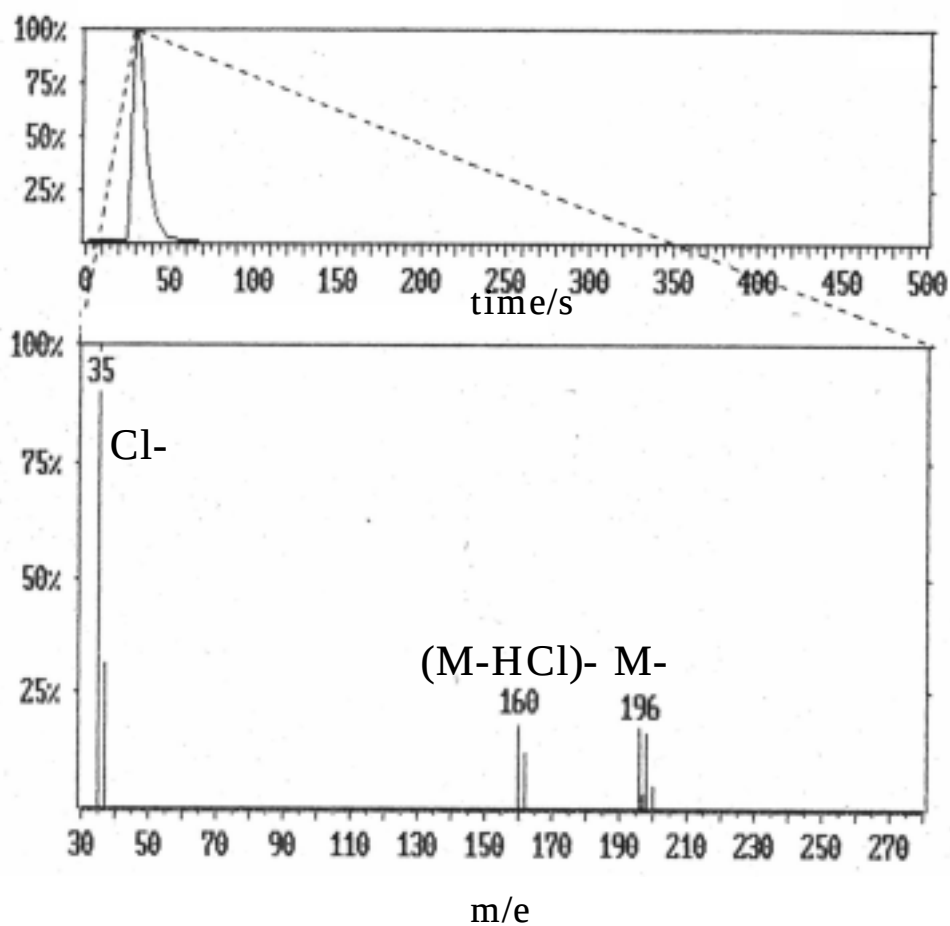


Fig. III-4 Total ion chromatogram (TIC) and negative chemical ionization (NCI) mass spectrum at the peak of TIC for 2,4,5-TCP. The spectrum was measured with the ion source temperature of 423 K.

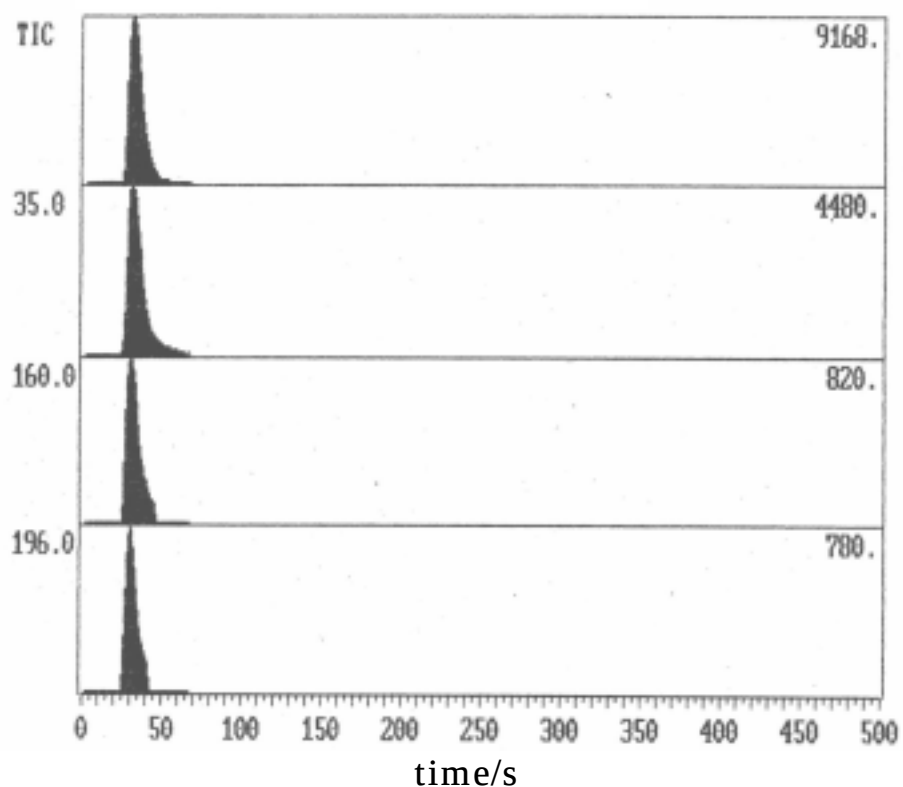


Fig. III-5 Total ion chromatogram (TIC), ion chromatogram of Cl^- ($m/e=35$), ($\text{M} - \text{HCl}$) (M =parent molecule, $m/e=160$), and M^- ($m/e=196$) for 2,4,5-TCP. The signal intensity was measured at 423 K. The longitudinal axes show the ion signal intensity normalized by the peak height.

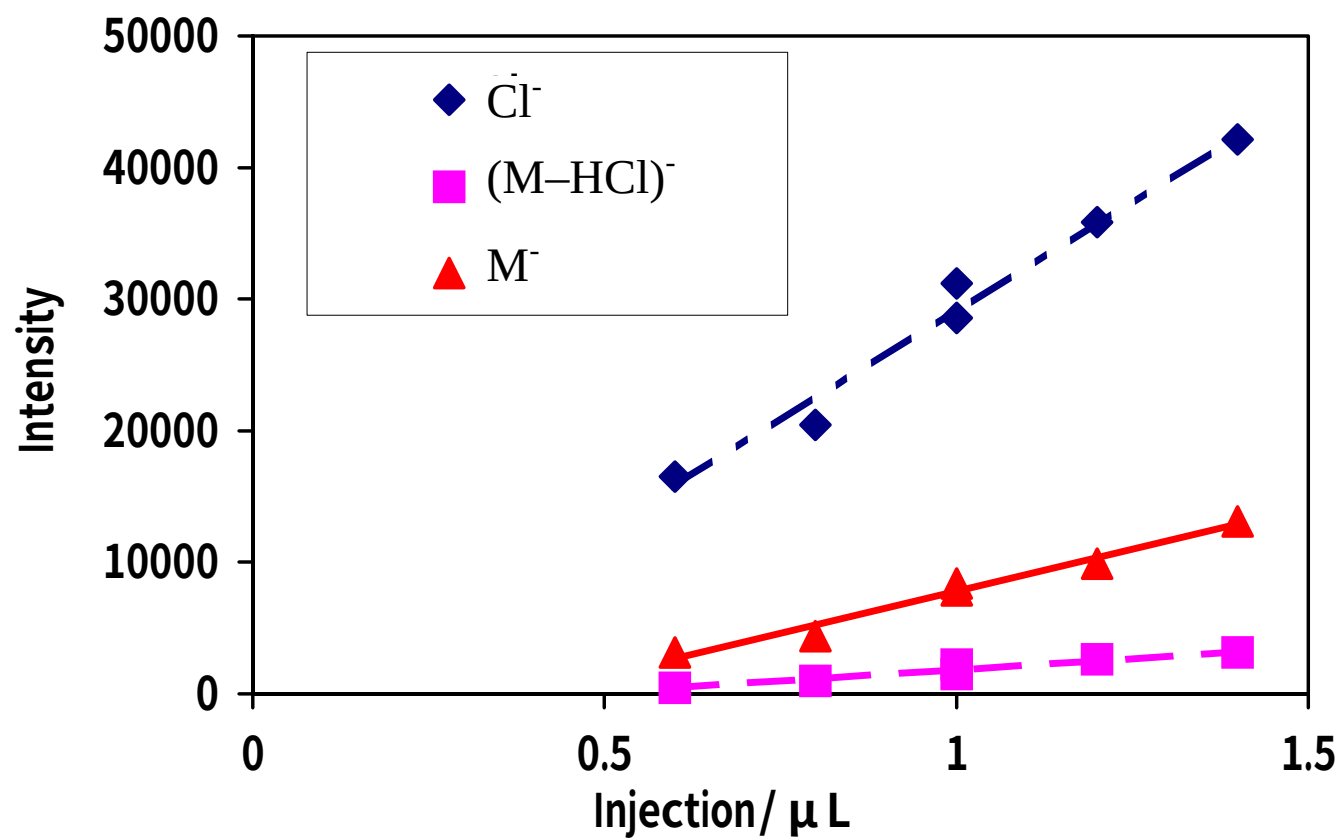


Fig. III-6 Plots of ion intensities against the injection quantity: Cl^- , $(\text{M} - \text{HCl})^-$ (M =parent molecule), and M^- for 2,3,4-TCP. The ion intensity was observed with the ion source temperature of 423 K.

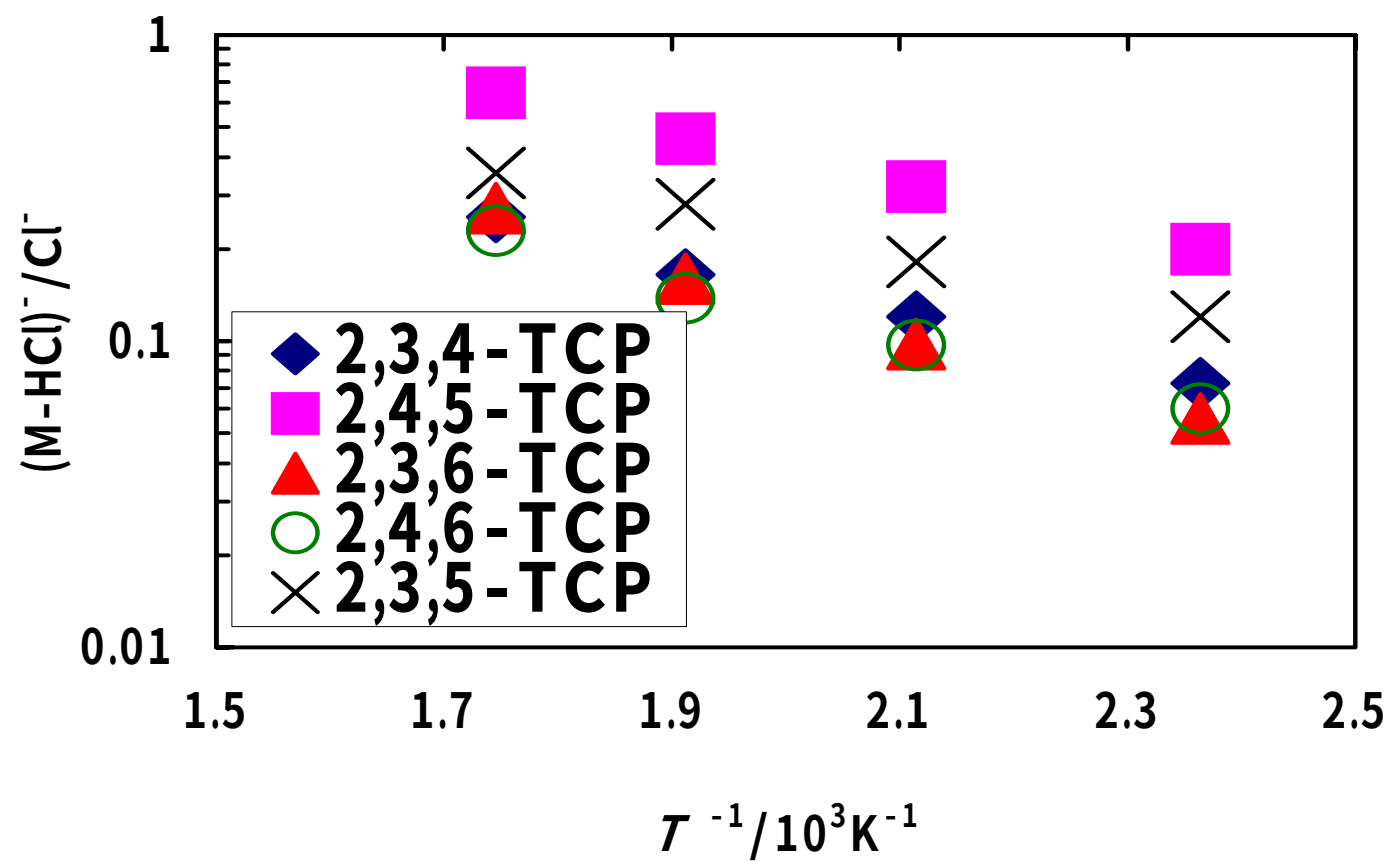


Fig. III-7 The temperature dependence of the branching ratio of (M - HCl)/Cl⁻ for various TCP derivatives.

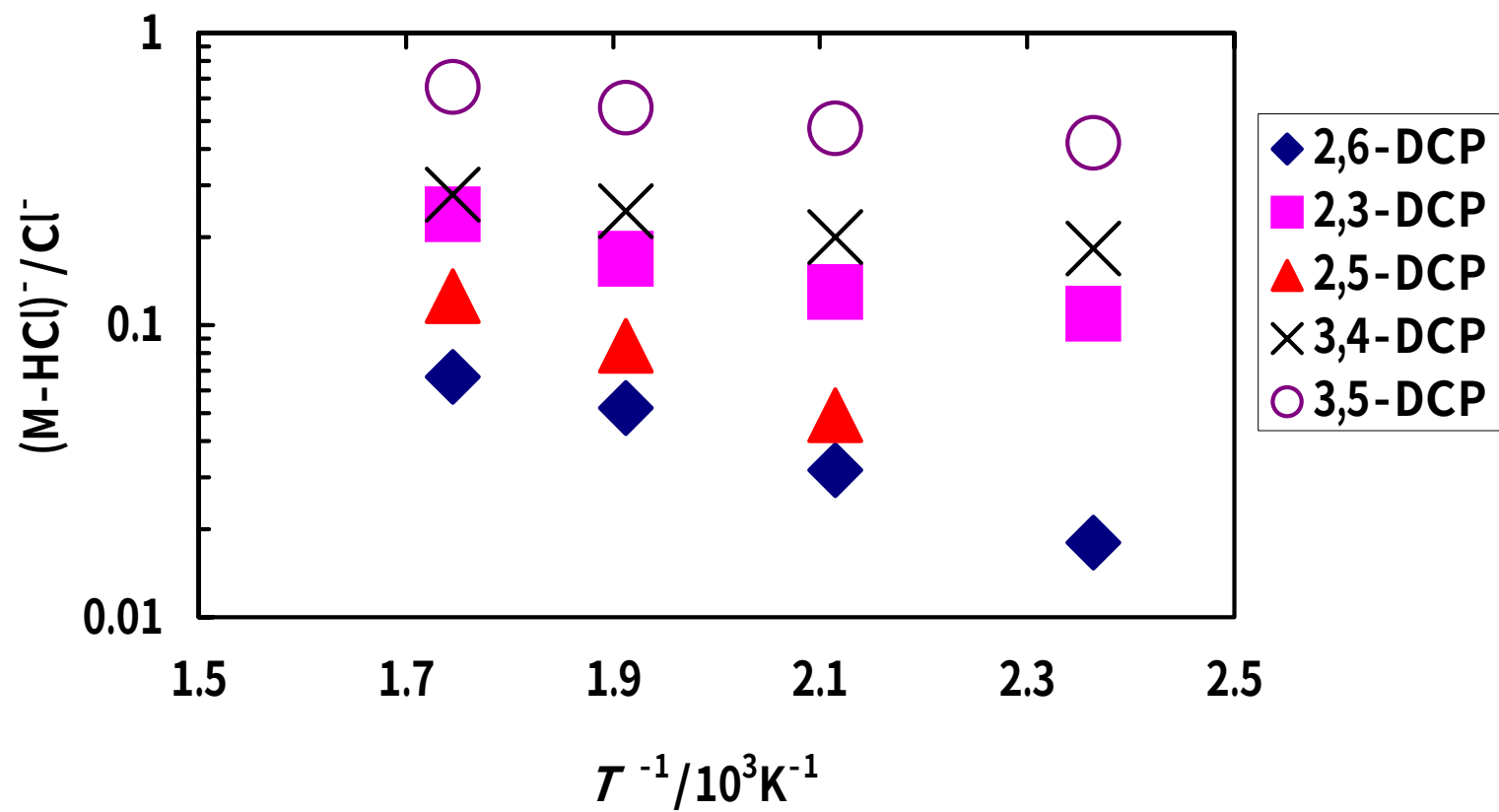


Fig. III-8 The temperature dependence of the branching ratio of $(\text{M} - \text{HCl})^-/\text{Cl}^-$ for various DCP derivatives.

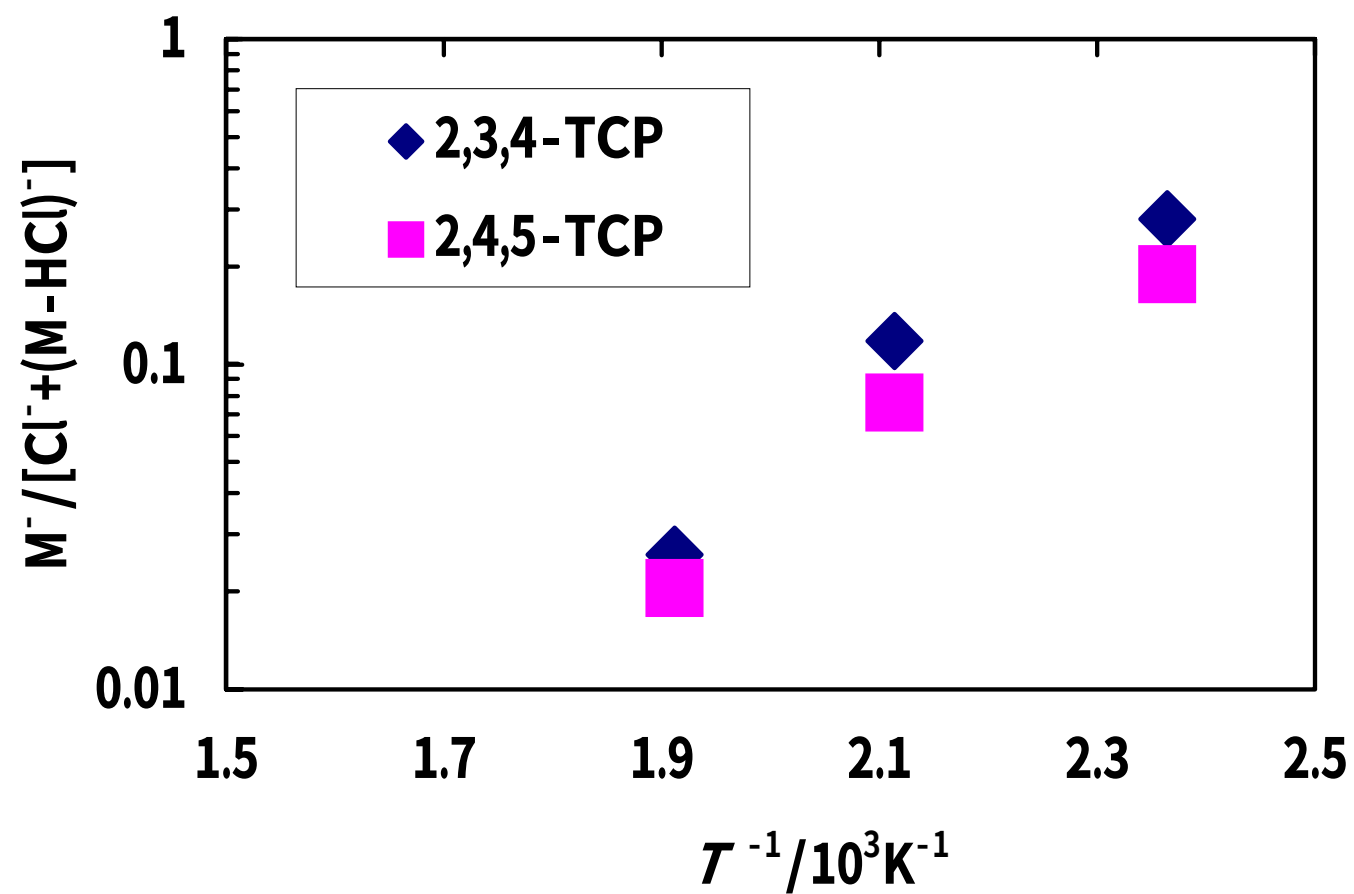


Fig. III-9 The temperature dependence of the branching ratio of $M^-/[Cl^-+(M-HCl)^-]$ for 2,3,4- and 2,4,5-TCP.

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IV. Comparison of REMPI and NCI measurements

1. Fragmentation mechanism

Both the Cl elimination and the CO elimination occur for the three-photon ionization process due to the excess energy of 4.5 eV for 3-ClP⁺. Only parent cations were observed with the lower laser power, indicating that the excess energy (0.2 eV) of two-photon ionization should be insufficient for either elimination.

On the other hand, the cleavage of the C-Cl bond takes place by thermal electron attachment for almost halogenated phenol anions studied. For the latter case, it suggested that the energy of the C-Cl bond should decrease by the resonant interaction of the unoccupied molecular orbitals (MO) and the excess electron, when the thermal electron approaches to the molecule. For example, it is known that the single occupied MO (SOMO) of C₆F₆⁻, which corresponds to the lowest unoccupied MO (LUMO) of C₆F₆ with π^* character, becomes the σ - π conjugated orbital.¹

The MOs of the cation and the anion of 3-ClP were calculated by Gaussian98 program with B3LYP/D95 method.² The obtained MOs are shown in Fig. IV-1. For the cation, the antibonding of the C-Cl is found to

be the orbital of LUMO+2. On the other hand, the LUMO has the character of the antibonding of the C-Cl for the anion. It is the evidence that the energy level of the $\sigma^*(\text{C-Cl})$ orbital in the anion decreases rather than that in the cation for chlorinated phenols.

The cyclohexadienone type intermediate produced through the hydroxylic hydrogen transfer to the ortho position was postulated for the HCl elimination from the anion of 3,4- and 3,5-DCP. As described in the previous chapter written about the HCl loss from 2-ClP⁺, the HCl elimination from the chlorinated phenol anion, which possesses the ortho-Cl atom, maybe take place before the hydroxylic hydrogen transfer to form the cyclohexadienone type intermediate. On the other hand, it is suggested that the cyclohexa-2,4-dienone isomer should be produced as the intermediate of the CO loss from the phenol cation.³ The similar type isomer can be expected for the CO loss from the chlorinated phenol cation. The process and the structure of the intermediate for the HCl loss from the anion and the CO loss from the cation will be similar.

2. Detection limit

The detection limit of chlorinated phenols for the analytical use is discussed by comparing of REMPI-TOF technique in a super sonic jet and NCI spectrometry. The signal intensity of REMPI is proportional to the absorption coefficient of the molecule. The signal intensity will be much larger if water clusters are not present in a supersonic jet. We must use the two-color two-photon ionization technique and keep the sample temperature to be higher than 373 K to avoid the production of the water clusters for the measurement of chlorinated phenols with more than two chlorine atom substituents.

On the other hand, the electron affinity of the molecule is important for NCI method. The detection efficiencies for trichlorophenols are about 100 times larger than mono-chlorinated phenols.

The efficiency and the condition of each measurement may be different for the detection of each sample. It is necessary to use the most adequate measurement for the detection of the substance.

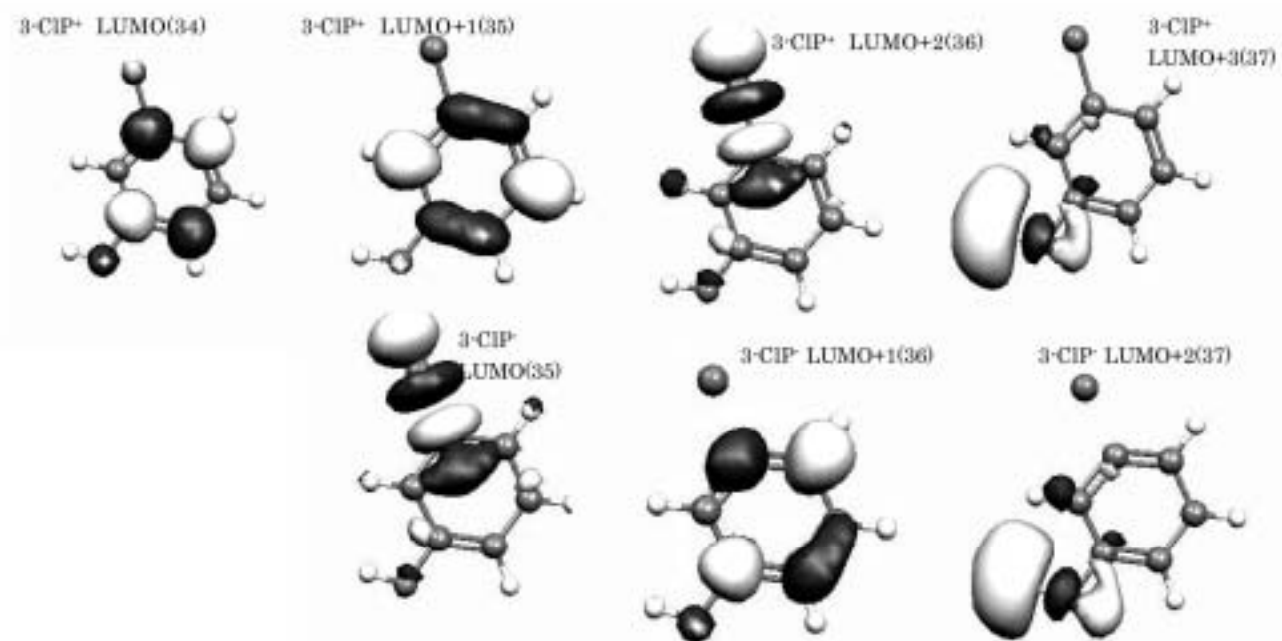


Fig. IV-1 The unoccupied molecular orbital for the cation and the anion of 3-ClP.

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V. Conclusion

Resonant enhanced multiphoton ionization (REMPI) excitation spectra of jet-cooled 3-chlorophenol (3-ClP) were measured with time-of-flight (TOF) mass spectrometry. The REMPI-TOF excitation spectra of the parent ion (3-ClP⁺) well corresponded to the ion current spectrum reported. Some new bands observed in the spectra were assigned with the aid of CIS and DFT calculations. In the TOF mass spectra, 3-ClP-water cluster cation and fragment ion as well as the parent ion were observed. The main fragment ion was C₃H₃⁺ produced through the S₁ state of the parent molecule. When the vapor pressure of the sample in the reservoir was increased, the dimer cation was also observed. The dimer cation was supposed to be produced from the dehydration of the dimer-water cluster cations due to their excess energy. The detection limit of the 3-ClP pressure was estimated to be in the order of ppm at the backing pressure of 0.4 atm Ar and the laser power of 4 μJ/pulse.

The temperature dependence of the formation of negative ions from chlorinated phenols was studied using negative chemical ionization mass spectrometry. For all compounds, Cl⁻ was produced and the intensity of the

Cl^- increased with increasing the number of Cl atoms possessed in the molecule. For some chlorinated phenols, $(\text{M} - \text{HCl})^-$, $(\text{M} - \text{H})^-$, and M^- (M = parent molecule) were also observed. The intensities of the fragment ions such as Cl^- and $(\text{M} - \text{HCl})^-$, increased with increasing temperature, though that of the parent anion decreased. There may be two mechanisms to produce $(\text{M} - \text{HCl})^-$. One is the HCl elimination of the hydroxylic hydrogen atom and the ortho-Cl atom. The other is the HCl elimination followed by the migration of the hydroxylic hydrogen atom to the ortho position for 3,4- and 3,5-dichlorophenol. The branching ratio of $[(\text{M} - \text{HCl})^-]/[\text{Cl}^-]$ depends on the length of the H-Cl bond of the intermediate for the former mechanism.

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