

Detection of Chlorobenzene Derivatives using Single Photon Ionization Time-of-Flight Mass Spectrometry

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Introduction

Chlorinated aromatic compounds are important environmental pollutants, and have been suggested to be suitable surrogates for monitoring polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F). One of the most effective methods to reduce PCDD/F formation and the concentration in incinerator fuel gas is to control the operation of incinerators. Continuous on-line monitoring of toxic trace gas is essential to enable feedback control of incinerators.

Chlorobenzenes are correlated with the PCDD/F concentration in flue gas.^{1,2} Therefore, chlorobenzene derivatives have been used as an indicator to estimate PCDD/F emission.² Multi-photon ionization (MPI) methods are useful to detect chlorobenzenes. The resonance-enhanced multiphoton-ionization time-of-flight mass spectrometry (REMPI-TOFMS) technique has been used for the on-line measurement of chlorobenzenes.²⁻⁹ The detection limits of chlorobenzenes by REMPI-TOFMS were less than 100 parts per trillion volume (pptv).²⁻⁹

Vacuum ultraviolet single-photon ionization time-of-flight mass spectrometry (VUV-SPI-TOFMS) has been applied to diagnose several chemical systems. This technique provides the threshold ionization of chemical species. VUV-SPI is a soft ionization technique that can be adjusted to be nearly fragmentation free. Quantitative detection then becomes possible because the single-photon ionization cross-sections tend to be more uniform from molecule to molecule than those for multi-photon ionization.

We demonstrated the detection of chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol using time-of-flight mass spectrometry coupled with vacuum ultraviolet single-photon ionization. In the present work, the photoionization cross-sections (σ_{ion}) of halogenated benzenes and phenol at 10.2 eV (121.6 nm) were estimated. The ionization potentials and appearance potentials leading to

fragmentation were calculated using quantum chemical calculations. We now have a detection limit on the order of tenth ppbv for chlorobenzene.

Methods and Materials

The apparatus consists of a pulsed valve incorporated into a source chamber of the molecular beam machine, which is equipped with a time-of-flight (TOF) mass spectrometer. The mass spectrometer can be operated as a Wiley-McLaren-type TOF mass spectrometer. The field drift free region was 130 cm.

The sample gases were expanded from a pulsed valve (0.8 mm orifice diameter) with a stagnation pressure of 760 Torr and collimated by a skimmer 1.0 mm in diameter. A molecular beam was introduced into the TOF mass spectrometer. Ionization was accomplished by photoionization at 10.2 eV. Coherent VUV laser light was obtained by frequency tripling in phase-matched Kr/Ar gas mixtures adjusted to achieve the optimum phase matching. A frequency-tripling gas cell was sealed at the end opposite to an MgF_2 lens (70 mm focal length at 121.6 nm) by a fused silica window. A lens with a focal length of 15 cm was used to focus the output of an excimer pumped dye laser in a cell containing rare-gas mixtures. The laser was operated at 10 Hz. The VUV and the residual dye laser light passed through a MgF_2 lens and onto the molecular beam. The focusing MgF_2 lens had a lower refractive index at a longer wavelength; hence, the residual UV beam was mildly divergent. A LiF prism monochromator was also used to separate the VUV and the residual dye laser light. It consisted of a doubled coaxial cylinder; the outer cylinder was connected to a frequency-tripling cell, while an inner one was installed in a prism on the cylinder axis and connected to a vacuum chamber via a 15 cm long arm. The dispersed UV light was blocked out by a plate. The TOF signal was detected by a two-stage microchannel plate. The output of the signal from the MCP was fed to a digital oscilloscope. The TOF spectra were accumulated over 200 laser pulses (20 second measurement time).

A diluted mixture of chlorobenzene in He was used without further purification. The premixed sample gases (0.1% to 1% mixtures in the He buffer gas) were prepared and stored in glass bulbs, and then used to determine the ionization cross sections.

Results and Discussion

Mass spectra obtained by SPI at 10.2 eV

Table 1 gives the ionization potentials of chlorobenzene derivatives and the appearance potentials of $C_6H_4X^+$ ions. The ionization potentials of the chlorobenzene derivatives are located around 9 eV. We calculated the appearance potentials to form $C_6H_5Cl^+$ and $C_6H_5OH^+$ ions in the ionization of *o*-chlorophenol by G3//B3LYP/6-31G(d) level of theory. The calculated appearance potentials are listed in Table 1. The appearance potentials of $C_6H_4X^+$ ions are more than 12 eV, which are much higher than the photon energy of 10.2 eV used in the present study. Thus, fragmentation-free measurements of the mass spectra for chlorobenzene derivatives are expected in the SPI at 10.2 eV. Figure 1 shows the mass spectra of chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol obtained by the SPI at 10.2 eV. The parent molecular ions were exclusively observed. In the present study, fragmentation-free mass spectra were obtained with the threshold ionization of these species at 10.2 eV photon.

The ion signal intensity in the mass spectrum monochromatically increased with increasing pulse energy. The slopes in logarithmic plots of the ion signal intensity versus the VUV laser power are 1.04 ± 0.01 , 1.05 ± 0.02 , and 1.09 ± 0.02 for chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol, respectively. These values indicate that the ionization process occurs in the single-photon process and that the ionization resulting from the multiphoton process by combining the VUV and UV lasers could be ruled out. No fragment ion was observed within the laser fluence considered in the present study.

Table 1: Ionization potentials of chlorobenzenes and the appearance potentials of $C_6H_4X^+$ ions

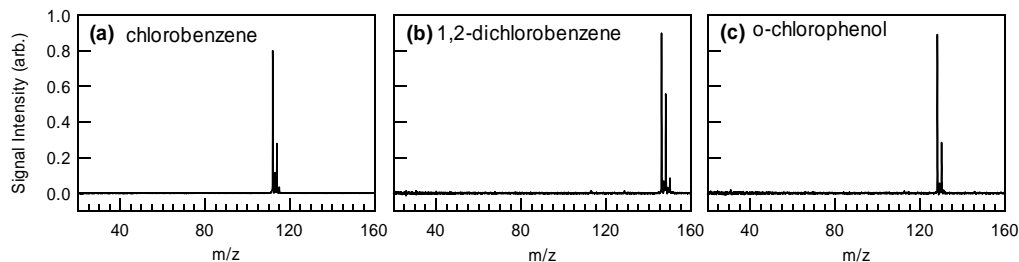
Ionization process		Ionization Energy /eV
C_6H_5Cl	$\rightarrow C_6H_5Cl^+ + e^-$	9.02
	$\rightarrow C_6H_5^+ + Cl + e^-$	12.6
$C_6H_4Cl_2$	$\rightarrow C_6H_5Cl_2^+ + e^-$	9.06
	$\rightarrow C_6H_4Cl^+ + Cl + e^-$	12.9
<i>o</i> - $C_6H_4Cl(OH)^a$	$\rightarrow o-C_6H_5Cl(OH)^+ + e^-$	9.28 ^b
	$\rightarrow C_6H_4OH^+ + Cl + e^-$	12.92 ^c
	$\rightarrow C_6H_4Cl^+ + OH + e^-$	13.60 ^c
C_6H_6	$\rightarrow C_6H_6^+ + e^-$	9.24
NO	$\rightarrow NO^+ + e^-$	9.26

a. *cis*-isomer.

b. Ionization potentials of *m*- and *p*-chlorophenol are 8.65 eV.

c. Calculated value by G3//B3LYP/6-31G(d) level of theory.

Figure 1: Photoionization mass spectra of (a) chlorobenzene, (b) *o*-dichlorobenzene, and (c) *o*-chlorophenol obtained by single-photon ionization at 10.2 eV.



Photoionization cross-sections

Photoionization processes of chlorobenzene derivatives have been well established by photoionization and photoelectron spectroscopy. To our knowledge, however, the absolute photoionization cross-sections of chlorobenzene, *o*-chlorophenol, and *o*-dichlorobenzene have never been determined. We thus estimated the photoionization cross-sections of these compounds at 10.2 eV. The same concentrations of NO and chlorobenzene derivatives were photoionized at 10.2 eV, and the signal intensities of molecular ions were measured. The photoionization cross-section of NO at 121.6 nm is known to be $2.0 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. Using this value, the photoionization cross-sections of chlorobenzene derivatives are estimated by

$$\sigma_{\text{ion}}(\text{CB}) = \sigma_{\text{ion}}(\text{NO}) \frac{I(\text{CB})}{I(\text{NO})},$$

where $\sigma_{\text{ion}}(\text{CB})$ is the photoionization cross-section of the chlorobenzene derivative at 10.2 eV, $\sigma_{\text{ion}}(\text{NO})$ is the photoionization cross-section of NO at 10.2 eV, and I is the signal intensity of the molecular ion. Table 2 gives the estimated photoionization cross-sections at 10.2 eV. The absolute photoionization cross-sections of chlorobenzene, *o*-chlorophenol, and *o*-dichlorophenol are $(2.6 \pm 0.4) \times 10^{-17}$, $(1.3 \pm 0.1) \times 10^{-17}$, and $(2.1 \pm 0.2) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, respectively. The photoionization cross-section of benzene at 10.2 eV is *ca.* $0.8 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. Thus, the detection sensitivity of chlorobenzene derivatives in the VUV-SPI-

TOFMS is expected to be higher than benzene derivatives (*e.g.* benzene, toluene, and xylene).

Table 2: Photoionization cross-sections (σ_{ion}) of chlorobenzene species at 10.2 eV

Species	$\sigma_{\text{ion}} / 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$
$\text{C}_6\text{H}_5\text{Cl}$	2.6 ± 0.4
$\text{C}_6\text{H}_4\text{Cl}_2$	1.3 ± 0.1
$\text{C}_6\text{H}_4\text{Cl}(\text{OH})$	2.1 ± 0.2
C_6H_6	0.8
NO	0.2

Estimate of the detection limit

Figure 2 shows the SPI mass spectrum of 200 ppbv chlorobenzene calibration gas for a measurement time of 20 sec. The detection limit for a signal-to-noise (S/N) ratio of 2 was estimated using the formula $\text{DL} = 2\sigma c/h$, reported by Muhlberger *et al.*,¹⁰ where c is the concentration of the chlorobenzene standard; σ , the standard deviation of the noise between a mass of 105 and a mass of 111, and h , the signal peak height at a mass of 112. The detection limit estimated using this formula is 20 ppbv. A series of measurements at calibration gases were also performed to estimate a calibration curve and the sensitivity limits for chlorobenzene. Figure 3 shows plots of the ion signal intensity versus the chlorobenzene concentration. The measurement time for each point in Figure 3 was 20 sec. The plots show a good linear relation over a wide dynamic range of four orders magnitude. The detection limit for $\text{S/N} = 2$ is located at around 14 ppbv.

Figure 2: Photoionization mass spectrum of a calibration gas mixture containing 200 ppbv of chlorobenzene in helium to estimate the detection limit.

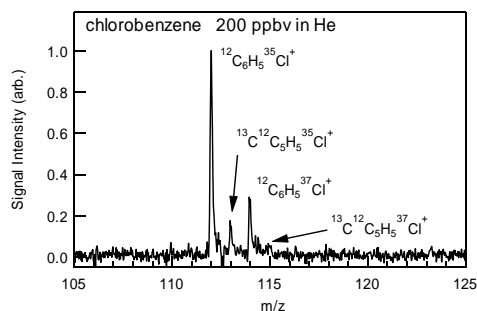
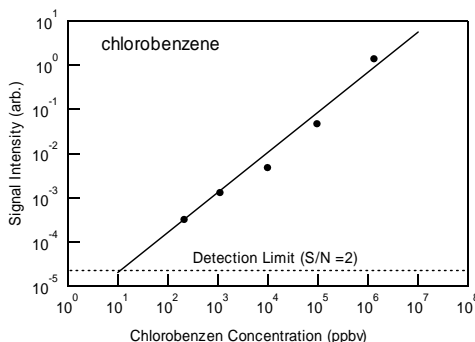


Figure 3: Ion signal intensity versus a sample concentration plot for chlorobenzene.



We briefly tried the VUV-SPI-TOFMS detection of chlorobenzenes at 118 nm (10.5 eV) generated by frequency tripling at 355 nm laser light. The detection limit for chlorobenzenes by the SPI at 10.5 eV was almost identical with the SPI at 10.2 eV. Since the ionization cross-sections at 10.2 and 10.5 eV are almost the same, this result is reasonable. Muhlberger *et al.*¹⁰ estimated the detection limits in the 100 ppb range for benzene derivatives by VUV-SPI-TOFMS at 10.5 eV. They did not optimize the phase-matching conditions for the third-harmonic generation process. Therefore, the detection limits in the present study are an order of magnitude higher than their values.

In summary, the VUV-SPI-TOFMS for chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol at 10.2 eV gives a fragmentation-free mass spectrum. The photoionization cross-section is an important parameter in VUV-SPI-TOFMS. This method is useful to detect other halogenated compounds such as bromobenzene derivatives.

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