Detection of Chlorobenzene Derivatives Using Vacuum Ultraviolet Ionization Time-of-Flight Mass Spectrometry

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Vacuum ultraviolet single-photon ionization time-of-flight mass spectrometry (VUV-SPI-TOFMS) has been applied for the detection of chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol as surrogates for polychlorinated dibenzo-*p*-dioxine/furans (PCDD/F). The photoionization mass spectra of these compounds appear to be fragmentation free in the ionization processes by the VUV-SPI at 10.2 eV (121.6 nm). Quantum chemical calculations support no fragmentation in the photoionization of chlorobenzene derivatives at around 10 eV. The absolute photoionization cross-sections of chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol were estimated at 10.2 eV. The photoionization cross-section is an important parameter in the detection of chlorobenzene derivatives by the single-photon ionization technique. The detection limit for chlorobenzene is on the order of tenth parts-per-billion volume (ppbv) in the present experimental setup.

(Received April 21, 2003; Accepted May 30, 2003)

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. Quantitative analysis of PCDD/F by gas chromatography interfaced with a mass spectrometer takes more than one week due to complicated sampling and extracting processes. Instead of direct analysis of dioxin, therefore, real-time analysis of surrogates of dioxin is attracting attention.

Chlorobenzenes are correlated with the PCDD/F concentration in flue gas.^{1,2} Therefore, chlorobenzenes 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 Zimmermann *et al.*²⁻⁶ constructed mobile instruments for on-line monitoring of polyaromatic hydrocarbons and other aromatic species in the flue gas of industrial incineration plants. Oser *et al.*⁷⁻⁹ also performed REMPI mass spectrometry to detect chlorinated aromatic compounds. The detection limits of chlorobenzenes by REMPI-TOFMS were less than 100 parts per trillion volume (pptv).²⁻⁹ Imasaka *et al.*^{10,11} have been examined the pulse-width effect of a laser in the multiphoton ionization efficiency of halogenated

benzenes and phenols at 248 nm. They indicated that an ultrashort laser pulse is very useful to improve the ionization efficiency for halogenated benzenes and phenols.

The threshold ionization technique has been widely used to avoid fragmentation in the ionization process. Vacuum ultraviolet single-photon ionization time-of-flight mass spectrometry (VUV-SPI-TOFMS) has been applied to diagnose several chemical systems.¹²⁻¹⁷ 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. Recently, Muhlberger *et al.*^{18,19} applied VUV-SPI-TOFMS to the detection of aromatic species from automobile exhaust gas. It would, therefore, be expected that this technique could be used to detect dioxins and their precursors.

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.

Experimental

A schematic view of the experimental setup is shown in Fig. 1. The apparatus consists of a pulsed valve incorporated into a source chamber of the molecular beam machine, which is

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Fig. 1 Schematic diagram of the experimental apparatus.

equipped with a time-of-flight (TOF) mass spectrometer. The mass spectrometer can be operated as a Wiley-McLaren-type²⁰ TOF mass spectrometer, described in detail elsewhere.^{21,22} The field drift-free region was 130 cm.

The sample gases were expanded from a pulsed valve (General Valve Series 9, 0.8 mm orifice diameter) with a stagnation pressure of 760 Torr and collimated by a skimmer 1.0 mm in diameter. The pulsed valve was heatable up to 200°C to minimize the wall adsorption effects. The distance between the ionization region and the pulsed valve was 45 mm. A molecular beam was introduced into the TOF mass spectrometer. An Einzel lens and deflectors were located just above the ion acceleration regions.

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.²³ A frequency-tripling gas cell was sealed at the end opposite to an MgF₂ 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 (Lambda Physik LPX 110 + Lambda Physik LPD 3002) in a cell containing rare-gas mixtures. The laser was operated at 10 Hz. The typical laser intensity at 364.8 nm was 5 mJ pulse⁻¹. The VUV and the residual dye laser light passed through a MgF₂ lens and onto the molecular beam. The focusing MgF₂ lens had a lower refractive index ($\eta = 1.6275$ at 121.6 nm compared with $\eta = 1.386$ at 364.6 nm) 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. Figure 1 shows this experimental configuration. 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 spot size of the VUV laser light at the point of molecular beam was about 1 mm. The VUV laser light was monitored using a NO contained photoionization cell. Because a NO molecule has an ionization potential of 9.24 eV, an incident VUV photon at 10.2 eV can ionize the NO molecules. The resultant photocurrent by an ejected electron or ionized NO was monitored to measure the relative intensity of the VUV light ($\approx 10^{8-10}$ photons pulse⁻¹).²³

The TOF signal was detected by a two-stage microchannel plate (MCP; Hamamatsu F4655-10). The output of the signal from the MCP was fed to a 500 MHz, 1 GS/s digital oscilloscope (Tektronix TDS 520C) and transferred to a

Table 1 Ionization potentials of chlorobenzenes and the appearance potentials of C₆H₄X⁺ ions

Ionization process	Experimental ^a /eV	G3/eV
C ₆ H ₅ Cl → C ₆ H ₅ Cl ⁺ + e ⁻	9.02	9.13
→ C ₆ H ₅ ⁺ + Cl + e ⁻	12.6	12.47
C ₆ H ₄ Cl ₂ → C ₆ H ₃ Cl ₂ ⁺ + e ⁻	9.06	9.08
→ C ₆ H ₄ Cl ⁺ + Cl + e ⁻	12.9	12.91
<i>o</i> -C ₆ H ₄ Cl(OH) ^b → <i>o</i> -C ₆ H ₃ Cl(OH) ⁺ + e ⁻	9.28 ^c	8.70
→ C ₆ H ₄ OH ⁺ + Cl + e ⁻	----- ^d	12.92
→ C ₆ H ₄ Cl ⁺ + OH + e ⁻	----- ^d	13.60
C ₆ H ₆ → C ₆ H ₆ ⁺ + e ⁻	9.24	9.31
NO → NO ⁺ + e ⁻	9.26	9.36

a. Taken from Refs. 26–34.

b. *Cis*-isomer.

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

d. No experimental data.

Pentium personal computer via a general purpose-interface bus. The TOF spectra were accumulated over 200 laser pulses (20 second measurement time).

A diluted mixture of chlorobenzene in He (Nippon Sanso) was used without further purification. Other samples were purchased from Aldrich and were used without further purifications. 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 C₆H₄X⁺ ions. The ionization and appearance potentials calculated at the G3 level of theory²⁴ using Gaussian 98 series of programs²⁵ are also listed in Table 1. The energy differences between the experimental and G3 energies are less than 0.13 eV, except for *o*-chlorophenol. For *o*-chlorophenol, the *cis*-isomer is more stable than its *trans*-isomer. The difference in the heat of formation between *cis*- and *trans*-*o*-chlorophenol is 13.06 kJ mol⁻¹ in the G3 energy. Thus, we only considered the *cis*-isomer for *o*-chlorophenol. The ionization potentials of the chlorobenzene derivatives are located around 9 eV. To our knowledge, the appearance potentials to form C₆H₅Cl⁺ and C₆H₅OH⁺ ions in the ionization of *o*-chlorophenol have never been reported. The calculated appearance potentials are listed in Table 1. The appearance potentials of C₆H₄X⁺ ions are more than 12 eV, which are much higher than the photon energy of 10.2 eV used in the present study.²⁶⁻³⁴ Thus, fragmentation-free measurements of the mass spectra for chlorobenzene derivatives are expected in the SPI at 10.2 eV. Figure 2 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. The 70 eV electron impact library spectra for chlorobenzene derivatives show fragmentation.³⁴ In the present study, fragmentation-free mass spectra were obtained with the threshold ionization of these species at 10.2 eV photon. As shown in Fig. 1 (a), the isotope distributions were observed with a ratio of 73:23 for masses of 112 and 114. This is in reasonable agreement with the isotope distribution calculated from the natural abundances, which are 75.8% for a mass of 112 and 24.2% for a mass of 114. For *o*-dichlorobenzene and

Fig. 2 Photoionization mass spectra of (a) chlorobenzene, (b) *o*-dichlorobenzene, and (c) *o*-chlorophenol obtained by single-photon ionization at 10.2 eV.

o-chlorophenol, the isotope distributions are also in reasonable agreement with the isotope distributions calculated from the natural abundances. The mass spectra of chlorobenzene, *o*-dichlorobenzene, and *o*-chlorophenol were not changed with two experimental configurations; one was no separation of the residual dye laser light at 364.8 nm and the VUV light at 121.6 nm. The other used a LiF prism monochromator. Thus, the residual dye laser light at 364.8 nm was not affected in the ionization process under the present experimental conditions.

Figure 3 shows the VUV laser power dependence of the molecular ion signals for chlorobenzene derivatives. The laser power dependencies were observed under the condition of no separation of the UV laser light and the VUV laser light. 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.

Photoionization cross-sections

In the REMPI scheme, the detection sensitivity of halogenated benzenes is affected by the lifetime of the S_1 excited state, which is attributed to intersystem crossing by a spin-orbit interaction.¹⁰ Therefore, there is the influence of the chlorine atoms substituted on a benzene ring in the REMPI. On the other hand, the detection sensitivity in the VUV-SPI scheme is

Fig. 3 Relationships between the intensities of molecular ions and the VUV laser pulse energy for (a) chlorobenzene, (b) *o*-dichlorobenzene, and (c) *o*-chlorophenol.

governed by the photoionization cross-section below the appearance potential leading to fragmentation. Thus, the absolute photoionization cross-section is an important parameter in trace gas detection by SPI mass spectrometry.

Photoionization processes of chlorobenzene derivatives have been well established by photoionization and photoelectron spectroscopy.^{26,27} Sergeev *et al.*²⁶ measured the photoionization efficiency curves of chlorobenzene with the formation of a molecular ion and a $C_6H_5^+$ ion. The photoionization efficiency curve of *o*-dichlorobenzene was measured by photoelectron spectroscopy.²⁷ 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 $2.0 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.³⁵ 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

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

Species	$\sigma_{\text{ion}}/10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$	Ref.
$\text{C}_6\text{H}_5\text{Cl}$	2.6 ± 0.4	This work
$\text{C}_6\text{H}_4\text{Cl}_2$	1.3 ± 0.1	This work
$\text{C}_6\text{H}_4\text{Cl}(\text{OH})$	2.1 ± 0.2	This work
C_6H_6	0.8	36
NO	0.2	35

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.* $8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.³⁶ 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). Muhlberger *et al.*¹⁸ estimated the detection limits (DL) of NO and benzene by the SPI-TOFMS at 10.5 eV (118 nm). The ratio of the detection limits, $\text{DL}(\text{NO})/\text{DL}(\text{benzene}) = 6.9$, was derived by Muhlberger *et al.*¹⁸ This value is in reasonable agreement with the ratio of $\sigma_{\text{ion}}(\text{benzene})/\sigma_{\text{ion}}(\text{NO}) = 4$ at 10.5 eV.

Estimate of the detection limit

Figure 4 shows the SPI mass spectrum of 200 ppbv chlorobenzene calibration gas for a measurement time of 20 s. 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.*,¹⁸ 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 5 shows plots of the ion signal intensity *versus* the chlorobenzene concentration. The measurement time for each point in Fig. 5 was 20 s. The plots show a good linear relation over a wide dynamic range of four orders magnitude. The detection limit for $S/N = 2$ is located at around 14 ppbv.

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,²⁶ this result is reasonable. Muhlberger *et al.*¹⁸ 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.

Further improvement

The detection limits of chlorobenzene derivatives by REMPI-TOFMS were reported to be less than 100 pptv.²⁻⁹ Zimmermann *et al.*² observed the chlorobenzene concentration in the 100 to 800 pptv region in a 22MW hazardous-waste incineration plant. The current VUV-SPI-TOFMS gives a detection limit of 20

Fig. 4 Photoionization mass spectrum of a calibration gas mixture containing 200 ppbv of chlorobenzene in helium to estimate the detection limit.

Fig. 5 Ion signal intensity versus a sample concentration plot for chlorobenzene.

ppbv for chlorobenzenes derivatives. The monitoring of trace of chlorobenzene derivatives using the VUV-SPI-TOFMS requires an improvement of the sensitivity by two orders.

The density $n(x)$ of chlorobenzene in the ionization region can be estimated by the following equation:³⁷

$$n(x) = n_0 0.15(x/D)^{-2}, \quad (2)$$

where D is the nozzle diameter (0.8 mm), x is the distance from the nozzle, and n_0 is the concentration for $x = 0$. In the present apparatus, $n(x)/n_0$ is 4.7×10^{-4} ($x = 45 \text{ mm}$). If x decreases to 15 mm, the density of chlorobenzene in the ionization region increases up to $n(x)/n_0 = 4.3 \times 10^{-4}$. In the present apparatus, a Chevron assembly is used for MCP. The gain of the Z-stack assembly is an order of magnitude higher than that of the Chevron assembly. Improvements in sample introduction and the detector will give a two orders of magnitude higher sensitivity.

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. Further improvement is necessary for monitoring the trace of chlorobenzene derivatives. In a future study we plan to construct an improved apparatus.

Acknowledgements

The authors thank Prof. M. Kawasaki (Kyoto University) for useful comments. This work was supported in part by the Steel Industry Foundation for the Advancement of Environmental Protection Technology.

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