Measurement of Mass and Multiphoton Ionization Spectra Using Small Quantities of Dioxins and Their Surrogates

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Introduction

Multiphoton ionization-mass spectrometry (MPI-MS) has a potential application in on-line real-time monitoring of polychlorinated dibenzo-*p*-dioxins/furans (PCDD/F) and their surrogates.[1,2] In particular, selective analysis can be achieved by using each compound's resonance transition wavelength. Although some MPI spectra of these substances have been reported,[3,4] those of more highly chlorinated congeners have not been measured. Several factors make it difficult to measure the MPI spectra of PCDD/F, as follows.

(1) Shorter excited-state lifetimes. The lifetimes of PCDD/F are expected to be ~10-100 ps, mainly due to the heavy atom effect. It is reported that ionization efficiency is increased when the laser pulse width is identical to the lifetime of the sample.[5] A distributed-feedback dye laser system with a pulse width of ~100 ps has been used for precursors of PCDD/F.[6]
(2) Necessity of a two-color laser system. When a PCDD/F is ionized by using a laser emitting at the 0-0 transition wavelength, three (or more) photons are required, resulting in a lack of ionization efficiency. Instead of this one-color three-photon ionization process, a two-color two-photon ionization technique is commonly used. However, adjusting two laser beams both spatially and temporally is a complicated task. Recently, a two-color three-photon ionization technique was reported for selective and sensitive analysis of an aromatic hydrocarbon.[7]
(3) The use of a considerable amount of sample (on the order of milligrams, for example). In the MPI-MS method, the sample is placed in a reservoir and heated to vaporize. Once this is done, however, the sample is introduced into a vacuum chamber, resulting in the difficulties of controlling the concentration and start/stop sample introduction. In particular, the use of large amounts of extremely toxic PCDD/F causes serious environmental problems and is harmful to the human body.

In this study, a sample introduction technique using gas chromatography (GC) is demonstrated. Although techniques for interfacing MPI-MS with GC have been reported elsewhere,[8,9] the GC system in this study is used only to introduce the sample, not to separate it. The analyte can be introduced into the vacuum chamber by slow injection over a certain period of time and at a fixed concentration. Using this technique, mass spectra and MPI spectra can be measured using a quite small amount of sample.

Methods and Materials

The sample of chlorobenzene was purchased from Wako Pure Chemical Industries, and 2,3,8-trichlorodibenzofuran (2,3,8-TriCDF, 50 ng/μL in nonane) and 1,2,3,8,9-pentachlorodibenzofuran (1,2,3,8,9-PeCDF, 50 ng/μL in nonane) were purchased from Cambridge Isotope Laboratories. The sample of chlorobenzene was diluted with methanol (10 pg/μL), and the others were used without further purification.

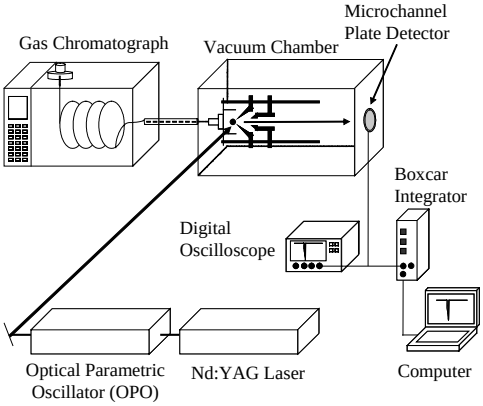

Figure 1 Experimental apparatus.

A schematic of the experimental apparatus used in this study is shown in Figure 1. The end of the capillary (5 m long, 0.32 mm i.d.) in a GC system (Agilent Technologies, 6890GC) was introduced directly into the vacuum chamber. When the mass spectra and MPI spectra were measured, the end of the capillary was processed narrow by melting, in order to generate a supersonic molecular beam.[1] The sample solution was injected into a GC column using a micro-syringe pump driven by a translational stage. The injection speed was programmed as follows: 1 μL/min for chlorobenzene, or 5 μL/min for 2,3,8-TriCDF or 1,2,3,8,9-PeCDF. The second harmonic emission of an optical parametric oscillator (Spectra Physics, MOPO-730, 1 mJ, 6 ns) was focused by a quartz lens (focal length 30 cm) into a sample molecule. The induced ions were accelerated by a repulsive potential into a flight tube (30 cm) and were subsequently detected by an assembly of three microchannel plates (Hamamatsu, F4655-10). The MPI spectrum was measured by monitoring the signal of a specified mass peak by means of a boxcar integrator. The mass spectra were measured 200 times, and the signals were averaged by means of a digital oscilloscope (IWATSU, WaveRunner, DS-4264M). The mass resolution was typically 330 at m/z = 112. The mass spectrum, however, was sometimes recorded under a poor mass resolution to improve the S/N ratio.

Results and Discussion

Figure 2a shows the variation over time in the ion signal intensity of chlorobenzene. The wavelength of the ionization laser is adjusted to a 0-0 transition wavelength. The signal of chlorobenzene appears 30 seconds after the translation stage is driven, and the signal intensity is relatively stable. The injection speed is 1 μL/min and the injection time is 5 min. The amounts of solution and solute (chlorobenzene) in this measurement are calculated to 5 μL and 50 pg, respectively. Figure 2b shows a MPI spectrum of chlorobenzene. The injection condition of the sample is the same as that of Figure 2a, except for the sample injection time (ca. 10 min). The scan speed of the ionization laser is 0.005 nm/s. The total amounts of solution and solute to scan the wavelength of that laser in this range are determined to be 10 μL and 100 pg, respectively.

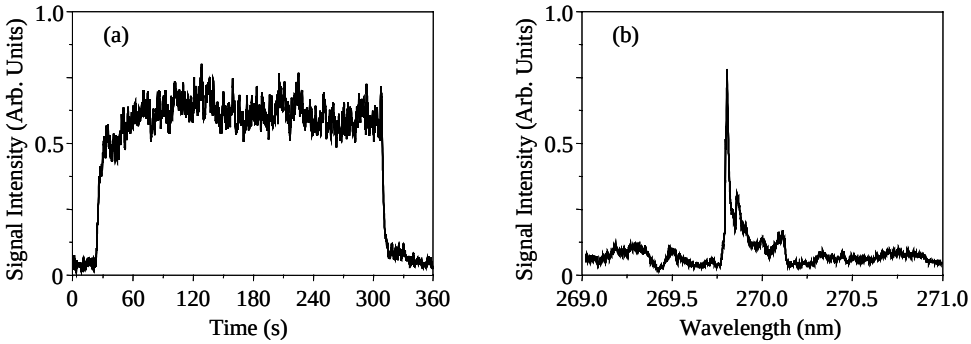

Figure 2 (a) Variation in ion signal intensity of chlorobenzene against time. (b) MPI spectrum of chlorobenzene. The laser was began scanning 60 seconds after the sample was injected.

In addition to helium as a carrier gas, methanol is also mixed and expanded during this measurement. It is therefore thought that the cooling effect is not so achieved. As shown in Figure 2b, however, the spectral resolution is enough to recognize a 0-0 transition wavelength.

Figure 3a shows the mass spectrum of 2,3,8-TriCDF. The total amount of 2,3,8-TriCDF to measure this mass spectrum, averaged 200 times, is calculated to be ca. 80 ng. In Figure 3a, the main peak at t = 22 μs corresponds to 2,3,8-TriCDF, and few peaks are observed at smaller mass numbers, indicating fragment ions. Figure 3b shows a MPI spectrum of 2,3,8-TriCDF. The scan speed of the ionization laser is 0.05 nm/s. The total amount of this molecule used during scanning in the 20-nm range is ca. 3 μg. Unfortunately, no structured signals are observed in the MPI spectrum, mainly because of the short excited-state lifetime resulting from the heavy atom effect. However, several peaks would be expected to measure when the picosecond transform-limited dye laser is used, as described previously.

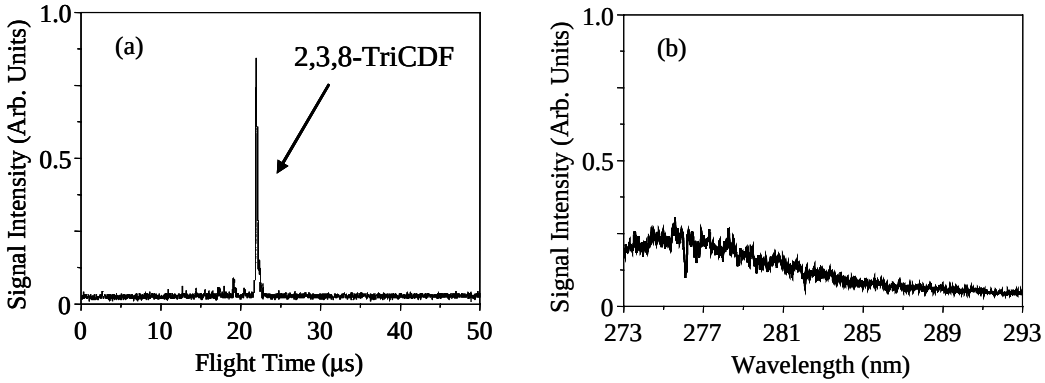

Figure 3 (a) Mass spectrum (laser wavelength: 245.6 nm) and (b) MPI spectrum of 2,3,8-TriCDF.

Figure 4 shows a mass spectrum of 1,2,3,8,9-PeCDF. This mass spectrum is obtained using a total amount of ca. 80 ng. Several fragment peaks are observed, unlike the case in the mass spectrum of 2,3,8-TriCDF (Fig. 3a). It has been reported that ultrashort laser pulse was very useful for reducing these fragment ions and enhancing molecular ions.[5] On the other hand, there are no structured peaks in the MPI spectrum of this molecule (not shown), as in the case of 2,3,8-TriCDF (Fig. 3b). To know the resonance wavelength of PCDD/F, a transform-limited picosecond laser pulse is strongly required. This pulse can maintain the spectral resolution of the peaks of the MPI spectra.

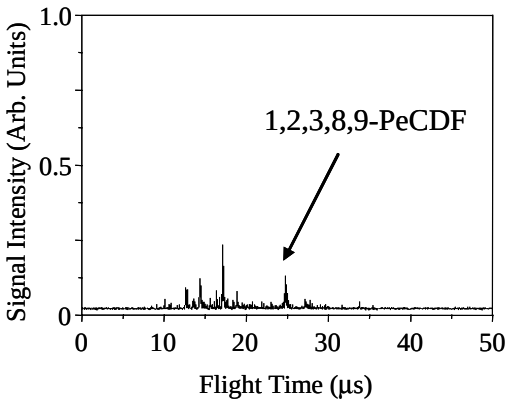

Figure 4 Mass spectrum of 1,2,3,8,9-PeCDF. Laser wavelength: 263.9 nm.

This study demonstrated an interface between MPI-MS and GC to measure the mass spectra and MPI spectra of PCDD/F in small quantities. This method makes it possible to measure these spectra without a health risk to the researcher.

Acknowledgements

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