Highly Sensitive Droplets by the Surface Laser Two-Photon Ionization

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The laser two-photon ionization technique has been applied to a liquid droplet (100 - 3 µl) in order to determine the analytical potential of this technique for a small amount of sample. Surface photoionization was effective to remove the leakage current and allowed use of water as the solvent. Irradiation at the top surface of the liquid drop showed a wider linear range of the analytical curve than irradiation at its middle body. The detection limit of pyrene was 0.3 pg.

Keywords Laser, two-photon ionization, aromatic molecule, droplet, solution surface

Water is the most important solvent for us. Although the laser two-photon ionization method has been found very sensitive in non-polar solvents and on metal surfaces, its application to aqueous solutions has had difficulty due to the large leakage current of water. Photoionization on the solution surface has, however, overcome most of such difficulty.

The amount of sample needed for an analysis should be as small as possible, especially for a chromatographic detector and a clinical application. Microcolumn HPLC and capillary electrophoresis techniques require a very small and very sensitive detector. When a liquid droplet (4 µl) was used as a windowless fluorescence cell, a detection limit of 0.75 pg was obtained for aflatoxin. A liquid droplet was also used as a windowless photoionization cell for an HPLC detector. The detection limit was excellent for a normal-phase HPLC: 1.6 pg for pyrene in an iso-octane droplet. It was, however, rather unsatisfactory for a reversed-phase HPLC due to the large leakage current of the polar solvent: 50 ng for anthracene in an acetonitrile droplet. A surface technique will be able to suppress the large leakage current of polar solvents in a liquid droplet. If this is the case, it would be useful for a detector of a chromatographic system.

In the present paper, we are reporting surface two-photon ionizations of several aromatic molecules in small water droplets.

Experimental

The schematic diagram of the experimental apparatus is shown in Fig. 1. A liquid droplet (100, 50, 10 µl) was placed on a plate (20X20 mm; copper or nickel); a small droplet (3 µl) was, however, placed on a small rod (diameter: 2 mm; stainless steel). A nitrogen laser (Moletron UV-24; 337 nm, 9 mJ, 10 Hz) was focused softly by a quartz lens either on the droplet surface (Fig. 1: A) or into the droplet body (Fig. 1: B); the laser beam was narrowed with a pinhole. The photoionization signal was measured and compared for the two irradiation positions. The laser pulse energy was monitored with a photodiode (Hamamatsu S 1336-8BQ) and a calorimeter (SCIENTECH 36-0001). A positive electrode (stainless-steel mesh) was located 8 mm above the base electrode on which the droplet was placed. The positive electrode was held at 1750 V using a high voltage power supply unit (Ikegami HD2.5K-M). The base electrode was connected to a current amplifier (Keithley...
The time profile of the photoionization current was integrated, and its area was used as a signal. The photoionization signal was accumulated for 32 pulses of the laser, and an average of eight sets of such data was taken as an observed result.

The liquid drop was prepared using a microsyringe; a certain amount (100 µl to 3 µl) of the sample solution was placed softly on the base electrode. The water was distilled, deionized, filtered and distilled in a quartz vessel. Aromatic molecules (research grade) were used without further purification. They were dissolved in water by ultrasonic vibration and their concentrations were confirmed by a UV/VIS spectrophotometer (Shimadzu UV-2200) and a fluorescence spectrophotometer (Hitachi F-4010).

Results and Discussion

A typical time profile of the photoionization signal is shown in Fig. 2. It has a fast and a slow component as in the case of photoionization on solution surface. The fast component can be assigned to electrons ejected from the surface, and the slow component to oxygen anions.

The laser irradiated the liquid droplet at two positions: its top surface (A in Fig. 1) and its middle body (B in Fig. 1). Typical analytical curves of pyrene at two irradiation positions are compared in Fig. 3. When the laser irradiates the top surface of the droplet, the photoionization proceeds only on the surface. The analytical curve is straight, because the signal should be proportional to the analyte concentration staying on the top surface. Meanwhile, when the laser irradiates the middle body, the photoionization in the bulk of the droplet proceeds as well as on the surface. The signal may be larger, but is complicated. Then, the signal may not be proportional to the concentration. Such behavior of the analytical curve has been found also in the case of solution surface as for the irradiation angle.

The photoionization signal depended on the applied voltage. At higher applied voltage, the escape probability of electrons from the surface would increase, and the signal increases. In addition, electrons fly faster in a higher electric field (the velocity and the electric field should be proportional), and more electrons arrive to the positive electrode before being captured by oxygen molecules; thus, the signal becomes sharper, and its detection becomes more efficient. However, the background signal of water increased more steeply than the photoionization signal at a higher voltage. The best signal-to-background ratio was obtained at about 1.5 kV. Further experiments were carried out at this voltage.

A molecule with a large absorptivity at the laser wavelength shows a larger photoionization signal. This is also true for surface photoionization on a droplet as shown in Fig. 4. The absorptivity at 337 nm was measured at 1×10^5 M in hexane, because most of the samples was not soluble enough in water to measure an absorption spectrum. The photoionization signal was approximately proportional to the molar absorptivity; this finding indicates that the first step for photoionization is excitation to a resonant state.

The analytical curves were linear up to three orders of magnitude above the detection limits when irradiated on the top surface. Detection limits of several aromatic molecules were determined using irradiation on the top surface. They were obtained as a concentration where the signal-to-noise ratio was 3, and are summarized in Table 1 for the case of 3 µl droplet.
The concentration limit was 0.3 pg of pyrene, which corresponded to $5.0 \times 10^{-10}$ M. The concentration detection limit was almost constant for four sizes of droplets, as shown in Fig. 5; this finding indicates that the largest source of noise was the blank signal of water, which reduced proportionally as the droplet size became smaller.

A molecule with a large absorptivity gave a larger photoionization signal, probably because the photoionization efficiency depends on the first step of photon absorption for a series of similar molecules in an identical solvent. Thus, a molecule with a large absorptivity at the laser wavelength indicated a lower detection limit, as shown in Fig. 6. This technique is more efficient for such molecules.

The present technique indicates that highly sensitive detection is possible for a small water droplet. The application to a reversed-phase HPLC detector should follow.

### Table 1 Detection limits of several aromatic molecules in a droplet of 3 µl

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorptivity/dm⁻³ mol⁻¹ cm⁻¹</th>
<th>Detection limit/mol dm⁻³</th>
<th>Detection limit/pg</th>
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</thead>
<tbody>
<tr>
<td>Pyrene</td>
<td>15000</td>
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<tr>
<td>1-Aminopyrene</td>
<td>13000</td>
<td>$8.9 \times 10^{-10}$</td>
<td>0.57</td>
</tr>
<tr>
<td>3,4-Benz[a]pyrene</td>
<td>7300</td>
<td>$6.7 \times 10^{-8}$</td>
<td>5.1</td>
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<td>Anthracene</td>
<td>5900</td>
<td>$5.4 \times 10^{-8}$</td>
<td>2.9</td>
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<tr>
<td>2-Aminoanthracene</td>
<td>4000</td>
<td>$7.2 \times 10^{-8}$</td>
<td>4.2</td>
</tr>
<tr>
<td>2-Methylandthracene</td>
<td>5100</td>
<td>$8.0 \times 10^{-8}$</td>
<td>4.6</td>
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<tr>
<td>9-Methylandthracene</td>
<td>4100</td>
<td>$8.9 \times 10^{-8}$</td>
<td>5.1</td>
</tr>
<tr>
<td>9,10-Dimethylandthracene</td>
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<tr>
<td>Tetrathene</td>
<td>10000</td>
<td>$1.9 \times 10^{-8}$</td>
<td>1.3</td>
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### References


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