RECENT PROGRESS IN LASER MULTI-PHOTON IONIZATION SPECTROMETRY

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Abstract - A conductivity measurement of electrons and ions produced in laser multi-photon ionization is a simple and sensitive analytical technique. Aromatic molecules in solution excited by pulsed (266, 337 and 355 nm) or continuous (Ar) lasers showed detection limits as low as 1.7 ppt. Surface molecules can be detected below the monolayer coverage.

Key words laser, photoionization, conductivity, aromatic molecules

INTRODUCTION

A non-linear optical process has been a challenge for an analytical laser application. A molecule can be photoionized in an intense laser field by absorbing two or more photons successively or simultaneously. A simple and sensitive method to detect photoionization is conductivity measurements [1-5]. One atom detection in a gas phase [1] and a ppb level detection in a solution [5] have been reported. Recent progresses of this technique for molecules in solution and on surface will be discussed in the present paper.

DYNAMICS OF PHOTOIONIZATION IN SOLUTION

Two or three photons of a laser can photoionize a molecule in solution; the first photon excites the molecule, and the second (or third) one ionizes it, as follows: A + hv → A*, A* + hv → A⁺ + e. This successive absorption of two photons has reasonable probability if the molecule has a strong absorption band at the laser wavelength. It is possible to ionize a molecule with a simultaneous absorption of two or three photons, but this process is less probable and less useful for an analytical application.

The ionization potential of an aromatic molecule in the gas phase lies in the 6-10 eV range: eg. benzene (9.2 eV), toluene (8.8 eV), naphthalene (8.1 eV) and pyrene (7.4 eV). The ionization potential in solution decreases by 1 - 3 eV due to electron affinity of solvent and polarization energy of the ion. Thus, two photons of a Nd-YAG laser (4.7 eV(266 nm) or 3.5 eV (355 nm)) or a N₂ laser (3.7 eV) can photoionize variety of aromatic molecules in solution.

The conductivity technique is sensitive for a detection of photoionization in solution. The time profile of the photoionization signal has two components as shown in Fig. 1; the fast component is due to electrons and the slow component is due to ions [6]; they are produced as below:

A + hv → A⁺, A⁺ + hv → (A⁺⋯e) → A⁺ + e
A + e → A⁻
The sharp signal of the fast component is more useful for a high sensitive detection. The probability \( P(E) \) of an electron escaping from the geminate pair is proportional to the applied electric field.

Photoionization current depends on the absorptivity of the molecule. Its wavelength dependence is similar to the optical absorption spectrum [7]. However, since a photon with a higher energy can give more energy to the geminate pair, its ionization efficiency is larger, as shown in the following equation [8] and in Fig. 2.

\[ i = B' (2h\nu - I_p)^{5/2}. \]

HIGH SENSITIVE DETECTION IN SOLUTION

A typical experimental apparatus is shown in Fig. 3, and a typical photoionization cell in Fig. 4. A beam of a nitrogen or Nd-YAG laser was focused at a space between the two electrode in the solution. The current produced by photoionization was converted into a voltage signal and was measured with a boxcar technique.
The photoionization current was proportional to the applied voltage and quadratic to the laser pulse energy. These findings are consistent with the above mechanism and show the photoionization is a two-photon process.

Table 1. Photoionization detection limits (S/N=3) of aromatic molecules in hexane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar absorptivity l/cm·mol·cm·mol</th>
<th>Detection limit ng/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>337 nm 266 nm</td>
<td>337 nm 266 nm</td>
</tr>
<tr>
<td>Bensene</td>
<td>- 120 -</td>
<td>- 3.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>- 300 -</td>
<td>- 1.2</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>- 4750 -</td>
<td>- 0.064</td>
</tr>
<tr>
<td>Anthracene</td>
<td>5900 730</td>
<td>0.01 0.72</td>
</tr>
<tr>
<td>Pyrene</td>
<td>15000 18600</td>
<td>0.006 0.061</td>
</tr>
</tbody>
</table>

- : no absorption and no successive two-photon ionization

Analytical applications of this technique for the detection of organic molecules in solution were reported first by Voigtman et al. [2] and then by us [3]. The detection limits of this technique are shown in Table 1; an N₂ laser is used for the excitation at 337 nm and the 4th harmonics of a Nd-YAG laser for the excitation at 266 nm. The detection limits are closely correlated with the molar absorptivity (ε) at the laser wavelength as shown in Fig. 5, indicating the first step of photoionization is the excitation to states of the laser photon energy.

The simultaneous action of 355 nm and 1064 nm, or 355 nm and 532 nm has increased detection sensitivity considerably [9]. A typical detection limit of anthracene by the two-color method was 1.7 pg/ml. The photocurrent enhancement would be due to photoexcitation of the excited state for the 532 nm light and of the geminate electron-ion pair for the 1064 nm light.

HIGH SENSITIVE DETECTION ON SURFACE

Most of the current high sensitive technique on surface requires the sample to be in high vacuum. The laser photoionization technique on surface can offer a sensitive method without evacuation just as in the case of solution. The experimental apparatus is shown in Fig. 6. The photocurrent time profile in air has a fast and a slow components as in the case of solution as shown
in Fig. 7. No slow component appears in N₂, and no fast component in SF₆. Thus, we can conclude that the fast component is due to electrons and the slow component to O₂⁻ produced in electron capture of oxygen. The motion (speed) of slow component is proportional both to the pressure and to the electric field; mobility of O₂⁻ was determined to be 2.3 cm²/s·V⁻¹.

The photocurrent signal depends on the molar absorptivity, indicating the initial step is the excitation to the states of the laser photon energy. The detection limit of pyrene on platinum was about 5x10⁻¹⁵ mol/cm², which is about one-thousandth of the monolayer coverage. The analytical curve was linear for five orders of magnitude above the detection limit.

PHOTOIONIZATION BY AN ARGON LASER

Laser two-photon ionization has been investigated with a pulsed laser, because a two-photon ionization probability is quadratically proportional to the peak energy of the laser and a pulsed laser has a larger peak energy. However, a continuous laser is more stable and more coherent, and it has its own merits if two-photon ionization is possible with a continuous laser.

Since a continuous laser can be focused more tightly than a pulsed laser, a two-photon ionization probability differs little if the sample is sufficiently small as in the case of microcolumn HPLC. For a solution sample in a cell, a simple calculation indicates that there are about 5 orders of magnitude difference in the S/N ratio of the photoionization current induced by the two lasers. Since typical detection limit by the dye laser is 0.1 ng/ml, expected detection limit by the Ar laser would be 10 μg/ml. However, in the case of an application to micro-column HPLC, the most of the merit of the dye laser would disappear and the S/N ratio would be much closer.

With an apparatus similar to Fig. 3 with an Ar laser, we have obtained a photoionization signal from naphthacene and fluoranthene in hexane; the former should be photoionized successively and the latter simultaneously.

REFERENCES

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