

Investigation on Production of Cluster Ions Using Surface-Assisted Laser Desorption/Ionization Mass Spectrometry



NIE Long-Hui¹, WANG Wei-Guo^{2,*}

¹ Department of Materials and Chemical Engineering, Hubei University of Technology, Wuhan 430068, China

² Key Laboratory of Separation Science for Analytical Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

Abstract: Surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS) has become an indispensable tool in analysis of macromolecule and small molecule in solid and liquid samples. However, there were few studies focusing on the ionization mechanisms especially for the small molecules. In this work, the compounds of pyrene, coronene and rubrene with similar molecular structures were used to investigate the ionization mechanism via SALDI-MS. Additionally, the effect of laser power on product ions was also investigated. It was found that strong cluster ions peaks nM^+ ($M = \text{pyrene, coronene}$) were observed for pyrene and coronene, and daughter ions of coronene by loss of C_2H_2 were also observed. On the contrary, no cluster ion was obtained for rubrene, only daughter ions with the losses of nC_6H_5 ($n = 1, 2, 3$) were acquired. Finally, the ionization mechanism was discussed. The formation of clusters of pyrene and coronene was attributed to the interaction of π - π bonds. For rubrene, the spatial barrier weakened the interaction of π - π bonds because the four phenyl groups were not on the same plane of skeleton structure, thus impeding the formation of cluster ions.

Key Words: Surface-assisted laser desorption/ionization mass spectrometry; Polycyclic aromatic; Ionization; π - π bond interaction; Spatial barrier

1 Introduction

Laser ionization mass spectrometry technique, combining laser with mass spectrometry, was widely used in directly analyzing solid and liquid samples with advantages of simple preparation of samples and wide applications. The first paper on laser ionization mass spectrometry was published in 1963 by Honig *et al.*^[1], who detected and identified product ions, electrons, and neutral atoms emitting from solid surface using a laser ion source double focusing mass spectrometer. With the rapid development of laser technique and mass spectrometry technique, laser ionization mass spectrometry attracted many attentions in the fields of analyses of inorganic trace elements^[2-5], environmental pollutants^[6], biological

macromolecules^[7,8], and so on.

At present, laser ionization mass spectrometry techniques for solid and liquid analysis were mainly divided into two categories: matrix assisted laser desorption/ionization mass spectrometry (MAIDI-MS)^[9,10] and surface assisted laser desorption/ionization mass spectrometry (SALDI-MS)^[11-15]. MAIDI-MS, as an important biological analysis technique, was firstly developed by Hillenkamp's group^[7] for detection of macromolecules. The principle of MAIDI-MS is that matrix adsorbs energy from laser when the mixture of sample and matrix is irradiated by a certain intensity of laser. Therefore, sample evaporates and sample ions are produced via charge transfer reactions, and then the ions are detected using MS. However, a strong background signal from small organic

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*Corresponding author. Email: wwg1978@dicp.ac.cn

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matrix interferes with the detection of small molecular compounds. SALDI-MS makes use of the techniques of surface assisted adsorption of sample molecules and laser ionization, which can efficiently avoid the interference with small molecular compounds. Thus, SALDI-MS can be used for detection of both macromolecules and small molecules.

One of important application fields for SALDI-MS is asphaltene chemistry^[16–23]. Asphaltenes are composed of aromatic rings and aromatic heterocycles^[16,17]. By studying the molecular weight distribution of asphaltenes, the age and region of its formation can be traced. Previous studies showed that the molecular weight distribution obtained from different laser power was very different, and average molecular weight was from 2000 to 50000 D^[22,23]. Al-Muhareb *et al.*^[22] observed the distribution of peak mass 50000 under high laser power, and they believed that low laser power was not enough to desorb large mass of asphalt. However, Al-Muhareb *et al.*^[21] and Hortal *et al.*^[22] thought that the large laser power would cause molecular polymerization to produce clusters with large mass during the desorption/ionization processes. Therefore, it is of great significance to investigate the mechanism of SALDI. In this paper, pyrene, coronene and rubrene with similar and highly symmetric structure containing several benzene rings (Fig.1) were selected to investigate the evolutions of product ions in SALDI-MS under different experimental parameters. It was found that a lot of cluster ions were observed for pyrene and coronene with coplanar π bond structure. However, only a large number of daughter ions were acquired for rubrene. The effect of laser power on the product ions and their distribution was also investigated. Also the formation mechanism of product ions was analyzed and discussed. This study can provide references for spectrum analysis and ion identification with laser ionization mass spectrometry in the future.

2 Experimental

2.1 Instrument and reagents

Home-made surface-assisted desorption/ionization time-of-flight mass spectrometer was used in the experiment. Toluene was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.; pyrene was from Bailinwei Technology Limited; coronene and rubrene were purchased from Dalian Ruikaimu Petrochemical Company Limited. All reagents were analytical pure.

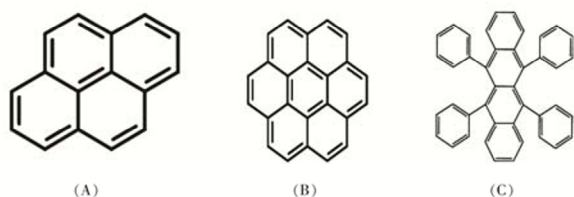


Fig.1 Chemical formula of pyrene (A), coronene (B) and rubrene (C)

2.2 Experimental method

Firstly, the standard solutions (2 mg mL⁻¹) of pyrene, coronene and rubrene were prepared by using toluene as solvent, respectively. Then, 2 and 6 μ L of standard solutions were dropped on sample target. After solvent toluene volatilizing for 10 minutes, the sample for test was obtained on a disc of 2.3 mm in diameter on the target surface. Afterwards, the sample entered into the desorption/ionization chamber of mass spectrometer and was used for detection with time of flight mass spectrometry.

The Nd:YAG laser with a wavelength of 355 nm was used in this experiment, and the laser power could be adjusted from 1000 nJ to 6000 nJ. The diameter of the laser spot at the sample was about 0.5 mm. Data acquisition card included micro-channel board, high-speed transient data acquisition card and preamplifier. The pressure in the detection chamber was maintained at the level of 10⁻⁴ Pa order. Mass spectra were recorded in positive ion mode with a mass range of 0–20000.

3 Results and discussion

3.1 Spectra analysis for pyrene, coronene and rubrene

Typical mass spectra for pyrene, coronene and rubrene are shown in Fig.2, where cluster ions and daughter ions peaks could be observed for pyrene and coronene. The maximum number in cluster ions was up to 4 for pyrene, and more than 10 for coronene (clusters ions with number above 6 was not shown in Fig.2). With the increase of the molecule number in the cluster ions, the signal intensity approximately showed exponential decay. The divergence between pyrene and coronene could be ascribed to the difference in molecular structure. The π - π bond interaction of coronene molecule was stronger than that of the pyrene molecule, while the steric hindrance of the rubrene molecule hindered the polymerization

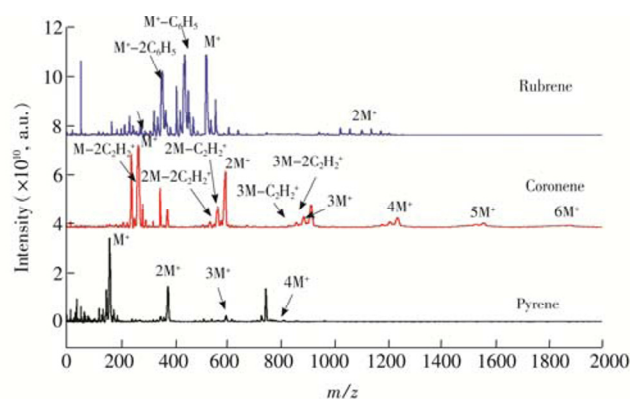


Fig.2 Typical SALDI-MS spectra for pyrene, coronene and rubrene at 3000 nJ of laser power, where M represents the corresponding molecule and digital number represents the number of molecules

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