Applying a Spray-jet Method for Measuring Naphthalene Derivatives by Nanosecond Laser MPI TOF-MS

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(Received November 12, 2004; CL-041362)

A molecular-beam apparatus with a spray-jet method was applied for the laser TOF-MS study of naphthalene derivatives, 2-naphthoic acid (2NA), and 1,5-dihydroxynaphthalene (DHN). The results obtained by this method are compared with those obtained by the traditional sample-heating inlet method. The spray-jet method strongly improved the signal-to-noise ratio (S/N), compared to the traditional method. In addition, the intermolecular clusters due to hydrogen-bond formation were observed in case of the DHN system.

The sample-heating inlet method to generate a supersonic-jet molecular beam, which is a combination of an ultrahigh vacuum and a pulsed nozzle, has become a popular method in the spectroscopic field studying the gas phase.[1] This method enabled us to introduce electronic neutral molecules into a vacuum chamber as a molecular beam, while reducing the load on the evacuation systems. This traditional sample inlet method is not suitable for the sample molecules which are non-volatile, or thermally unstable. Rizzo et al.[2] developped a method to combine a thermospray with a thermal desorption. According to their report,[2] a brass block was heated upto 230 °C in case of tryptophan experiment. Therefore their method is not always suitable for the sample molecules which are non-volatile, or thermally unstable. To overcome these difficulties on the traditional sample-inlet method, we have developed a molecular beam apparatus with a spray-jet method that produces a neutral molecular beam.[3] The details of this apparatus are described elsewhere.[3–5] Briefly, a thick mist of sample solution is initially prepared with the nebulizer, and then flowed into the inlet chamber, from which a molecular beam is ejected into vacuum through the pulsed nozzle.

On the other hand, recently, several unique methods to introduce non-volatile large molecules (or heavy-molecular-weight molecules) into vacuum, to carry out the MS measurement, such as electrospray (ES),[6] MALDI TOF-MS,[7] and laser desorption jet-cooling[8] have been developed. All of these methods are very sensitive and excellent methods for precise mass analyses. The ES deals with the pre-ionized molecules, i.e., the pre-ionized sample molecules are introduced into a vacuum chamber through a capillary, and they are subsequently mass selected by a quadrapole or an octapole for mass analyses. In contrast to the ES, our spray-jet deals with not pre-ionized sample ions but neutral molecules. While in the MALDI TOF-MS, the matrix molecules are photoionized in vacuum by laser radiation. Subsequently the ionization of the sample molecules takes place. Produced cations are mass analyzed by a TOF-MS. Thus, the MALDI involves rather complicated processes for producing the cations to be mass analyzed. In contrast to MALDI, in case of the spray-jet method, the sample molecules in the molecular beam are directly photoionized. In case of laser desorption jet-cooling,[8] sample molecules produced by a laser desorption process are seeded in the supersonic carrier gas flow. On the other hand, our spray-jet method does not require the laser desorption process.

Aromatic molecules, especially benzene derivatives and naphthalene derivatives,[9,10] have been widely and precisely studied by the combination of a traditional pulsed sample-inlet method and a pulsed-laser technique, since they are the ones of the most basic polycyclic molecules. In addition, a series of dioxins including biphenyl derivatives and dibenzofuran derivatives, are known to be one of the most important endocrine disrupters. These dioxins are also polycyclic molecules, which attract much interest due to the demand for real-time detection of these molecules in the field of environmental chemistry.[11]

We have applied the spray-jet method on liquid crystal (5CB),[3] laser dyes (DCM, Rhodamin B),[4,5] and larger molecular systems (porphyrin derivatives, dendrimer, etc.), but we have not applied it to the basic polycyclic molecules, so far. Under these circumstances, it is very important to examine the applicability of the spray-jet method for naphthalene derivatives as species of basic polycyclic molecules. In the present study, we apply the spray-jet method to the naphthalene derivatives, 2-naphthoic acid (2NA) and 1,5-dihydroxynaphthalene (DHN), which have melting points of 185–187 °C and 259–261 °C, respectively. It is expected that these samples have low vapor pressure.

In this study, methanol (MeOH) solutions of each sample molecule with a concentration of 2.5 mM were prepared for the spray-jet experiments, while the sample molecular vapor ob-

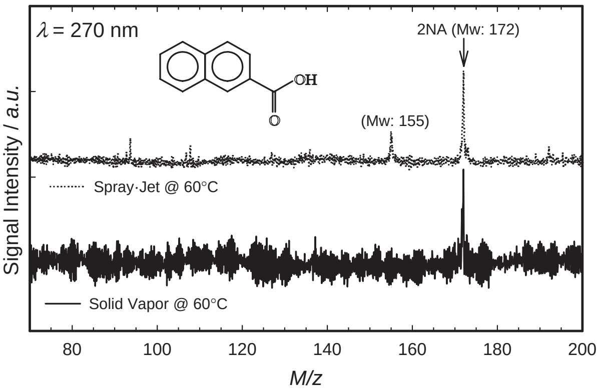

Figure 1. TOF-mass spectra of 2NA obtained by spray-jet method (dotted line) compared with that obtained by traditional sample inlet method (solid line). The molecular structure of 2NA is also shown in this figure.

tained by heating solid sample was introduced into vacuum in case of traditional measurements. Our laser sytem consists of a Nd:YAG laser and an optical parametric oscillator (OPO). A signal output from an OPO, pumped by the third harmonic of a Nd:YAG laser, is frequency doubled (225–320 nm, typically 1.3 mJ/pulse) and slightly off-focused to enable MPI TOF-MS measurement.

The mass spectrum of 2NA obtained by the spray-jet method is compared with that obtained by the traditional sample-heating method in Figure 1. In case of 2NA measurement, a laser beam with a 270-nm wavelength was applied. In both cases, the sample was heated to 60 °C. As can be seen in Figure 1, the signal-to-noise ratio (S/N) of the obtained mass spectrum by the spray-jet method (S/N = 7.2) is better compared with that obtained by the traditional method (S/N = 2.2). The weak parent-ion signal obtained by the traditional method implies that the heating temperature of 60 °C was not sufficient to generate sample vapor pressure. The second significant peak observed at $m/z = 155$ in the spray-jet method is tentatively assigned due to the desorption of the –OH group from the carboxyl group from the mass number.

Figure 2 shows the mass spectra of DHN obtained by the spray-jet and the traditional heating methods. In the DHN measurement, the laser beam with a wavelength of 300 nm was applied in both cases. In our experiment, the parent cation signal of DHN was not detected below 100 °C, even though very weak parent signal was observed at 140 °C by means of the traditional sample-heating method (S/N = 8.7). In contrast, a very intense parent cation signal was detected at $m/z = 160$, even at 60 °C, by means of the spray-jet (S/N = 156.1).

Figure 3 shows the TOF-mass spectrum of the DHN clusters obtained by the spray-jet method. Hydrogen bond clusters, DHN–MeOH, DHN–$(MeOH)_2$, and $(DHN)_2$ were observed at $m/z = 192$, 224, and 320, respectively. The signal intensities of the observed clusters tend to fluctuate compared to that of bare DHN. No cluster signal has been observed, according to previous reports,[3–5] and the DHN/MeOH system is the first to show intermolecular clusters between a non-volatile sample molecule and solvent molecule(s) (as well as DHN dimer) by the spray-jet method. This is due to the strong intermolecular hydrogen-bond formation between the –OH groups of DHN and MeOH.

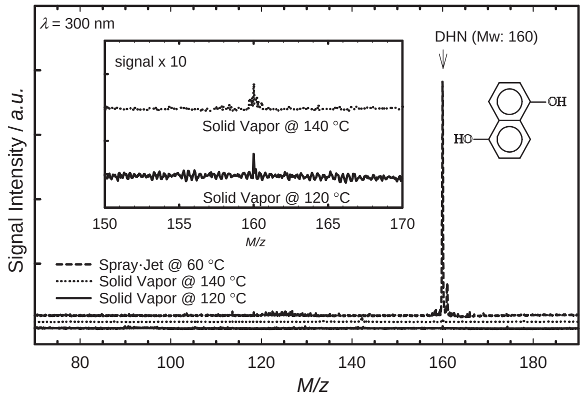

Figure 2. TOF-mass spectra of DHN obtained by spray-jet method (dotted line) compared with those obtained by traditional sample inlet method. The inset shows the enlarged mass spectra obtained by the traditional methods at 120 °C (solid line) and 140 °C (dotted line), respectively. The molecular structure of DHN is also shown in this figure.

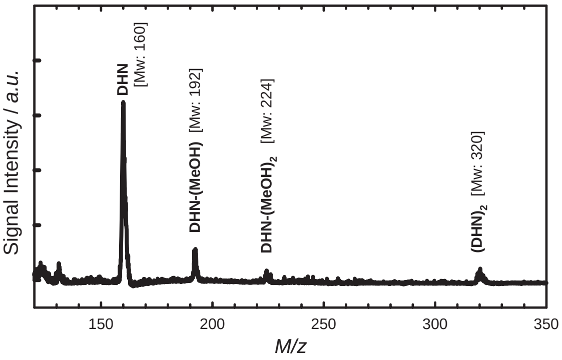

Figure 3. TOF-mass spectrum of DHN obtained by spray-jet method. The hydrogen bonding clusters of DHN–(MeOH), DHN–$(MeOH)_2$, and $(DHN)_2$ are observed at m/z of 192, 224, and 320, respectively.

As can be seen from Figures 1–3, we have successfully observed the parent cation signals for 2NA and DHN introduced by the spray-jet method as well as the intermolecular clusters of DHN. Compared to the traditional method, the spray-jet method improved the S/N ratio of mass spectra for both of 2NA and DHN. Furthermore, in case of DHN, a very intense parent ion signal was obtained at much lower temperature (60 °C) compared to the traditional method (140 °C). To obtain the REMPI spectra of not only these naphthalene derivatives but also their intermolecular clusters is the next step to be achieved with this spray-jet method.

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Published on the web (Advance View) January 15, 2005; DOI 10.1246/cl.2005.234