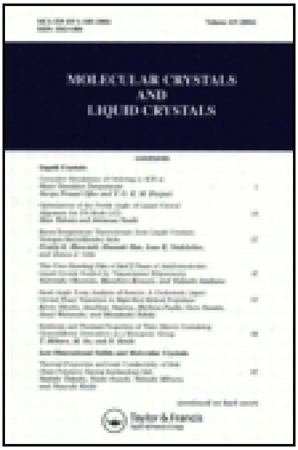

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Analysis of a Molecular Beam Produced by the Spray-Jet Technique with Femtosecond Laser Mass Spectroscopy

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We previously developed a molecular beam apparatus with the spray-jet technique to produce a molecular beam of non-volatile molecules under high vacuum from sprayed mists of sample solutions. The apparatus is used in spectroscopic studies or is a means of molecular beam deposition. We analyzed the molecular beam with femtosecond laser mass spectroscopy and conventional nanosecond laser mass spectroscopy. The information obtained from both mass spectroscopy methods provided insight into non-volatile, solvent, and carrier-gas molecules in the molecular beam.

Keywords: femtosecond laser mass spectroscopy; nanosecond laser mass spectroscopy; non-volatile molecule; spray-jet technique

INTRODUCTION

We previously developed a molecular beam apparatus by using a spray-jet technique, which enabled us to produce a molecular beam of non-volatile and/or thermally labile molecules in a vacuum from sprayed mists of sample solutions [1–9]. The apparatus was used for spectroscopic studies and molecular beam deposition. The apparatus for spectroscopic studies consists of (1) an ultrasonic inlet system with an ultrasonic nebulizer, an inlet chamber, and a pulsed nozzle or (1′) a pneumatic inlet system with a pneumatic nebulizer, an inlet cap, and a modified pulsed nozzle; (2) a set of skimmers; and (3) a high-vacuum

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chamber equipped with a time-of-flight mass spectrometry (TOFMS) unit in which pulsed-laser photoionization and mass detection are carried out. The apparatus for molecular beam deposition consists of basically the same components, but the TOFMS unit is replaced by an ultra-high-vacuum (UHV) chamber equipped with a unit for molecular beam deposition and one for transferring a sample plate to a low-temperature scanning tunneling microscope (LT-STM).

A dense mist of sample solution is initially prepared by the ultrasonic nebulizer (or the pneumatic nebulizer) and then introduced into the inlet chamber (or the inlet cap) from which a molecular beam is ejected into the vacuum chamber through the pulsed nozzle (or the modified pulsed nozzle) and skimmers. For a molecular beam deposition experiment, a substrate is located in the path of a molecular beam. After deposition, the substrate is transferred into an ultra-high-vacuum scanning tunneling microscope (UHV-STM), without breaking the vacuum, to analyze the molecular overlayer deposited by the spray-jet technique. We previously investigated the molecular overlayer consisting of chloro[tri-*tert*-butyl-subphthalocyaninato]boron(III) (TBSubPc) molecules and the one consisting of 5,15-bis(4-ethynylphenyl)-10, 20-bis(3,5-di-tert-butylphenyl)porphyrin (trans-BETBPP) molecules, deposited by the spray-jet technique from their sample solutions [5–7]. In spectroscopic studies, we investigated various sample molecules, such as 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM); and Rhodamine B; 1,5-dihydroxy-naphthalene (DHN); and with nanosecond laser mass spectroscopy [1–4]. Resonantly enhanced multi-photon ionization (REMPI) time-of-flight mass spectra and REMPI excitation spectra were recorded, and these spectra provided us with information on the electronic states of the sample molecules as well as mass spectroscopic information. The spray-jet technique in conjunction with nanosecond laser mass spectroscopy provides information different from that provided by the supersonic jet [10], the matrix-assisted laser desorption ionization (MALDI) [11,12], and the electrospray ionization (ESI) [13] techniques.

Thus, the spray-jet technique enabled us to produce a high-quality molecular beam with which spectroscopically characterized sample molecules and deposited them on clean surfaces in a vacuum. However, we do not have sufficient information about the molecular beam; that is, carrier gas, solvent, and non-volatile sample molecules. With nanosecond laser mass spectroscopy, it is generally difficult to simultaneously obtain information about carrier gas, solvent, and non-volatile sample molecules because they have different electronic structures, e.g., ionization potential and excited electronic states. This motivated us to perform femtosecond laser mass spectroscopy.

Intense-field laser ionization with femtosecond lasers (10^{12}–10^{15} W/cm^2), that is, non-resonant multi-photon ionization/tunneling ionization, occurs for all kinds of molecules at the laser beam spot. This enables us to analyze carrier gas, solvent, and non-volatile sample molecules simultaneously.

We report on analyses of the molecular beam produced by the spray-jet technique from a solution of non-volatile trans-BETBPP molecules by using femtosecond laser mass spectroscopy and conventional nanosecond laser mass spectroscopy. Both mass spectrometric methods provide insight into the molecular beam produced by the spray-jet technique.

EXPERIMENTAL

Figure 1 shows the apparatus used in this study. The spray-jet inlet system consists of a pneumatic nebulizer (Mainhard, HEN-170-A0.2), an inlet cap, and a pulsed nozzle (Paker Hannifin, 9-279-900). The pulsed nozzle has an 800-µm pinhole. The inlet cap is made of aluminum and is shaped like the diagram of the one in Figure 1, and it has an approximate inner volume of 1320 mm^3. The diameter of the inlet cap exit pinhole is 1 mm. The inlet cap and the pulsed nozzle were usually heated to 10°C below the solvent's boiling point. Atomization of a sample solution initially occurs by pneumatically converting a bulk liquid into small droplets. A sample solution was pumped at 100 µL/min with a syringe pump, and N_2 flowed with a stagnation pressure of 0.4 N/mm^2 (0.4 MPa) to pneumatically produce

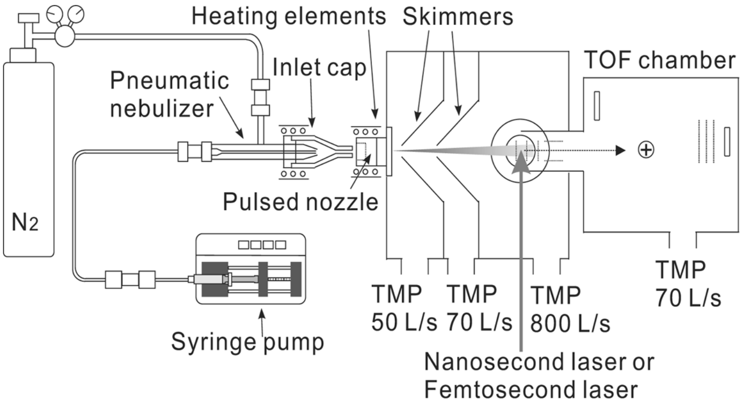

FIGURE 1 Spray-jet molecular beam apparatus used in conjunction with nanosecond and femtosecond laser mass spectroscopy.

the droplets. Droplets in the inlet cap were carried with a carrier gas (N_2) towards the pulsed nozzle, and then a molecular beam was ejected into the vacuum through the pulsed nozzle and skimmers. The vacuum system consists of three chambers separated by skimmers and a TOF chamber that is differentially pumped by turbo molecular pumps. The operation time and repetition frequency of the pulsed nozzle were 0.9 ms and 5 Hz. The vacuum was maintained at approximately 8×10^{-6} Torr during the measurements. Our nanosecond laser system consists of a Nd:YAG laser and an optical parametric oscillator (OPO). The signal light from the OPO, pumped by the third harmonic of the laser, is frequency-doubled (225–320 nm, 5 ns, typically 1.5 mJ/pulse). The laser beam has a wavelength of 310 nm. The typical laser power density at the molecular beam is $10^6 - 10^7\,\mathrm{W/cm}^2$ 2 in current nanosecond laser mass spectroscopy. Details on the vacuum and nanosecond laser systems are described elsewhere [1,3,8]. Our femtosecond laser system consists of a mode-locked Ti:sapphire laser, Q-switched, frequency-doubled Nd:YLF laser, and a regenerative amplifier (Spectra Physics, Hurricane). Amplified pulses (125 fs, 0.8 mJ/pulse) were obtained at a repetition rate of 5 Hz. We used a beam expander to expand the laser beam spot by a factor of 3 and then tightly focused it onto the molecular beam with an $f = 200$-mm achromatic lens. The obtained maximum laser power density at the molecular beam was $3 \times 10^{15}\,\mathrm{W/cm}^2$ in the current femtosecond laser

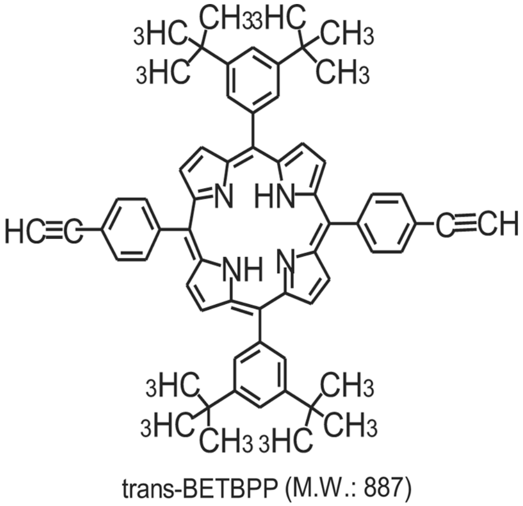

FIGURE 2 Chemical structure of trans-BETBPP.

mass spectroscopy, which is a typical laser power density at which non-resonant multi-photon ionization/tunneling ionization occurs for all kinds of molecules in the laser beam spot. The conventional knife-edge method was used to measure the laser beam spot size at the molecular beam.

A chloroform solution of trans-BETBPP (0.5 mM) was used as the sample solution. The trans-BETBPP, whose chemical structure is shown in Figure 2, is a derivative of the typical porphyrin, tetrakis-di-tertiary-butyl-phenyl porphyrin (TBPP). Trans-BETBPP cannot be thermally evaporated due to two reactive ethynyl groups [6].

RESULTS AND DISCUSSION

Figure 3 shows a nanosecond laser TOFMS spectrum obtained for a chloroform solution of trans-BETBPP. A strong peak from the parent radical cation (m/z = 887) of trans-BETBPP is clearly observed. Since the ionization potential of porphyrin is 6.6 eV [14], the ionization potential of trans-BETBPP would be around 6.6 eV. Therefore the production of the parent trans-BETBPP radical cation is due to two-photon ionization of neutral trans-BETBPP under our experimental conditions (310 nm, ~4.0 eV). The ion intensity of trans-BETBPP radical cation against laser power was 1.95 power, which is approximately 2.

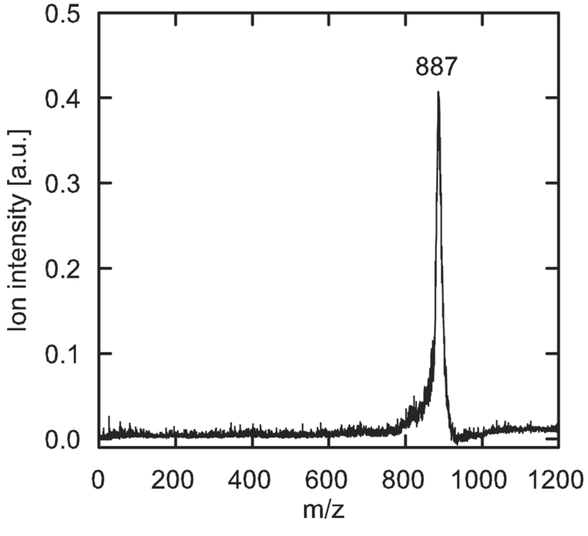

FIGURE 3 Nanosecond laser mass spectrum obtained from trans-BETBPP/chloroform solution.

The signal due to the parent radical cation $CHCl_3^+$ is negligible. Since the ionization potential of chloroform is 11.37 eV [15], three-photon ionization is required to attain it. The signal due to N_2^+ is also negligible. Since the ionization potential of N_2 is 15.581 eV [16], four-photon ionization is required. These observations indicate the non-volatile molecule (trans-BETBPP) is predominantly observed, while the solvent ($CHCl_3$) and carrier gas (N_2) molecules are negligible because carrier gas, solvent, and non-volatile sample molecules have different electronic structures, e.g., ionization potential and excited electronic states.

We then determined the intense-field laser ionization with a femtosecond laser, that is, we measured non-resonant multi-photon ionization/tunneling ionization occurs for a Xe beam produced by a conventional supersonic-jet technique [9,10] under a Xe stagnation pressure of 2 atm. Xenon is a standard atom used for intense-field laser ionization experiments involving femtosecond lasers [17,18]. Xenon ions (Xe^+, Xe^{2+}, Xe^{3+}, Xe^{4+}) were observed in the femtosecond laser mass spectrum and a plot of Xe ion yield versus laser intensity showed a tendency of saturation toward the maximum laser power density ($3 \times 10^{15}\,\mathrm{W/cm^2}$). The Keldysh parameter, γ [19], has conventionally been used for qualitative classification of non-resonant multi-photon and tunneling ionizations and is given by

$$\gamma = (\mathrm{IP}/(1.87 \times 10^{-13} I\lambda))^{1/2}, \tag{1}$$

where IP is ionization potential in eV, I is ionizing laser intensity in $\mathrm{W/cm^2}$, and λ is laser wavelength in μm. Tunneling ionization is expected in the region of $\gamma < 0.5$ and non-resonant multi-photon ionization is predominant for $\gamma > 0.5$ [20]. Using the ionization potential of Xe (12.13 eV) and maximum laser power density ($3 \times 10^{15}\,\mathrm{W/cm^2}$), we determined the Keldysh parameter is $\sim$0.16. Therefore, tunneling ionization is expected at this laser power density.

Figure 4 shows the femtosecond laser TOFMS spectrum obtained for a trans-BETBPP chloroform solution. The TOFMS spectrum was recorded at the maximum laser power density ($3 \times 10^{15}\,\mathrm{W/cm^2}$) attained by our laser system and optics. The small peak appearing at $m/z = 887$ is attributable to the parent trans-BETBPP radical cation. Further smaller peaks in the smaller mass range than 887, which might be the fragment ions of trans-BETBPP, are scarcely discernible, but these are not identified at present. The peaks appearing at $m/z = 119$, 84, and 48 are attributable to $CHCl_3^+$, $CHCl_2^+$, and $CHCl^+$. The ionization potential of chloroform is 11.37 eV. Previous research showed that its dissociation threshold is about 11.52 eV (0.15 eV above its ionization potential) [15], and its dissociation process is

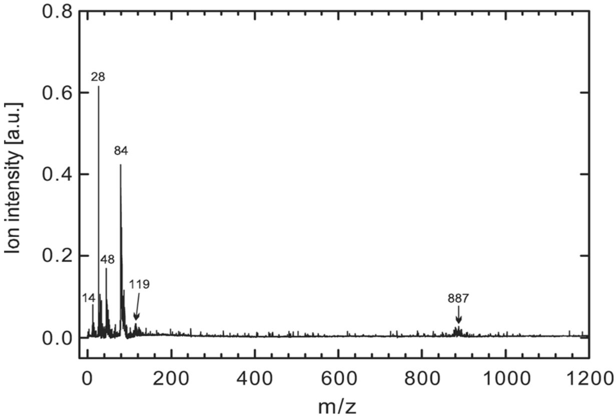

FIGURE 4 Femtosecond laser mass spectrum obtained from trans-BETBPP/ chloroform solution.

($CHCl_3^+ \rightarrow CHCl_2^+ + Cl$). Therefore, it is reasonable to observe $CHCl_2^+$ as a strong peak. The peaks appearing at $m/z = 28$ and $m/z = 14$ is attributable to N_2^+ and N_2^{2+}. We found that intense-field laser ionization with a femtosecond laser occurs for carrier gas, solvent, and non-volatile solute molecules in the laser beam spot, in contrast to nanosecond laser mass spectroscopy. Since the ionization potentials of $CHCl_3$, N_2, and trans-BETBPP are 11.37, 15.581, and ~6.6 eV, the Keldysh parameters of these chemicals are 0.16, 0.19, and ~0.12. Therefore, tunneling ionization is expected for $CHCl_3$, N_2, and trans-BETBPP at this laser power density.

We calculated the summed ion intensity ratio of the trans-BETBPP radical cation to the $CHCl_3$ radical cation and related fragment ions to the N_2 radical cation and the doubly charged N_2 ion. The ratio was 1:70:40. Since the summed ion intensity of each component is proportional to the concentration of each component in the molecular beam, this ratio provides information about each component in it. However, an evaluation the relative sensitivity factor [17] for ionization of each molecular component is required for a more detailed analysis.

CONCLUSION

We used nanosecond laser and femtosecond laser mass spectroscopy to analyze a molecular beam produced by the spray-jet technique from a solution of non-volatile trans-BETBPP molecules. In the nanosecond laser mass spectrometry, a peak from the parent trans-BETBPP radical cation was predominantly observed produced by two-photon ionization at the excitation at 310 nm (4 eV), while peaks from $CHCl_3$ and N_2 radical cations, which are produced by three- or four-photon ionization, were negligible. The difficulty in simultaneously observing non-volatile solute, solvent, and carrier gas molecules by nanosecond mass spectroscopy comes from these molecules having different electronic structures (excited electronic states and ionization potential). In femtosecond laser mass spectrometry, the parent trans-BETBPP radical cation, $CHCl_3$ radical cation and related fragment ions, and the N_2 radical cation and the doubly charged N_2 ion were simultaneously observed by intense-field laser ionization at the excitation at 800 nm (1.55 eV). The parent trans-BETBPP radical cation was observed as a small peak, and the $CHCl_3$ radical cation and related fragment ions, and the N_2 radical cation and the doubly charged N_2 ion were observed as large peaks in the TOFMS spectrum. Analysis of the TOFMS spectrum provided insight into the component molecules in the molecular beam created by the spray-jet technique.

Recently, polycyclic aromatic hydrocarbons have been extensively investigated using femtosecond laser mass spectroscopy [21,22]. Finally, we would like to emphasize the importance of spray-jet technique applications in conjunction with femtosecond and nanosecond laser mass spectroscopy for studying non-volatile molecules.

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