High-temperature pulsed slit nozzle for supersonic jet spectrometry

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An interface converting a cone flow into a rectangular flow is attached to a conventional nozzle with a circular orifice. This assembly can be heated to 300 °C, due to a metal-to-metal contact between an orifice and a plunger and to a Teflon-insulated copper wire of an electromagnet. At the top of the interface, two razor blades are attached to convert the rectangular flow into a slit flow. The enhancement factor (long axis/short axis) is 6 in fluorescence measurements. The signal intensity obtained by the slit nozzle is four times larger than the best value obtained by the conventional circular nozzle.

Supersonic jet spectroscopy provides sharp line structure in the ultraviolet and visible spectra.[1-3] This method has great selectivity and is applied to analytical spectroscopy, allowing discrimination of a specific compound against those with similar chemical structure. In order to improve selectivity, this method may be further combined with other separation techniques such as gas, liquid, and supercritical fluid chromatographies.[4]

The gas density is greatly reduced by jet expansion of a sample molecule into a vacuum. Thus sensitivity is rather poor in supersonic jet spectrometry. Many researchers have developed a pulse nozzle in order to increase the gas density to match pulsed laser excitation. Jet expansion from a pulsed slit nozzle further improves sensitivity by increasing the interaction length between the sample gas and the laser beam. In current studies, a slit nozzle consisting of a plunger with a flat-top board and a slit orifice has been developed.[5] However, it requires high precision in its construction, and it is difficult to eliminate a gas leak completely without using a seal component such as a rubber O-ring. Because of this practical reason, the operating temperature is restricted to −50–80 °C. A slit nozzle, which can be operated up to 200 °C, is reported elsewhere.[6] This nozzle is constructed from two concentric cylinders; the diameter of the internal cylinder is matched to the diameter of the rotating external cylinder with a slit (0.2 mm wide, 35 mm long) within a tolerance of 0.02 mm. However, it is mechanically driven and is difficult to control electronically. In this paper, we report a pulsed slit nozzle with an interface converting a cone flow into a slit flow, which can be operated up to 300 °C and can be driven electronically.

Figure 1 shows a structure of the high-temperature pulsed slit nozzle developed in this study. Part A is a high-temperature pulsed nozzle with a circular orifice (0.8-mm i.d.) reported elsewhere.[7] The orifice and the plunger are made of stainless steel. The nozzle is sealed by a metal-to-metal contact, and no seal component such as an O-ring is used. A copper wire insulated by Teflon is used for construction of an electromagnet, so that it can be heated up to 300 °C. Part B is an interface mass of brass, which converts a cone flow into a rectangular flow. The channel width is 1 mm, the channel volume being 50 mm^3. Two razor blades are attached to the top of the interface to convert a rectangular flow into a slit flow. The slit length is 32 mm, and the slit width is adjustable from 0 to 0.5 mm. The pressure in the interface is not measured but might roughly be estimated to be 1/10 of the nozzle pressure from the difference between the cross sections of the slit and the orifice. In this work the nozzle temperature was raised up to 300 °C. The temperature might be increased further by using a ceramic-insulated copper wire (Dipsol) for an electromagnet.

The experimental apparatus used in this study is reported in detail elsewhere.[8]

Figure 2 shows the relationship between the fluorescence intensity and the nozzle pressure (pressure of carrier gas in nozzle). The fluorescence intensity is greatly enhanced by using a slit nozzle. The enhancement factor, which is defined as the ratio of the fluorescence intensities obtained by placing the slit parallel and perpendicular to the laser beam (long axis/short axis), is 6 at 760 Torr. Furthermore, the signal intensity obtained by the slit nozzle (long axis) is four times larger than the best value obtained by a circular nozzle. Thus the present slit nozzle is useful to improve sensitivity in supersonic jet spectrometry. It is noted that the optimum nozzle pressure is 160 Torr for a circular nozzle and 760 Torr for a slit nozzle. Thus the present slit nozzle is directly applicable to an atmospheric sample. One possible explanation for extension of the optimum pressure to higher pressure might be less-efficient formation of van der Waals complexes. The spectral lines of the van der Waals complexes formed by expansion from a high-pressure nozzle are known to be red shifted relative to the bare molecule.[9] Formation of van der Waals complexes reduces the number of bare molecules to be excited at the specified wavelength. The pressure of a sample gas expanded into a vacuum is much lower (about ten times) in the case of a slit nozzle, as described. So, formation of the van der Waals complexes might be less-efficient when a slit nozzle is used.

The present slit nozzle was also applied to anthracene. The excitation and fluorescence spectra are shown in Fig. 3. Sharp vibrational structure is observed in both the spectra. From the linewidth observed at the pure electronic transition (0–0 transition), the rotational temperature was estimated to be <20 K.[10] This value is consistent with a translational temperature (<37 K) calculated by assum-

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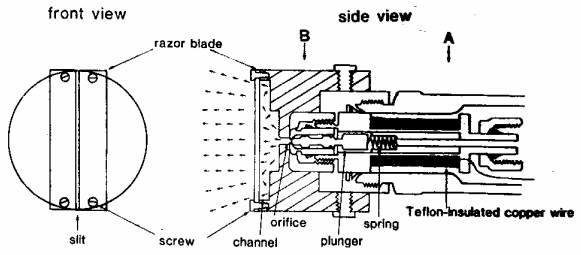

FIG. 1. Part A: high-temperature pulsed nozzle with circular orifice; part B: interface for slit jet expansion (shaded part). The arrows indicate directions of the molecular flow. Many collisions occur and the sample molecules are not cooled in the interface.

ing the jet expansion from a circular nozzle with the same cross section to the slit nozzle. The enhancement factor was improved from 1 to 4 by decreasing the slit width from 0.4 to 0.1 mm. In order to obtain a large enhancement factor, the slit width should be optimized. If the width is too small, the gas density of a jet is decreased and no cooling effect is observed in the extreme case. If the width is too large, the jet is formed by the sample gas is located only in the center part of the jet. It works as a circular nozzle, and no signal enhancement is observed. The optimum slit width is also affected by a stagnation pressure. Thus the slit width must be carefully adjusted, depending on the experimental conditions used.

The nozzle developed in this study may be applied to several spectrometric methods. One of them might be the application to absorption spectrometry. The enhancement factor is restricted by the limited slit height of the monochromator in fluorescence spectrometry. On the other hand, the enhancement factor is proportional to the interaction length between the sample gas and the laser beam in absorption spectrometry. Thus the present nozzle may be more advantageous in absorption spectrometry. Since the

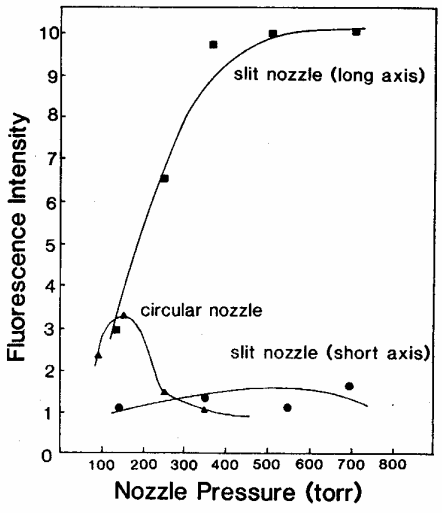

FIG. 2. Relationship between fluorescence intensity and nozzle pressure for aniline. Experimental conditions: slit width, 0.25 mm; orifice diameter, 0.8 mm; sample, room temperature; carrier gas, argon.

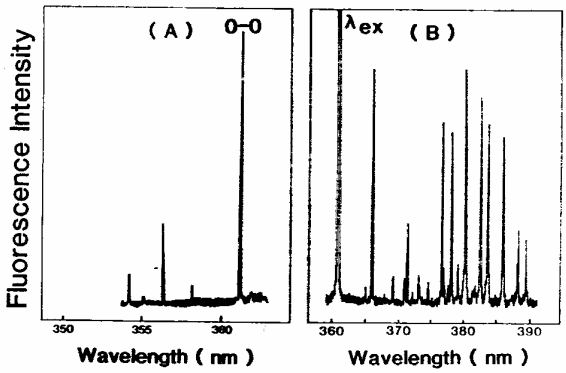

FIG. 3. (A) excitation and (B) fluorescence spectra of anthracene, indicating sufficient cooling by jet expansion. An excimer-laser-pumped dye laser was used as an exciting source. 0–0, wavelength of pure electronic transition; λ_{ex}, exciting wavelength.

present nozzle can be heated to 300 °C, it may be applied to measurements of large aromatic hydrocarbons with sufficient vapor pressures at an elevated temperature. The present nozzle might also be used in multiphoton ionization/mass spectrometry. In this case, it is necessary to use a slit skimmer to form a planar molecular beam. When the laser beam is focused by a cylindrical lens, the ionization region becomes a square plane, which well matches the dimension of a microchannel plate. This configuration reduces the radiation flux of the laser beam at the ionization region, and then the space charge effect is minimized. It is possible to increase the intensity of the parent ion peak by increasing the output power of the laser. Thus a slit nozzle combined with a slit skimmer is very suitable for application to multiphoton ionization/mass spectrometry.

Recently, a pulsed nozzle has been used in many applications, e.g., a frequency conversion of the laser beam by third-harmonic generation,[11] four-wave mixing,[12] etc. The efficiency is improved by increasing the interaction length, and a pulsed slit nozzle is advantageous to improve the efficiency. The present slit nozzle can be operated in a wide temperature range, e.g., even at a liquid-nitrogen temperature, since no rubber O-ring is used as a seal component. Then, this nozzle is useful to introduce a cold gas as well as a hot gas into a vacuum chamber or even into a high-pressure vessel.

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