Development of a Supercritical Fluid Jet Technique for Supersonic Jet Laser Spectroscopy of Nonvolatile and Pyrolytic Molecules

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A new supersonic jet technique, for nonvolatile and pyrolytic molecules, such as biomolecules, called the supercritical fluid jet (SCF-jet) technique was developed. This method enables the vaporization of such molecules without hard heating. To demonstrate the SCF-jet technique, we applied it to 1-naphthol and measured the resonant enhanced multiphoton ionization spectrum.

Mass spectrometry has been one of the indispensable tools for life science, which is demonstrated by the fact that the 2002 Nobel Prize in Chemistry was awarded to the developers of electrosplay ionization (ESI) and matrix-assisted laser desorption ionization (MALDI).[1] These techniques enable one to vaporize nonvolatile or pyrolytic molecules, such as proteins. The techniques used to vaporize such molecules will be applicable to not only mass spectrometry but also the supersonic jet laser spectroscopy, which gives detailed information about the geometrical and electronic structures as well as the reaction dynamics. It can possibly be a powerful tool and bring about breakthroughs in biochemistry research.

For such applications, those techniques, ESI and MALDI, have difficult points. ESI can be applied to only ionic species. In addition, it is difficult to obtain a jet-cooling condition that can be realized by supersonic jet expansion. In the case of MALDI, a temporally steady vaporization is hardly realized. Of course, it is not necessary for mass spectrometry, though it is especially important for supersonic jet laser spectroscopy, which takes a long time for measurements due to the scanning laser frequencies.

To realize supersonic jet laser spectroscopy for nonvolatile or pyrolytic molecules, a new vaporization technique must be developed. In this letter, we offer a new technique, supercritical fluid jet (SCF-jet), which enables the vaporization of such molecules without hard heating. The principle of this technique is simple: to vaporize by direct jet-expansion of the SCF solution of the samples to a vacuum. By SCF-jet, both vaporization and supersonic expansion are achieved. In this letter, we demonstrate the availability of the SCF-jet technique for supersonic jet laser spectroscopy by measurements of the resonant enhanced multiphoton ionization (REMPI) spectrum of 1-naphthol.

Figure 1 shows a schematic diagram of the experimental setup for SCF-jet. The apparatus consists of 4 parts: 1) a generator of a supercritical fluid and an extractor of samples, 2) a jet-expansion chamber, 3) a mass spectrometer, and 4) a tunable laser system.

By using a CO_2 delivery pump (Jasco: SCF-Get), liquefied CO_2 is generated and delivered to an HPLC column oven (Jasco: SCF-LRO) in which liquefied CO_2 is heated at 50 °C to obtain a supercritical fluid. In the oven, some entrainer, which enhances the efficiency of the extraction, can be mixed with supercritical CO_2 by an HPLC pump (Jasco: PU-2080). The supercritical CO_2 that flows out the oven is branched to an extraction sample holder and a back-pressure regulator (Jasco: SCF-Bpg), which keeps the supercritical CO_2 at a certain pressure. The sample is extracted in a sample holder, which is heated at 50 °C just above a pulsed valve.

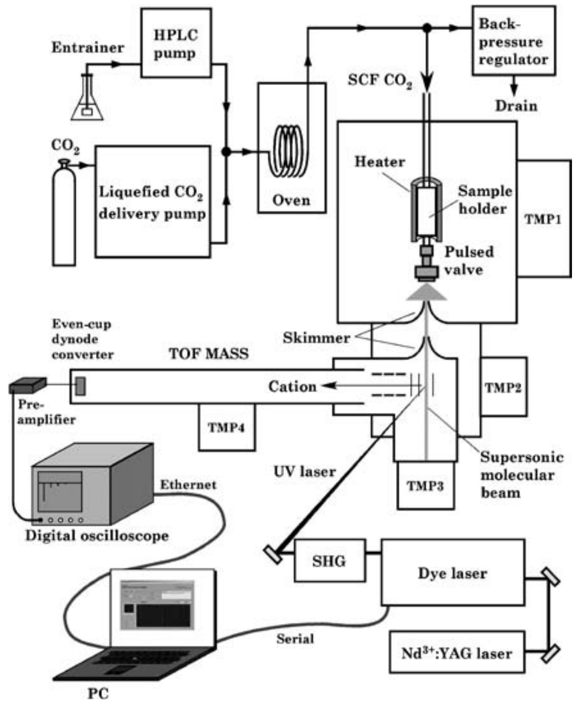

Figure 1. Experimental setup for SCF-jet laser spectroscopy.

To obtain the SCF-jet, we employed an Even–Lavie valve,[2] which can open and close rapidly up to 100 bars. Through a 0.2-mm diam conical nozzle, the SCF is expanded to a first chamber that is pumped by a 1600 L/s turbo molecular pump (TMP1). The SCF-jet is delivered to second and third chambers, each of which is pumped by 480 L/s TMP2 and TMP3, trough 2-mm diam skimmers. In the third chamber, the excitation and ionization laser is irradiated to the SCF molecular beam.

The produced cation is extracted to a linear time-of-flight mass spectrometer, by a Wiley–McLaren electrode.[3] The drift tube is pumped by a 480 L/s TMP4. The cation is detected by an Even-cup dynode converter.[4] The signal from the detector is amplified by a preamplifier (NF ELECTRONICS: BX-31A) and recorded by a digital oscilloscope (IWATSU-LeCroy: DS-4374). For measurements of REMPI spectra, the waveform of a certain mass peak is transferred to a personal computer at every

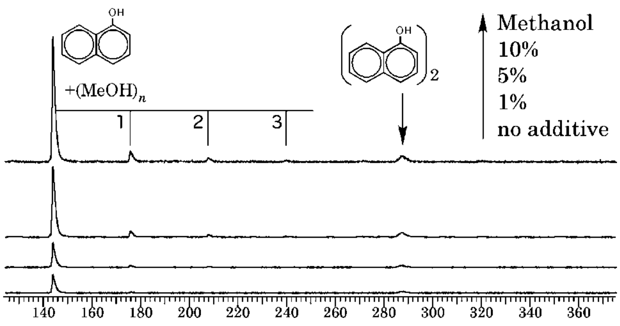

Figure 2. SCF-jet MPI mass spectrum of NpOH.

trigger and integrated. The intensity is continuously averaged and recorded as a function of the wavelength of the excitation laser.

A tunable UV laser is obtained by second harmonic generation (SHG) of the output of a dye laser (Sirah: Cobra Stretch) in a KDP crystal. The dye laser, which is controlled by the same PC for the data acquisition, is pumped by a Nd^{3+}:YAG laser (Spectra-Physics: INDI-40) at 20 Hz repetition, which is synchronized to the pulsed valve.

To demonstrate the SCF-jet technique, we selected 1-naphthol (NpOH) as a sample, which was investigated in detail by the conventional supersonic jet technique.[5–11] In the conventional method, the ion signal cannot be observed without heating over 100 °C in this apparatus because of low vapor pressure.

Figure 2 shows a SCF-jet multiphoton ionization (MPI) mass spectrum of NpOH. The temperature and the pressure of the SCF extraction were 50 °C and 100 bars, respectively. The UV laser was fixed at 315 nm, which does not resonant to any vibronic transitions of NpOH. To enhance the ability of SCF extraction, we added a small amount of methanol to the SCF CO_2. It is well known that the ability of SCF extraction for polar molecules can be drastically improved by adding a small amount of polar solvents,[12] which are called an entrainer. In each spectrum, a mass peak of NpOH was observed dominantly. In addition, the intensity of NpOH peak increases with an increase of the concentration of methanol. The intensities of the clusters also increase, which, however, are weaker, less than 1/10, than that of NpOH. Thus, it was found that the higher clusters are hardly produced in the SCF-jet.

We then measured the REMPI spectrum by monitoring the NpOH mass peak and scanning the UV laser (Figure 3). The concentration of methanol was 10%. An intense peak was observed at 31455.0 cm^{-1}, which corresponds to the S_1–S_0 transition between the zero vibrational levels of *trans*-1-naphthol,[6] where 1-naphthol has cis and trans conformers, according to the direction of the OH group. It is known that cis isomer is dominant.[7] In a higher energy region, many peaks were also observed. These peaks can be assigned to vibronic transitions of *trans*-1-naphthol. The spectral feature absolutely coincides with the REMPI spectrum measured by the conventional supersonic jet technique.[7] The observation of sharp peaks means that the jet-cooling effect is sufficient. Thus, it is concluded that the entrainer, at least methanol, does not disturb the jet-cooling effect of the SCF-jet expansion.

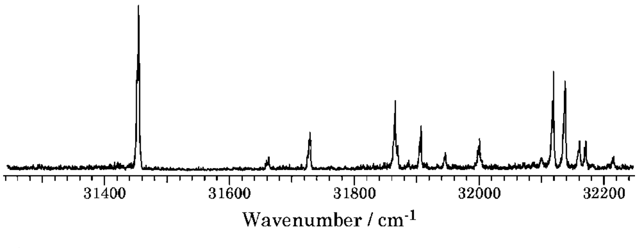

Figure 3. SCF-jet REMPI spectrum of NpOH with 10% methanol.

Here, it is very curious that the higher clusters are not produced in spite of being under a sufficiently jet-cooled condition. The jet-cooling is caused by energy transfers from a sample molecule to the carrier gas molecule/atom through 2-body collisions in the collision region of the supersonic expansion, which exists just at the outlet of the orifice. For the cluster formation process, 3-body or stepwise 3-body collisions are necessary; that is, the transient complex produced by the 2-body collision must be cooled by another collision with the carrier gas. Therefore, it is well known that the clusters are produced efficiently under good jet-cooled conditions. For the SCF-jet, however, such conditions do not cause the formation of many clusters. We cannot conclude at present whether this phenomenon is due to problems of our apparatus or is an intrinsic feature of the SCF-jet technique.

In conclusion, we demonstrated the SCF-jet technique by using NpOH, which is not pyrolytic and is rather volatile because the conventional supersonic jet technique is available with the hard heating of the sample. However, the result that the mass spectrum and the REMPI spectrum can be measured at low temperature, which gives no signal to the conventional method, shows a possibility that the SCF-jet technique will be useful for the mass spectrometry and the laser spectroscopy of nonvolatile or pyrolytic molecules, such as biomolecules.

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