Letters to the Editor

Laser Ablation / Supersonic Jet / Fluorescence Spectrometry of Large Aromatic Hydrocarbon

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Supersonic jet spectrometry provides sharp line structure in a spectrum, and therefore it has great selectivity in chemical analyses.¹⁻³ However, it is a gas-phase spectrometric technique, so that it is quite difficult to measure a sample molecule with low vapor pressure at even an elevated temperature. A laser ablation technique is useful to vaporize such a nonvolatile or thermally labile molecule transiently. Supersonic jet spectroscopy of inorganic molecules such as clusters of Cu, Mo, GaAs, *etc.* has already been reported by Smalley *et al.*⁴⁻⁶ The results indicate sufficient cooling of the molecule, the rotational temperature observed being 5 K.⁵ This technique has also been applied to organic molecules. Lubman *et al.* have reported resonant two-photon ionization spectrometry of aromatic hydrocarbons using pulsed laser desorption (ablation)/supersonic jet/mass spectrometry.⁷⁻¹⁰ They have measured multiphoton ionization and mass spectra for several polycyclic aromatic hydrocarbons, amino acids, and peptides by using a tunable dye laser or a wavelength-fixed fourth harmonic of a Nd:YAG laser as an exciting source. They have presented the advantage of rotational cooling obtained by jet expansion only for small molecules or their combined analogs, however. No sharp spectrum has been reported using a laser ablation/supersonic jet technique for a large molecule such as anthracene derivatives, whose π -electrons extend more than three aromatic rings. It is worth mentioning that such a large molecule surely requires a laser ablation technique. It is at present unknown whether such poor spectral features observed for a large molecule originate from laser ablation technique or from multiphoton ionization spectrometry.

In this study, we report efficient rotational cooling for a large molecule by using laser ablation/supersonic jet spectrometry. Instead of multiphoton ionization spectrometry we use a fluorescence technique to investigate the cooling effect, since we have been unable to observe a sharp multiphoton ionization spectrum for a large molecule such as anthracene or its derivatives.

Experimental

The design of the nozzle for laser ablation is essentially identical to that reported by Smalley *et al.*,⁴ but is slightly simplified. A nozzle throat (1.5 mm i.d., 8 mm long) is attached to a conventional pulsed nozzle.¹¹ A sample is placed in a pit located at the top of a brass rod (1 mm diameter), which is inserted vertically from the bottom into the nozzle throat. The distance between the sample and the nozzle top for jet expansion is 5 mm. The stagnation pressure is adjusted to 250 Torr. A fourth harmonic of a Nd:YAG laser (Quantel International, YG581C-20, 1.5 mJ, 266 nm) is focused into the sample (spot size <0.1 mm) by a quartz lens (focal length 20 cm, diameter 5 cm). The ablated molecules are mixed with a pulsed Ar gas in the throat and are expanded into a vacuum chamber evacuated by a 6-in. pumping system.¹² An excimer-laser-pumped dye laser (Lambda Physik, EMG102MSC, FL2002) excites the sample molecule in the jet 10 mm away from the nozzle. For fluorescence detection, a monochromator (Jasco, CT-100) equipped with a spectrometric multichannel analyzer (SMA, Princeton Instruments, IRY-700) was used in this study. The ablation laser is fired when the pulsed valve of the jet nozzle became fully opened. The timing of the excitation laser is adjusted to 40 μ s after the ablation laser pulse. The gate width of SMA is 20 μ s, the exposure time being 3.2 s.

Results and Discussion

In this study we use 9,10-dichloroanthracene (9,10-DCA) as a standard sample to investigate the cooling effect, since it has sufficiently low vapor pressure at room temperature. The fluorescence spectrum for 9,10-DCA excited at 385.35 nm is shown in Fig. 1. The observed sharp line structure indicates sufficient rotational cooling by supersonic jet expansion. However,

Fig. 1 Fluorescence spectrum for 9,10-DCA measured by spectrometric multichannel analyzer. The excitation wavelength is adjusted to 385.35 nm.

there is still a possibility that this signal originates from the sample continuously volatilized in the nozzle even at room temperature. Therefore, it was confirmed that no fluorescence signal could be observed when the ablation laser was not fired. Furthermore, the timing for laser ablation and the sampling gate of SMA was found to be critical, and it should be adjusted within an accuracy of 10 μ s. This also indicates that the sample is well-localized in a molecular jet, since the pulse width of the jet is much longer (1 ms). The observed spectral linewidth was 0.24 nm; the value was limited by the resolution of the fluorescence spectrometer.

In order to discuss the cooling effect with a better spectral resolution, the fluorescence excitation spectrum was measured at around pure electronic transition (0-0 transition). The wavelength of the monochromator was adjusted to that of the fluorescence band at 406.6 nm, and SMA was replaced with a photomultiplier in this experiment. The spectral width observed was so narrow (0.026 nm, 1.8 cm^{-1}) that the molecule was confirmed to be sufficiently cooled.

Laser ablation provides an effective means even for introduction of such a large molecule into a supersonic jet, and so it might be useful for analysis of large nonvolatile molecules. On the other hand, a sharp spectrum has been reported only for small molecules in laser ablation/multiphoton ionization spectrometry⁷⁻¹⁰, whose π -electrons extend only one or two aromatic rings. This limitation in the molecular size might be a

inevitable disadvantage of multiphoton ionization spectrometry. The reason for the difference is not clear at present, but probably includes the facts that the two-photon energy is too small to ionize such a large molecule and that power-broadening occurs in a three-photon ionization process. In fact, the molecules giving sharp structure in supersonic jet/multiphoton ionization spectrometry are mostly restricted to benzene derivatives or indole analogues, which have a rather low ionization potential relative to the two-photon energy. The present result indicates that laser ablation/supersonic jet/fluorescence spectrometry has no limitation in the size of the sample molecule and gives a sharp spectral structure. This is a distinct advantage of fluorescence detection over multiphoton ionization in supersonic jet spectrometry.

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