Fresenius J Anal Chem (1993) 346:543-544

Fresenius' Journal of Analytical Chemistry

Comparison of stimulated-emission-pumping fluorescence dip spectrometry and conventional fluorescence spectrometry in application to supersonic jet spectrometry *

Yoshiaki Murata, Cheng-Huang Lin, and Totaro Imasaka

Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812, Japan

Received January 18, 1993

Summary. A supersonic jet spectrum of 9,10-dichloroanthracene is measured by stimulated-emission-pumping fluorescence dip spectrometry and conventional fluorescence spectrometry. The performance obtained is compared for these spectrometric methods, providing same information concerned with the energy level of the ground state. The former is more preferential for measurement of a high-resolution spectrum, since the spectral resolution is determined by the linewidth of the dumping laser. On the other hand, the latter is more preferential for measurement with better sensitivity at the expense of the spectral resolution, since the fluorescence throughput can be improved by increasing the slit width of the monochromator.

Introduction

A sharp spectral structure is observed in a supersonic jet spectrum by rotational cooling of the sample molecule, and then information concerned with molecular vibration is obtained accurately [1-3]. The energy level of the excited state is measured by tuning the wavelength of the exciting laser. In this case, total fluorescence or fluorescence from a specified level is measured by isolating it with an optical filter or a monochromator. The spectral resolution is determined by the linewidth of the exciting laser. On the other hand, the energy level of the ground state is measured by scanning the wavelength of the fluorescence monochromator. The spectral resolution is determined by the slit width and the aberration of the monochromator used. Then, the sensitivity is substantially reduced, when a high-resolution spectrum is measured. Thus the spectral resolution and the sensitivity must be compromised in conventional fluorometry.

A stimulated-emission-pumping (SEP) technique has been developed for measurement of the energy level in the ground state [4-7]. In this approach, the sample molecule is excited to a specified level by a pumping laser and is stimulated to a level in the ground state. The population in the excited state is reduced when the frequency of the dumping laser coincides with the energy separation between the excited and ground levels. The reduction of the population is measured as a dip signal from a baseline level of the fluorescence. This technique has currently been used in spectroscopic studies, especially for recording a high-resolution spectrum. However, it has not yet been used in analytical spectroscopy.

In this study, we compare performance of conventional fluorescence spectrometry and SEP fluorescence dip (SEP/FD) spectrometry with respect to selectivity (wavelength resolution) and sensitivity by using 9,10-dichloroanthracene as an analytical sample.

Experimental

Apparatus

The experimental apparatus constructed in this study is shown in Fig. 1. The sample of 9,10-dichloroanthracene is placed in a reservoir made of a stainless steel tube, which is heated to 150 °C by a tape heater. The sample is diluted with argon and is expanded from a pulsed nozzle into a vacuum chamber, which is evacuated by an oil diffusion pump (Ulvac, ULK-06) followed by a mechanical booster pump (Shimadzu, MB-100) and a rotary pump (Shimadzu, KD-300). The vacuum pressure is maintained below 1×10^{-3} Torr during the experiment, which is measured by a pirani vacuum gauge (Ulvac, GP-2T).

Fluorescence measurement

A homemade dye laser pumped by an excimer laser (Lambda Physik, LP 205) is used for sample excitation. Fluorescence is collected by a lens (focal length, 10 cm; diameter, 8 cm) onto the slit of a monochromator (Jasco, CT-100) equipped with a photomultiplier (Hamamatsu, R1477). The signal is measured by a boxcar integrator (Stanford Research, SR250).

In SEP/FD experiments, another dye laser (Lambda Physik, FL2002) pumped by the same excimer laser is used as a dumping laser. The dumping beam is spatially and temporally superimposed to the exciting (pumping) beam. A SEP/FD spectrum is recorded by tuning the wavelength of the dumping laser.

Results and discussion

Figure 2 shows the SEP/FD spectrum of 9,10-dichloroanthracene. The pumping wavelength was adjusted to 358.35 nm, which corresponds to 0-0 (pure electronic) transition for

*Dedicated to Professor Dr. Wilhelm Fresenius on the occasion of his 80th birthday

Correspondence to: T. Imasaka

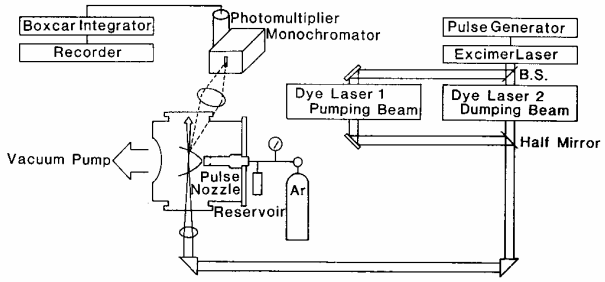

Fig. 1. Experimental apparatus for SEP/FD spectrometry and fluorescence spectrometry

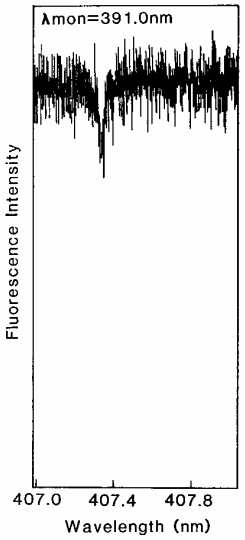

Fig. 2. SEP/FD spectrum of 9,10-dichloroanthracene

9,10-dichloroanthracene. The wavelength of the dumping laser is scanned from 407 to 408 nm. In this study, the fluorescence intensity was monitored at 391.0 nm, which corresponds to the transition to one of the vibrational levels in the ground state. The slit width of the monochromator was adjusted to 0.7 mm, which corresponds to a spectral bandpass of 0.56 nm. It is possible to monitor the fluorescence corresponding to the 0-0 transition. However, this was avoided due to a large background signal occurring from the scattered light of the exciting beam. A sharp signal peak is observed at 407.3 nm, the linewidth of the peak being 0.025 nm. The amplitude of the signal is 15% of the baseline fluorescence. Similar results were obtained, when the monitoring wavelength was adjusted to 405.1 or 409.9 nm.

Figure 3 shows the conventional fluorescence spectrum of 9,10-dichloroanthracene. The measurement was performed by interrupting the dumping laser without changing any experimental conditions except for the slit width of the monochromator, which was adjusted to 0.015 mm for measurement of a high-resolution fluorescence spectrum. The linewidths of the spectral peaks observed are 0.08 nm. The linewidth could not be further reduced by decreasing the slit width, due to limited performance of the monochromator used.

The linewidth observed in SEP/FD spectrometry is several times narrower than those in conventional fluorescence

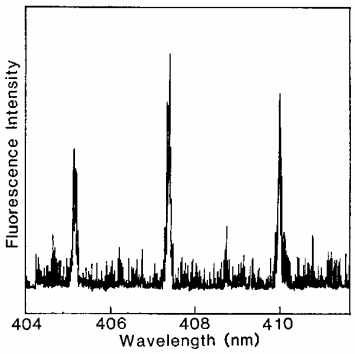

Fig. 3. Fluorescence spectrum of 9,10-dichloroanthracene

spectrometry. Thus the approach based on SEP/FD spectrometry has better spectral selectivity; i.e. many components included in the sample might be more accurately determined by SEP/FD spectrometry. However, this approach has several disadvantages as well. Firstly, the signal is observed as a dip from the baseline, and then the signal-to-noise ratio is rather poor since the variation of the pulse energy of the dye laser is ~ 10%. Secondly, the maximum signal observed in this study is only 15%, which is probably due to poor spatial and temporal overlaps of the pumping and dumping laser beams; the fluorescence from the non-intersected region gives a background signal from the baseline level. Thirdly, the signal peak observed is rather broad in comparison with the linewidth of the dumping laser, which is probably due to signal saturation. Above 0.5 mJ, the fluorescence intensity is saturated on the laser pulse energy. It means that some processes are competing with the SEP/FD process, in addition to the fluorescence process. Fourthly, this approach requires two lasers, which should be superimposed spatially and temporally, as described. Contrarily, a fluorescence spectrum can be easily measured by using a single laser and a monochromator. In fluorometry, the sensitivity can be improved at the expense of the spectral resolution. Roughly speaking, the sensitivity of SEP/FD spectrometry becomes better only when the spectral resolution must be better than 0.03 nm though such a high-resolution could not be obtained in conventional fluorometry by the monochromator used in this study. Thus the analytical advantage of SEP/FD spectrometry is quite limited now. In order to overcome this problem, fluorescence dip spectrometry may be replaced with ion dip spectrometry based on multiphoton ionization, which has a possibility to improve the sensitivity and to obtain additional information concerned with a molecular weight of the sample molecule [7-10].

References

1. Hayes JM, Small, GJ, (1983) Anal Chem 55:565A
2. Lubman DM (1987) Anal Chem 59:31A
3. Imasaka T (1991) Spectrochim Acta Rev 14:261
4. Kittrell C, Abramson E, Kinsey JL, McDonald SA, Reisner DE, Field RW, Katayama H (1981) J Chem Phys 75:2056
5. Vaccaro PH, Kinsey JL, Field RW, Dai HL (1983) J Chem Phys 78:3659
6. Ebata T, Imajo T, Mikami N, Ito M (1982) Chem Phys Lett 89:45
7. Ito M (1987) J Spectrosc Soc Jpn 36:177
8. Cooper DE, Klimbak CM, Wessel JE (1981) Phys Rev Lett 46:324
9. Cooper DE, Wessel JE (1982) J Chem Phys 76:2155
10. Murakami J, Kaya K, Ito M (1982) Chem Phys Lett 91:401