Generation of Multifrequency Laser Emission and Its Application as an Excitation Source in Supersonic Jet Spectrometry

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INTRODUCTION

Supersonic jet spectrometry provides a very sharp spectrum, so that it gives high selectivity in spectrometric analysis.[1-4] However, it has an inevitable disadvantage; the spectrum should be measured with a narrow-band dye laser so that many laser shots are required for recording a spectrum. The repetition rate of the pulsed dye laser is usually 10–20 Hz; a continuous-wave dye laser is also available but it is not practical due to a limited tunable range. Therefore, it takes more than 20 min to scan the wavelength to cover the single-dye-solution range (ca. 30 nm). The sample molecule is unknown prior to the experiment in analytical spectroscopy, and then the laser wavelength must be scanned from the ultraviolet to the visible region. In order to extend the tunable range, the dye solution must be changed frequently. In our laser system, it takes more than 1 h to replace a dye solution, and more than 10 dye solutions must be changed to cover from the near-ultraviolet to the visible region. Then, it takes more than 1 day to scan the whole wavelength region. This is far beyond the time acceptable in routine works.

Recently, many laser systems with wider tunable ranges have been developed, and some of them are already commercialized. For example, a titanium-doped sapphire laser has a wide tunable range in the near-infrared region, which might be extended to the visible and ultraviolet regions by a nonlinear optical effect such as frequency doubling or tripling using a nonlinear optical crystal such as β-barium borate (BBO). It is also possible to use an optical parametric oscillator, which allows a wavelength scan in the whole visible region and is further extended to the ultraviolet region by frequency doubling.[5] Thus, the problem concerned with the replacement of the dye solution will be solved in the near future. However, the repetition rate of the laser is 10–20 Hz, and then the time for recording a spectrum is much longer than several hours to scan the whole spectral region. It is further noted that the angle of the crystal in optical parametric oscillation and frequency doubling must be critically controlled to maximize the efficiency due to phase matching.

In order to overcome these problems, it is possible to use a multiplex excitation technique, such as Hadamard transform spectrometry or Fourier transform spectrometry. A multifrequency laser emission equally spaced is already generated by a stimulated Raman effect. The frequency separation of the multifrequency laser beam generated by a vibrational Raman effect is 4155 cm^{-1}, when molecular hydrogen is used as a Raman medium. This frequency conversion system is attractive, since the multifrequency emission is generated simply by focusing the laser beam into pressurized hydrogen. This method has already been used in analytical spectroscopy.[6,7] Unfortunately, the frequency separation (4155 cm^{-1}) is too large to cover a wide spectral region completely by using a single dye solution, since the tunable range is usually limited to ca. 30 nm; more than three dyes are necessary to cover the spectral region without a gap.[8] For continuous coverage of the whole spectral region, it might be possible to use a titanium-doped sapphire with a wider tunable range. Assuming that the line width of the signal peak is 1 cm^{-1} and the repetition rate of the laser is 10 Hz, the time for recording a spectrum is at least 4155 × 5 (points/peak)/10 Hz × 60 s = 35 min. In order to shorten the time for recording a spectrum further, the frequency separation must be decreased. It is possible to use D_2 (Raman shift frequency, 2987 cm^{-1}) or CH_4 (2917 cm^{-1}).[9] However, the frequency separation is not sufficiently small. There are other Raman media such as O_2 or N_2, but the conversion efficiencies are poor. When a rotational stimulated Raman effect is used instead of the vibrational Raman effect, the frequency separation can be reduced to 587 cm^{-1} for orthohydrogen and 354 cm^{-1} for parahydrogen.[10] Unfortunately, no higher-order Stokes and anti-Stokes rotational lines can be generated by the rotational stimulated Raman effect due to conversion of an angular momentum; only the first Stokes emission can be generated when a laser beam circularly polarized is focused into hydrogen and no rotational emission occurs with a linearly polarized beam.[11]

Recently, a multifrequency laser beam was generated by a two-color stimulated Raman effect.[12-17] The two-colored laser beam separated by 587 cm^{-1} is focused into pressurized hydrogen, and more than 40 emission lines are generated simultaneously from the ultraviolet to the near-infrared region. This is based on generation of vibrational and rotational stimulated Raman emissions. The threshold for generation of higher-order rotational lines is substantially

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(1) Hayes, J. M.; Small, G. J. *Anal. Chem.* 1983, 55, 565A.
(2) Johnston, M. V. *Trends Anal. Chem.* 1984, 3, 58.
(3) Lubman, D. M. *Anal. Chem.* 1987, 59, 31A.
(4) Imasaka, T.; Ishibashi, N. *Prog. Quantum Electron.* 1990, 14, 131.
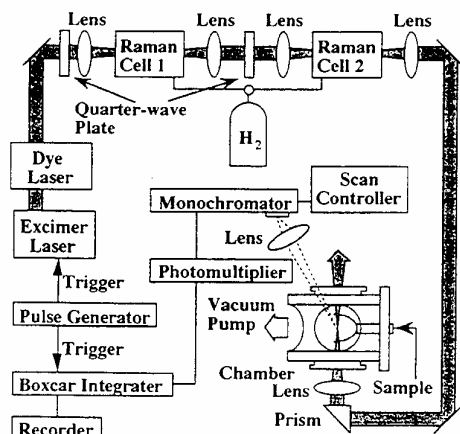(5) Bosenberg, W. R.; Cheng, L. K.; Tang, C. L. *Appl. Phys. Lett.* 1989, 54, 13.

(6) Leong, M. B.; D'Silva A. P.; Fassel, V. A. *Anal. Chem.* 1986, 58, 2594.
(7) Kawasaki, S.; Imasaka, T.; Ishibashi, N. *Anal. Chem.* 1987, 59, 419.
(8) Wilke, V.; Schmidt, W. *Appl. Phys.* 1979, 18, 177.
(9) Hanna, D. C.; Pointer, D. J.; Pratt, D. J. *IEEE J. Quantum Electron.* 1986, 22, 332.
(10) Rasetti, F. *Phys. Rev.* 1929, 34, 367.
(11) kawasaki, S.; Yoshikawa, S.; Imasaka, T.; Ishibashi, N. *Appl. Phys. B*, in press.
(12) Imasaka, T.; Kawasaki, S.; Ishibashi, N. *Appl. Phys. B* 1989, 49, 389.
(13) Imasaka, T.; Higashijima, T.; Kawasaki, S.; Ishibashi, N. *Appl. Opt.* 1990, 29, 1727.
(14) Kawasaki, S.; Imasaka, T.; Ishibashi, N. *Appl. Phys. B* 1991, 52, 211.
(15) Imasaka, T.; Yamanishi, S.; Kawasaki, S.; Ishibashi, N. *Jpn. J. Appl. Phys. Lett.* 1992, 64, 2206.
(16) Yoshikawa, S.; Imasaka, T. *Opt. Commun.* 1993, 96, 94.
(17) Losev, L. L.; Lutsenko, A. P.; Sazonov, S. N. *Sov. J. Quantum Electron.* 1990, 26, 878.

Figure 1. Block diagram of experimental apparatus. A multifrequency laser is used as an exciting source in supersonic jet fluorometry.

reduced by stimulated Raman mixing (four-wave mixing), and the angular momentum is reserved by using a two-colored linearly polarized pump beam.[8] More recently, either vibrational or rotational lines have been generated selectively by optimization of the experimental conditions such as the hydrogen pressure and the beam polarization.[18] However, the reported works so far are concerned with generation of wavelength-fixed multifrequency laser emission.

In this study, we first generate tunable multifrequency laser emissions based on the two-color stimulated Raman effect. More than four rotational lines are generated simultaneously and are used for excitation of the sample molecule in a supersonic jet. The wavelength is scanned repetitively between 378 and 387 nm (0–587 cm^{-1}) for multiplex excitation of anthracene derivatives. It is noted that this approach requires no complicated phase matching to maximize the efficiency. The method proposed herein is useful to shorten the time for recording a spectrum. However, it is unknown which line is used for sample excitation in this approach. Furthermore, sharp spectral lines originating from the scattered light appear in conventional excitation and fluorescence spectra. To overcome these problems, the multifrequency laser developed in this study is applied to supersonic jet/synchronous scan luminescence spectrometry. The unwanted signal peaks are removed, and the chemical species of interest are assigned without isolation of the respective emission line.

EXPERIMENTAL SECTION

Apparatus. A block diagram of the supersonic jet spectrometer, in which a multifrequency laser is used as an exciting source, is shown in Figure 1. The detail of the spectrometer is reported elsewhere,[19,20] and it is briefly described here. A dye laser (Lambda Physik, FL2002) is pumped by a XeCl excimer laser (Lambda Physik, LPX205), and 4,4'''-bis[(2-butyloctyl)oxy]-p-quaterphenyl (Exciton, BBQ) is used as a laser dye. The pulse energy of the dye laser was 15 mJ typically, the pulse duration being 10 ns. The laser beam is circularly polarized by passing it through a quarter-wave plate and is focused into Raman cell 1 filled with hydrogen pressurized to 5 atm, typically. The two-colored beam consisting of a fundamental beam and a rotational Raman emission is passed through a quarter-wave plate again, and the resulting linearly polarized beam is further focused into Raman cell 2 to generate a multifrequency laser beam. This is focused 10 mm away from the top of the pulse nozzle. The sample

heated in the gas chromatograph chamber (Shimadzu, GC-8A) is introduced into a pulsed nozzle maintained at 200 °C and is succeedingly expanded into a vacuum chamber, which is evacuated by an oil ejector pump (Ulvac, PBL-04) followed by a mechanical booster pump (Ulvac, PMB-001) and a rotary pump (Ulvac, D-330). Fluorescence is measured by a monochromator (Jasco, CT-25CP) equipped with a photomultiplier (Hamamatsu, R1477). The output signal is measured by a boxcar integrator (Stanford Research, SR-250). The scanning speed of the monochromator is adjusted to that of the dye laser by a scan controller in synchronous scan luminescence spectrometry.

Reagents. The polycyclic aromatic hydrocarbons 9-chloroanthracene, 9,10-dichloroanthracene, and 9,10-dicyanoanthracene are obtained from Wako Pure Chemicals.

RESULTS AND DISCUSSION

Generation of Single Rotational Line. The effect of hydrogen pressure on the pulse energy of the rotational first Stokes emission was investigated by using only the first Raman cell. Under present conditions, the first Stokes emission appeared at 3 atm, and the pulse energy reached a maximum value at 5 atm and decreased to a half-value at 10 atm. On the other hand, the pulse energy of the fundamental beam decreased rapidly from 3 atm and more gradually from 5 to 11 atm. The depletion of the fundamental beam at lower pressure (<5 atm) is due to the energy conversion into the rotational first Stokes emission. At higher pressure, the energy is more efficiently converted into vibrational emission. So the hydrogen pressure was adjusted to an optimum value of 5 atm for selective generation of a rotational line throughout this study. The effect of the beam polarization was also investigated in detail by rotating the quarter-wave plate. The rotational Stokes emission could be most efficiently generated, when the laser beam was purely circularly polarized. When the quarter-wave plate was rotated 45°, the energy of the rotational Stokes emission became negligibly small. The present result agrees quite well with the experimental result obtained in the infrared region using a CO$_2$ laser.[21]

Generation of Multifrequency Beam. The effect of hydrogen pressure in the second Raman cell was also investigated. The result was similar to the case of the first Raman cell; the optimum hydrogen pressure for generation of the multifrequency laser beam was located at around 5 atm. It is noted that multifrequency emission could not be generated by using a circularly polarized beam due to conservation of an angular momentum. Thus the two-colored linearly polarized beam is necessary for efficient generation of a multifrequency beam by four-wave mixing.[22] A single-colored elliptically polarized beam was also used to generate a multifrequency beam by using a couple of Raman cells, but the efficiency was relatively poor in comparison with the above experiment. This optical configuration was not used in this study. Thus multifrequency laser emission equally spaced (587 cm^{-1}) is generated efficiently by a combination of the single-colored dye laser, the rotational stimulated Raman effect, and the two-color stimulated Raman effect, in series.

Tunable Range. The wavelength of the multifrequency laser emission can be changed by scanning the wavelength of the dye laser. The tunable range obtained is shown in Figure 2. The tunable range is 17 nm for the fundamental dye laser emission, which can be extended to 47 nm without any gaps by using the rotational stimulated Raman emission. Thus the tunable range can be extended 2.8 times. Of course, it is possible to use this multifrequency beam directly without isolation of the respective emission lines. This provided us
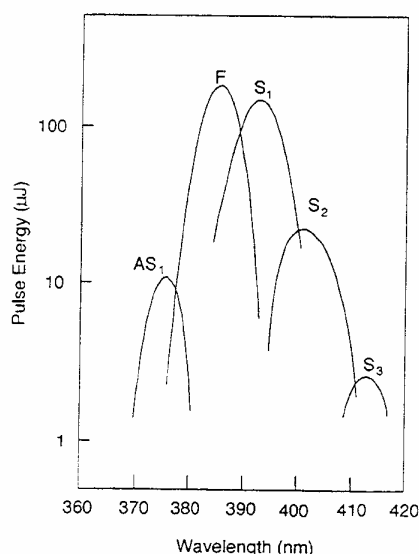
(18) Yoshikawa, S.; Kawasaki, S.; Imasaka, T.; Ishibashi, N. *Jpn. J. Appl. Phys. Lett.* 1991, 30, 283.

(19) Lin, C. H.; Fukii, H.; Imasaka, T.; Ishibashi, N. *Anal. Chem.* 1991, 63, 1433.

(20) Lin, C. H.; Imasaka, T.; Ishibashi, N. *Anal. Chem.* 1991, 63, 2346.

(21) Midorikawa; K. Ohashi, K.; Tashiro, H.; Nagasaka, K.; Toyoda, K.; Nambara, S. *Laser Res.* 1988, 16, 563 (in Japanese).

(22) Kawasaki, S.; Yoshikawa, S.; Imasaka, T.; Ishibashi N. *Appl. Phys. B*, in press.

Figure 2. Tunable range of multifrequency laser generated by two-color stimulated Raman effect. The wavelength can be turned from 370 to 415 nm by using anti-Stokes (AS₁), fundamental (F), and Stokes (S₁₋₃) emissions.

an opportunity to use it for multiplex excitation of the analytes, which may promise reduction of the time for recording a spectrum.

Conversion Efficiency. The major loss in frequency conversion is reflection of the beam at the surface of the optical components such as lenses and windows. The conversion efficiency from the fundamental beam to other emission lines is roughly estimated to be 0.5–1, though this estimate is not very accurate due to the nonflat spectral response of the diffuser window of the pyroelectric joule meter. The conversion efficiency may be further improved by (1) increasing the peak power of the laser, (2) using a multiple-pass Raman cell,[22] and (3) cooling hydrogen; the population of the lower state is increased by decreasing the temperature. The number of rotational lines may be increased by optimization of the conditions, since more than 11 rotational lines have already been generated simultaneously.[15,23,24] The conversion efficiency may be further improved by using parahydrogen instead of orthohydrogen;[25] the ratio of orthohydrogen and parahydrogen is 3:1 at a room temperature and only the orthohydrogen is valid in frequency conversion in this study. However, the content of parahydrogen can be increased to 100% by decreasing the temperature, and then parahydrogen is more useful to improve the efficiency. It also decreases the Stokes shift frequency (354 cm⁻¹) and is useful for increasing the number of emission lines. In order to obtain a flatter intensity distribution, a lesser with a higher peak power and a wider tuning range is needed. A nanosecond or picosecond titanium-doped sapphire laser is preferential for this purpose, and such a laser will be used instead of a dye laser in the future.

Conventional Fluorescence Spectrometry. Figure 3A shows the excitation spectrum for 9-chloroanthracene measured by using a multifrequency laser as an exciting source. A sharp peak is observed at 373.25 nm, which corresponds to the pure electronic (0–0) transition for 9-chloroanthracene. The molecule is excited by the first anti-Stokes emission. A strong peak (scaled out) is observed at 470 cm⁻¹, which
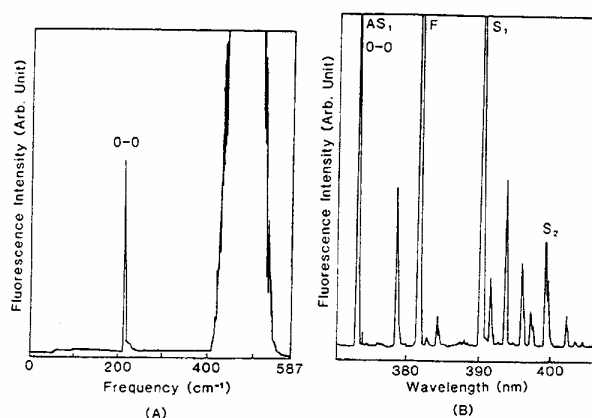
Figure 3. (A) Excitation spectrum for 9-chloroanthracene. The dye laser wavelength is scanned between 378 and 387 nm (0–578 cm⁻¹). Fluorescence is monitored at 394 nm, which is located at 470 cm⁻¹ in this spectrum. (B) Fluorescence spectrum for 9-chloroanthracene. The exciting wavelength is adjusted to 373.25 nm, which corresponds to the 0–0 transition for 9-chloroanthracene.

originates by coincidence of the fundamental wavelength of the dye laser and the wavelength of the monochromator for monitoring fluorescence occurring from excitation with the first anti-Stokes emission. Therefore, a strong unwanted peak is observed in the excitation spectrum.

Figure 3B shows the fluorescence spectrum for 9-dichloroanthracene. Several spectral lines are assigned to transitions to various vibrational levels in the ground state. However, peaks specified in the figure (AS₁, F, S₁, S₂) arise from the scattered light. These unwanted signals might be reduced by careful optimization of the fluorescence detection system, e.g, by using a light baffle to minimize the scattered light at the windows or by subtracting the background signal. However, it is difficult to eliminate the scattered light completely in the current work. Thus, the signal peaks occurring from the scattered light are unavoidable in conventional fluorescence spectrometry.

Synchronous Scan Luminescence Spectrometry. In order to remove unwanted peaks in the excitation and fluorescence spectra, the present multi-frequency laser is applied to supersonic jet/synchronous scan luminescence spectrometry reported elsewhere.[17,18,26,27] The spectrum shown in Figure 4A is obtained by monitoring resonance fluorescence; the monochromator wavelength is adjusted to the wavelength of the first anti-Stokes emission. Only a sharp signal peak is observed in the spectrum. A broad band is superimposed on the sharp peak, which is ascribed to the scattered light of the first anti-Stokes emission; the scattered lights at different wavelengths are removed by the monochromator. No sharp peak was observed when the monochromator wavelength was adjusted to the other emission lines. The present peak is apparently observed by exciting the sample with the first anti-Stokes emission. Thus, the synchronous scan luminescence technique is useful to isolate the contribution of the respective emission line.

Figure 4B is obtained by adjusting the monochromator wavelength to 21 nm longer than the wavelength of the first anti-Stokes emission. This wavelength separation corresponds to the energy difference between the vibrationless and one of the vibrational levels in the ground state. Only a signal peak is observed, and the broad background signal is suppressed almost completely. The scattered light is removed by differentiation of the wavelengths for sample
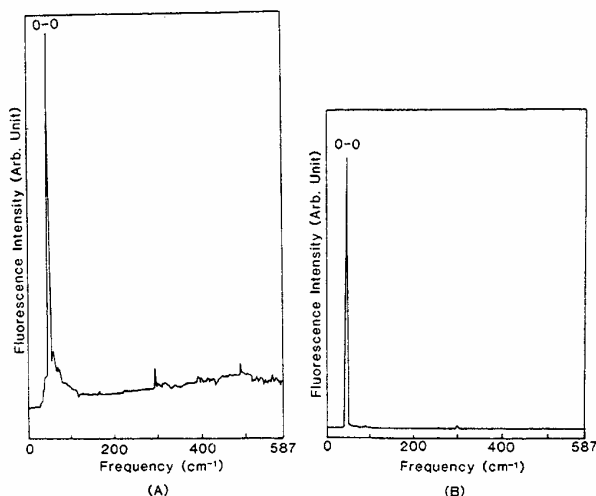
(23) Yoshikawa, S.; Imasaka, T., unpublished result.
(24) Imasaka, T.; yamanishi, S.; Kawasaki, S.; Ishibashi, N. *Appl. Opt.*, in press.
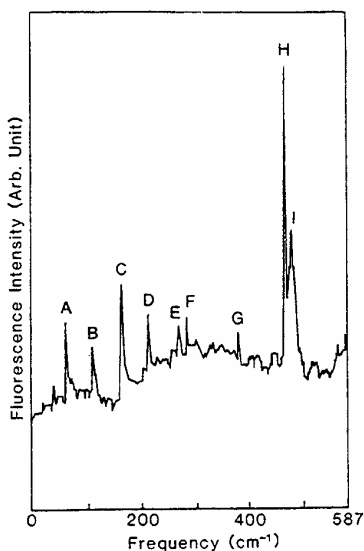(25) Kawasaki, S.; Imasaka, T.; Ishibashi, N. *J. Opt. Soc. Am. B* **1991**, *8*, 1461.

(26) Imasaka, T.; Tsukamoto, A.; Ishibashi, N. *Anal. Chem.* **1988**, *60*, 1362.
(27) Imasaka, T.; Maeno, I.; Ishibashi, N. *Analyst* **1990**, *115*, 73.

Figure 4. Synchronous scan luminescence spectrum for 9-chloroanthracene. The wavelength separation between sample excitation and fluorescence detection is adjusted to 0 (A) and 21 nm (B).

Figure 5. Excitation spectrum for a mixture of 9,10-dichloroanthracene, 9-chloroanthracene, and 9,10-dicyanoanthracene. Total fluorescence is measured by adjusting the wavelength of the monochromator to 0 nm.

Table I. Assignment of Spectral Lines

peak[a]	wavelength[b] (nm)	assignment[c]	peak[a]	wavelength[b] (nm)	assignment[c]
A	371.27		E	400.60	
	379.54	DCA(vib)		410.25	
	388.19		F	374.40	
	397.24			382.82	DCA(vib)
	406.72			391.62	
B	371.91			400.84	
	380.22			410.49	
	388.90		G	375.74	
	397.98	DCNA(0-0)		384.22	DCA(vib)
	407.51			393.09	
C	372.76			402.37	
	381.10	DCA(vib)		412.10	
	389.82		H	376.82	
	398.95			385.35	DCA(0-0)
	408.52			394.27	
D	373.27	9-CA(0-0)		403.61	
	381.64			413.40	
	390.39		I	377.13	
	399.54			385.67	DCA(vib)
	409.14			394.61	
E	374.20			403.96	
	382.61	DCA(vib)		413.77	
	391.40				

[a] Peak specified in Figure 5. [b] Wavelengths for first anti-Stokes, fundamental, first Stokes, second Stokes, and third Stokes emissions. [c] DCA, 9,10-dichloroanthracene; DCNA, 9,10-dicyanoanthracene; 9-CA, 9-chloroanthracene; 0-0, assigned from database constructed by accumulating wavelength of 0-0 transition for many hydrocarbons; vib, vibronic transition assigned from data reported in reference.
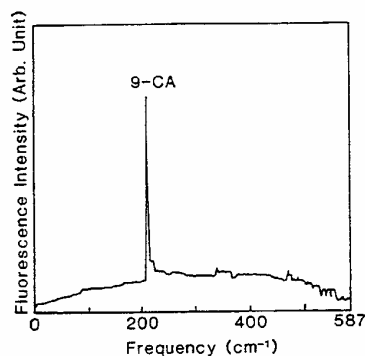
Figure 6. Synchronous scan luminescence spectrum for a mixture of 9,10-dichloroanthracene, 9-chloroanthracene, and 9,10-dicyanoanthracene. The spectrum is recorded by exciting the sample molecule without isolation of the respective emission line. The signal peak (9-CA) appears by excitation of 9-chloroanthracene with the first anti-Stokes emission. The wavelength separation between sample excitation and fluorescence detection is adjusted to 0 nm.

excitation and fluorescence detection using a monochromator. However, the spectral properties of the sample molecule should be known prior to the experiment in this case.

Mixture Sample. Figure 5 shows the excitation spectrum measured for a mixture sample containing three polycyclic aromatic hydrocarbons by adjusting the wavelength of the monochromator to 0 nm; total fluorescence is measured by using diffraction (reflection) of the zeroth order of the grating. Many spectral lines are observed, and a broad background signal is superimposed. The background signal is much larger than the case in synchronous scan luminescence spectrometry monitoring resonance fluorescence, since all the scattered light passes through the monochromator. Table I shows the wavelengths of the emission lines that possibly excite the sample molecules. From the database constructed by accumulating the 0-0 transition data,[28] the candidates of the

molecule contained in the sample are listed in the assignment column. The other vibronic bands are also assigned from the data reported in the references. Apparently, 9-chloroanthracene, 9,10-dichloroanthracene, and 9,10-dicyanoanthracene are excited by the first anti-Stokes, the fundamental, and the second Stokes emissions, respectively. Thus, the time for recording a spectrum can be reduced 5 times by using this multiplex excitation technique.

It is also possible to confirm this assignment by separating the spectrum into five parts using synchronous scan luminescence spectrometry. Figure 6 is obtained by scanning the wavelength of the multifrequency laser and by monitoring resonance fluorescence at the wavelength of the first anti-Stokes emission. Only a single peak is observed, which corresponds to the 0-0 transition for 9-chloroanthracene. Peak D in Figure 5 can readily be confirmed to appear by exciting the sample with the first anti-Stokes emission. Similar results

(28) Ishibashi, N.; Imasaka, T. Report for Grant-in-Aid for Scientific Research from the Ministry of Education of Japan; Project No. 01470065.

are observed for other peaks in Figure 5. Thus, a wide spectral region can be easily covered by application of the multifrequency laser. In synchronous scan luminescence spectrometry, only resonance fluorescence is monitored and then the sensitivity is poorer than in the conventional method. This is a distinct disadvantage of the method. However, it is emphasized that the above confirmation is not performed by separating the respective emission lines with a prism but by isolating resonance fluorescence with a monochromator. Experimentally, it is difficult to isolate a single oscillating line and to fix the direction of the beam passed through a prism since the beam direction changes during a wavelength scan. The present approach is simpler and more practical. It is noted that the measurement time cannot be reduced in synchronous scan luminescence spectrometry since the laser wavelength should be scanned repeatedly by monitoring resonance fluorescence at specified wavelenths in the present detection system. However, the time might be reduced by using an optical multichannel analyzer for recording a fluorescence spectrum since many synchronous scan luminescence spectra can be constructed at once by monitoring resonance fluorescence peaks simultaneously. The broad background signal that appears in Figure 6 could be reduced substantially by adjusting the wavelength separation between sample excitation and fluorescence detection to 21 nm.

CONCLUSION

In this study, we have investigated the advantage of multifrequency excitation in supersonic jet spectrometry. In the first step of the experiment, the excitation spectrum is measured by monitoring total fluorescence by adjusting the wavelength of the monochromator to 0 nm (reflection). All the fluorescence peaks appear in this spectrum, though a broad background signal originating from the scattered light is superimposed. In this approach, it is difficult to separate the contribution of the respective emission line. In the next step, the synchronous scan luminescence spectrum is measured. A simple spectrum is observed in this approach; a single component gives a single peak in most cases. It is noted that the assignment can readily be performed without isolation of the respective emission line. Thus, this technique may be used practically in spectrometric analysis. The background signal occurring from the scattered light can be further reduced by differentiating the wavelengths for sample excitation and fluorescence detection, though the spectral properties of the sample should be known prior to the measurement in this case. This method is useful for trace analysis. It is noted that this background signal can be removed in multiphoton ionization spectrometry. Thus, the present multifrequency laser may be used advantageously in various spectrometric analyses.

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