Reprinted from Analytical Chemistry, 1991, 63.

Suppression of Background Emission from High Vibrational Levels in the Excited State through Vibronic Mixing in Supersonic Jet Spectrometry by Using Synchronous Scan Luminescence

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When a sample molecule is excited to high vibrational levels in the excited state, rapid intramolecular relaxation occurs by an interaction with a dense manifold of vibrational levels in the ground state. Due to vibronic mixing, a combination of vibrational quanta is redistributed and the state is no longer identical with the initial state excited. Therefore, a complicated and broad-band structure appears in a conventional excitation spectrum, due to breakdown of selection rules. This common feature in supersonic jet spectrometry makes it difficult to assign a specific component even for a sample containing only a single interference compound. For example, selective detection of β-naphthol is difficult for a sample containing anthracene, and this situation is similar to *m*-toluidine and 2-methylnaphthalene. However, this unwanted photoemission is completely suppressed by a combination of supersonic jet spectrometry and synchronous scan luminescence spectrometry monitoring resonance fluorescence (SSJ/R-SSL). Furthermore, the number of spectral lines is reduced, giving a simpler spectrum. Thus SSJ/R-SSL spectrometry provides a useful analytical means for selective analysis of organic molecules such as polycyclic aromatic hydrocarbons.

Supersonic jet (SSJ) spectrometry provides sharp line structure in the ultraviolet/visible spectrum, and it provides great selectivity in spectrometric analysis (*1–4*). Even compounds with closely related structure such as isotopes (*5*) and isomers (*6*) could be determined selectively by this spectrometric method. Therefore, most people consider (or believe) that chemical species with completely different structures can be easily resolved, due to this ultrahigh selectivity. However, this optimistic expectation is not correct, and discrimination of an aromatic compound against even those with different numbers of aromatic rings is difficult in conventional SSJ spectrometry, to be mentioned in this paper. In other words, conventional SSJ spectrometry is useful only for discrimination between closely related compounds but is not useful for discrimination between completely different compounds. This is attributed to intramolecular vibronic mixing in the excited state, as described later.

Figure 1 represents an energy diagram for a typical polyatomic molecule. In SSJ spectrometry an optical transition occurs from the lowest energy level in the ground state, due to a cooling effect by supersonic jet expansion. Thus it is useful to simplify the spectrum. However, sharp vibrational lines are observed in the excitation spectrum only below an excess energy of 1000 cm^{-1} from the 0–0 transition. Above 3000 cm^{-1} a complicated spectral feature appears; many irregular spectral lines and sometimes even a diffuse band are observed. This is attributed to intramolecular vibronic mixing; the excited state is perturbed by a dense manifold of high vibrational levels in the ground state (*7, 8*). The character of the excited state is modified, so that selection rules effective to reduce the number of active vibrational modes are not valid anymore. Because of this reason, isolation of the spectral peak is difficult, when a spectral region interested is covered with complicated or broad-band structure occurring from the other molecule having a 0–0 transition at far below 3000 cm^{-1}.

To overcome this problem, SSJ spectrometry is combined with synchronous scan luminescence spectrometry monitoring resonance fluorescence (R-SSL). As already reported, this approach is useful for simplification of the SSJ spectrum and is useful for discrimination between closely related compounds (*9, 10*). In this work, conventional SSJ spectrometry is first applied to two sample mixtures consisting of anthracene (three aromatic rings) and β-naphthol (two aromatic rings) and of 2-methylnaphthalene (two aromatic rings) and *m*-toluidine (one aromatic ring). It is confirmed to be difficult to clearly resolve these compounds by conventional SSJ spectrometry. Alternatively, SSJ/R-SSL spectrometry is applied to the same sample mixtures. It is verified to be useful for discrimination between these compounds, due to better selectivity in spectrometric analysis.

EXPERIMENTAL SECTION

Apparatus. The experimental apparatus constructed in this study is shown in Figure 2. A Nd:YAG-laser-pumped dye laser (Quantel, YG581C-20, TDL50, UVX-2, DCC-3) was used for sample excitation. The vacuum system and the synchronous scan luminescence detection system are reported in detail elsewhere (*9–11*) and are briefly described here. For recording an excitation spectrum, fluorescence is collected by a quartz lens (focal length, 3 cm) onto a photocathode of photomultiplier 1 (Hamamatsu, R1477) after passing it through a color filter (cutoff wavelength, 350 or 317 nm) to discriminate against scattered light of the laser emission. The long pass filter is not suitable for efficient collection of sample fluorescence and enhances interference fluorescence, but the above filter is used in this study since a band-pass filter should be changed frequently by scanning the exciting wavelength. For recording a R-SSL spectrum, fluorescence is collected by a quartz lens (focal length, 10 cm) onto an entrance slit of a monochromator (Jasco, CT-25CP, 2.1 nm/mm) and is detected by the same photomultiplier placed at the position of photomultiplier 2. The wavelength of the monochromator was adjusted to $\lambda_{em} = \lambda_{ex}$ throughout this experiment. The fluorescence signal was measured by a boxcar integrator (Stanford, SR250).

Reagents. Anthracene, 2-methylnaphthalene, and *m*-toluidine were obtained from Tokyo Kasei and β-naphthol from Kishida Chemical. The laser dyes of R610 and DCM were purchased from Exciton.

RESULTS AND DISCUSSION

Mixture of β-Naphthol and Anthracene. Figure 3 shows the excitation spectrum for a mixture of β-naphthol and anthracene. Many sharp lines appear, and irregular and broad background fluorescence covers this spectral region. Com-

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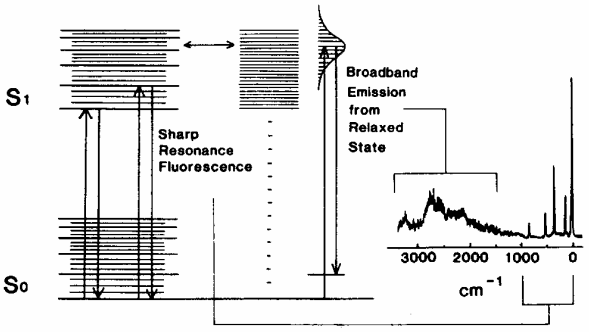

Figure 1. Energy diagram and spectral feature for a polyatomic molecule in supersonic jet spectrometry.

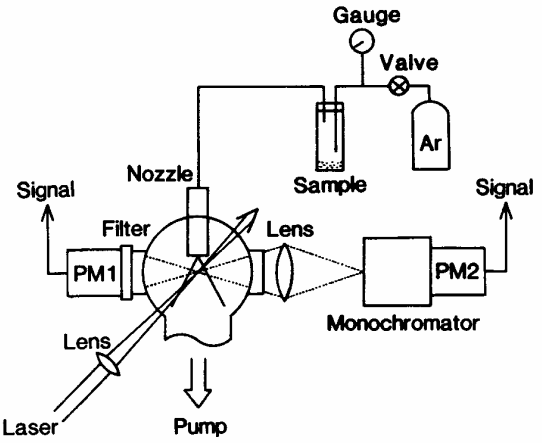

Figure 2. Experimental apparatus for SSJ spectrometry. A conventional excitation spectrum is measured by monitoring total fluorescence by photomultiplier 1 (PM1), and a R-SSL spectrum by monitoring only resonance fluorescence by photomultiplier 2 (PM2).

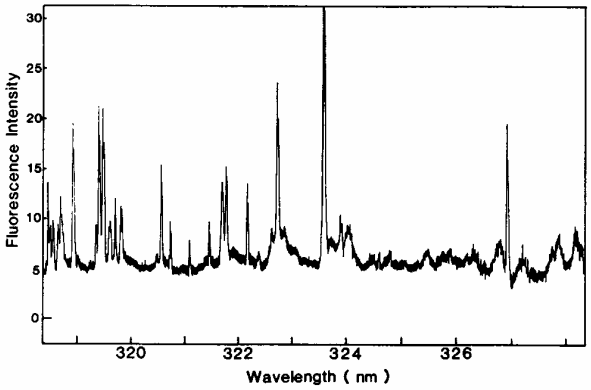

Figure 3. Excitation spectrum for a mixture of β-naphthol and anthracene.

plicated spectral features make it difficult to assign the components, and moreover background photoemission prevents sensitive analysis of a specific component because of a poor S/N ratio. Figure 4A,B shows the fluorescence excitation spectra for β-naphthol and anthracene, respectively. As seen in Figure 4A, β-naphthol provides sharp spectral lines but provides no background fluorescence, as observed in Figure 3. A sharp peak at 326.94 nm is assigned to the 0–0 transition peak for a cis form and a peak at 323.57 nm to that for a trans form of β-naphthol (*12*). In contrast to β-naphthol, anthracene gives only a diffuse spectrum. This is due to vibronic mixing as described; since the spectral region measured covers from 2700 to 3800 cm^{-1} above the 0–0 transition (361.08 nm), the initial state excited is relaxed rapidly by vibronic mixing, giving a broad-band structure. As seen in this spectrum, this

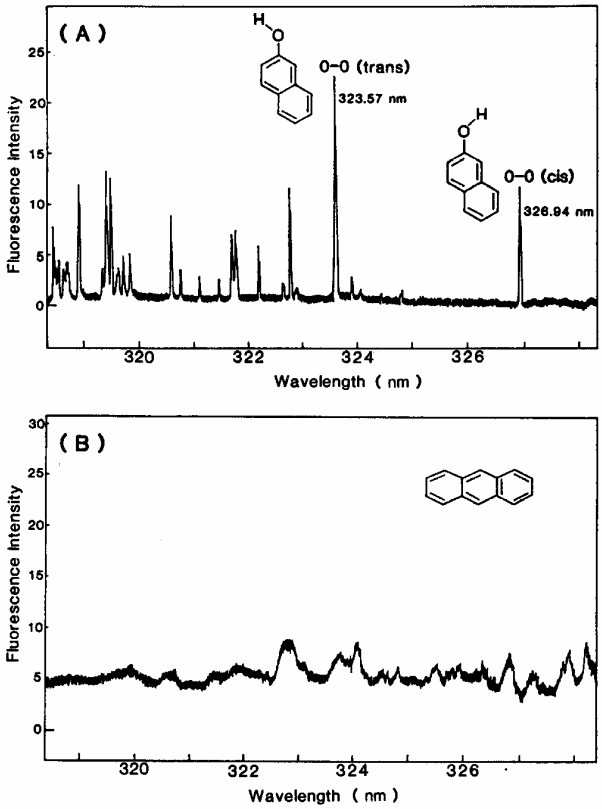

Figure 4. Excitation spectra for β-naphthol (A) and anthracene (B).

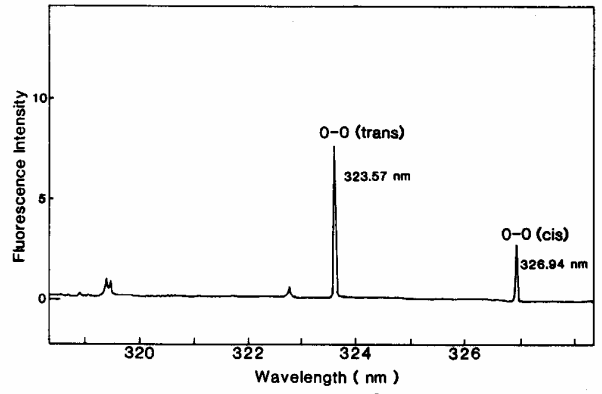

Figure 5. R-SSL spectrum for a mixture of β-naphthol and anthracene.

broad-band structure makes it difficult to isolate the sharp spectral peaks originating from β-naphthol, so that this background photoemission should be suppressed as much as possible, especially in trace analysis.

Figure 5 shows the SSJ/R-SSL spectrum for a mixture of β-naphthol and anthracene. Only two major peaks are observed, corresponding to 0–0 transitions for the cis and trans forms. This spectral simplification is ascribed to rejection of perturbed nonresonance fluorescence and to a "double-filter effect"; a small signal peak observed in the excitation spectrum is reduced further by a fluorescence isolation process due to a small Franck–Condon factor (*10, 11*). This result indicates that SSJ/R-SSL spectrometry provides an effective means for analysis of a mixture sample.

The discrimination ratio, i.e. the relative signal intensity of resonance fluorescence to nonresonance fluorescence for an interference molecule in the R-SSL spectrum, depends on the rate of intramolecular vibrational relaxation (IVR); a large molecule generally has a large freedom of vibration and the

IVR rate is fast, especially when a molecule is excited sufficiently above the 0–0 transition. This IVR minimizes the contribution of resonance fluorescence from the interference molecule, so that selectivity is substantially enhanced by R-SSL spectrometry. In the case of β-naphthol and anthracene the discrimination ratio is estimated to be >1000.

Mixture of *m*-Toluidine and 2-Methylnaphthalene. The excitation spectrum was measured for a mixture of 2-methylnaphthalene and *m*-toluidine in the 292–300-nm region. Many irregular peaks were observed in the spectrum, and it was difficult to assign these spectral peaks. Thus determination of the components was quite difficult, even though only two components were included in this mixture. A rather simple spectrum was observed for a sample containing *m*-toluidine only, and the spectral peak at 295.50 nm was assigned to the 0–0 transition (*13*). On the contrary, a complicated spectrum was observed for 2-methylnaphthalene, since the 0–0 transition reported to appear at 315.40 nm (*14*) was far below the present spectral region (<1600–2600 cm^{-1}). Thus many spectral peaks appeared in this spectral region, due to an intramolecular vibronic mixing and a large number of possible combinations in vibrational quanta for the excited state. In analytical spectroscopy, these complicated spectral features were troublesome for selective identification.

The R-SSL spectrum was measured in the same spectral region, and the spectral feature was greatly simplified and only a few major peaks were observed. The peak that appeared at 295.50 nm was readily assigned to the 0–0 transition for *m*-toluidine, and the peak at 294.0 nm to one of the resonance fluorescences to/from a high vibrational level for *m*-toluidine.

Comparison with Multiphoton Ionization/Mass Analysis. One of the competitive methods to SSJ/R-SSL spectrometry might be supersonic jet/resonance-enhanced multiphoton ionization time-of-flight mass analysis (SSJ/REMPI-TOFMS), since it provides us with an additional selectivity (MS) to discriminate against interference species. However, the discrimination ratio is not always satisfactory in SSJ/REMPI-TOFMS due to the fact that an isomer sometimes has a completely different structure; even the number of the aromatic ring is different. In this case, wavelength selectivity is necessary for discrimination, but it is sometimes difficult due to a broad spectral feature as described. On the other hand, nonresonance fluorescence giving broad background fluorescence is completely suppressed by R-SSL spectrometry. Furthermore, the IVR rate is generally fast at sufficiently above the 0–0 transition, due to a high density of vibrational levels in the ground state. Therefore, resonance fluorescence from the interference molecule is also discriminated, independent of the interference molecule. Thus the advantage of R-SSL is apparent, though R-SSL spectrometry also has several limitation, as pointed out in ref 11.

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RECEIVED for review April 16, 1991. Accepted July 29, 1991. This research is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan and by the Kurata Foundation.