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Application News

No. A573

Spectrophotometric Analysis

Spectrometry in Low-Temperature State – Utilization of CoolSpeK –

When a substance absorbs or emits light, those phenomena are accompanied by changes in its electronic state. In absorption, electrons change from the ground state to an excited state, and in light emission, the opposite change occurs, i.e., from an excited state to the ground state. There are energy levels of vibration in each of these states, and energy levels of rotation also exist at each vibrational level. At room temperature, substances display a broad spectrum because, in terms of energy, their electrons are distributed among several vibrational/rotational levels in the ground state, and they transit to the excited state from there. The distribution of the vibrational/rotational levels is influenced by ambient heat. Because distribution to high-order vibrational/rotational levels is suppressed if a substance is cooled, the spectrum becomes sharp, and it is possible to obtain peaks that cannot be measured at room temperature.

This article introduces measurements of liquids in a low-temperature state with an ultraviolet-visible (UV-Vis) spectrophotometer and spectrofluorophotometer by using CollSpeK (Unisoku Co., Ltd.)

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Absorption of Benzene in Low-Temperature State

Fig. 1 shows the appearance when CoolSpeK was attached to a UV-2600 UV-Vis spectrophotometer. CoolSpeK can be controlled in the range from -182 °C to +100 °C. Below room temperature (20 °C) flow control is performed with liquid nitrogen.*1

Fig. 2 and Fig. 3 show the results of measurements of a benzene solution (solvent: ethanol, 0.44 mg/ml) when the temperature was decreased from 20 °C to -120 °C. The spectra are normalized by the value of 280 nm. The measurement conditions are shown in Table 1.

*1 In some cases, a blackout curtain may be necessary in measurements.

Fig. 1 Condition of CoolSpeK Attached to UV-2600

Table 1 Measurement Conditions

Instruments	: UV-2600, CoolSpeK
Measured wavelength range	: 230 to 280 nm
Scanning speed	: Medium
Sampling pitch	: 0.2 nm
Slit width	: 0.5 nm

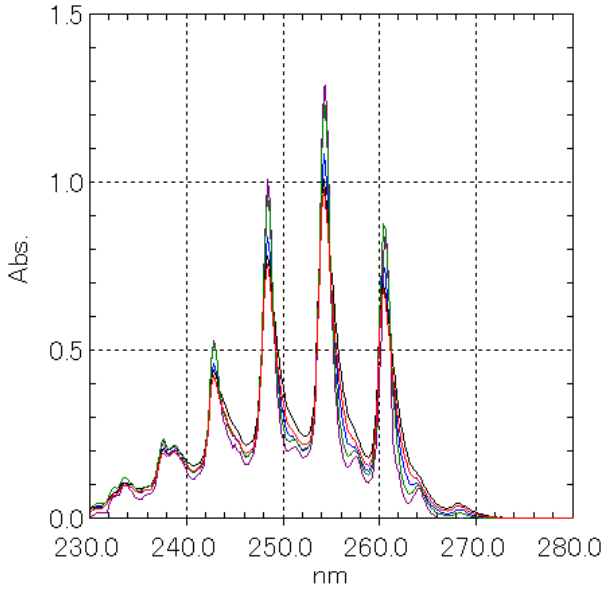

Fig. 2 Absorption Spectra
Black: 20 °C, Red: 0 °C, Blue: -40 °C, Green: -100 °C, Purple: -120 °C

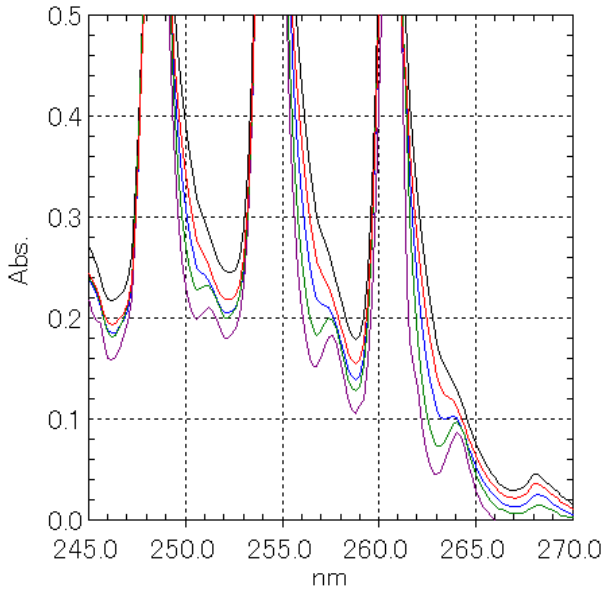

Fig. 3 Enlargement of Fig. 2

In Fig. 2, mainly four peaks (242 nm, 248 nm, 254 nm, 260 nm) can be observed at 20 °C and 0 °C. The respective peaks become sharper when the temperature is decreased, and in Fig. 3, peaks can also be observed at 264 nm and 257 nm at -100 °C and -120 °C. At room temperature, the energy states of benzene are widely distributed, extending to high-order vibrational/rotational levels of the electronic ground state due to the influence of heat, and as a result, the 264 nm and 257 nm peaks are included in the skirts of the main peaks. However, measurement of these peaks presumably became possible with the reduction in the distribution of high-order vibrational/rotational levels by cooling to a low-temperature state and the accompanying sharpening of the main peaks.

Light Emission of Benzophenone in Low-Temperature State

Fig. 4 shows the appearance when CoolSpeK was attached to a RF-6000 spectrofluorophotometer. By selecting the base part of the bottom of the CoolSpeK, it is possible to set the device not only on the UV-Vis spectrophotometers in the UV Series, but also on the RF-6000 spectrofluorophotometer.

Fig. 5 and Fig. 6 show the results when a benzophenone solution (solvent: ethanol, 2×10^{-5} mol/L) was measured at temperatures from 20 °C to -180 °C. The measurement conditions are shown in Table 2.

Although no light emission from the benzophenone solution can be observed from 20 °C to -100 °C, light emission can be observed from around -150 °C. In explaining this, it is estimated that the thermal energy deactivation process was predominant in the room-temperature state, but measurement of the emission process became possible as that process decreased in the low-temperature state.

Fig. 4 Condition of CoolSpeK Attached to RF-6000

Table 2 Measurement Conditions

Instruments	: RF-6000, CoolSpeK Cut filter IHU310
Excitation wavelength	: 265 nm
Measured wavelength range	: 350 to 600 nm
Scanning speed	: 200 nm/min
Data pitch	: 1.0 nm
Band width	: Ex 5.0 nm, Em 5.0 nm
Sensitivity	: Low

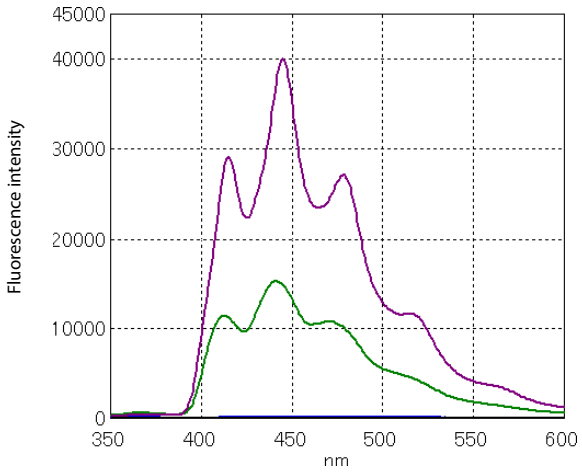

Fig. 5 Light Emission Spectra of Benzophenone Solution
Black: 20 °C, Red: -100 °C, Blue: -150 °C,
Green: -160 °C, Purple: -180 °C

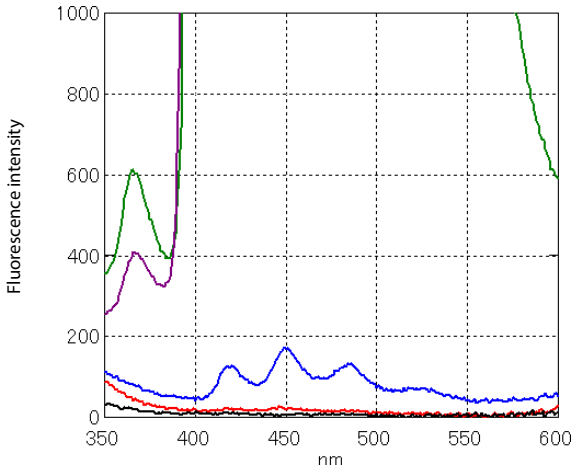

Fig. 6 Enlargement of Fig. 5

Conclusion

It was possible to measure the spectra of a benzene solution and a benzophenone solution in the low-temperature state by using a CoolSpeK with a spectrophotometer and a spectrofluorophotometer, respectively.

In the absorption spectra of the benzene measured with the UV-2600 UV-Vis spectrophotometer, signals that had been contained in the skirt of the main absorption peaks in the room-temperature state could be differentiated and observed by cooling to a low-temperature state.

In measurement of the benzophenone solution with the RF-6000 spectrofluorophotometer, it was found that a light emission spectrum that could not be observed at 20 °C to -100 °C could be observed from a low-temperature state of around -150 °C.

Reference
Shuichi Maeda, author and editor, *Saisho ni yomu hikarikagaku no hon* (First Book to Read on Photochemistry, in Japanese) (Nikkan Kogyo Shimbun, Ltd.)

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