UV–vis Absorption Spectra of Powdered Materials: Direct Measurements by Optical Waveguide Spectroscopy

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UV–vis absorption spectra of powders of naphthalene and salicylideneaniline were obtained using optical waveguide spectroscopy. It is demonstrated that the optical waveguide spectroscopy is an excellent method for the measurement of UV–vis absorption spectra of powdered materials as they are, without any treatment.

The UV–vis absorption spectrum of solid powdered materials is of great importance in chemistry and material science. However, there has been no way to obtain directly the absorption spectrum of powdered materials, because transmittance spectroscopy is not applicable. Accordingly, diffuse reflectance is measured.[1–3] However, observed reflectance is not only from diffuse reflections, the intensity of which obeys Lambert's law, but also from regular reflections, the intensity of which does not obey Lambert's law. Under the condition that regular reflections can be neglected, the Kubelka–Munk transformation of the diffuse reflectance spectrum gives a spectrum that can be regarded as an absorption spectrum. It is therefore essential to prevent a contamination of regular reflections into diffuse reflections in the measurement of materials, particularly with strong absorption. A most effective way to minimize the contamination of regular reflections is to dilute powdered materials with a diluent such as barium sulfate, magnesium oxide, etc. Without dilution, a spectrum corresponding to an absorption spectrum cannot be obtained from a diffuse reflectance spectrum. Thus, it is impossible to obtain an absorption spectrum of powdered materials as they are from diffuse reflectance spectrum. In addition, even with dilution, the Kubelka–Munk spectrum may be distorted if diluents interact with powdered materials.

Recently, a spectroscopy utilizing an optical waveguide has attracted considerable attention as a new analytical tool.[4–8] An incident light to the optical waveguide, which is usually a thin quartz plate, proceeds in the waveguide repeating total reflections. When a total reflection occurs, the so-called evanescent light emerges from the outer surface of the optical waveguide. The emerging distance is about a wavelength of the incident light. When the evanescent light is absorbed by the sample that is placed on the optical waveguide, the outgoing light from the optical waveguide decreases in intensity. As a result, an absorption spectrum of the sample on the optical waveguide is obtained. This spectrum is the absorption spectrum of the molecules that reside within a distance of 1 μm from the surface of the optical waveguide. This suggests that an absorption spectrum of solid powdered materials as they are can be obtained, if the powdered materials are placed on the optical waveguide.

We report here that UV–vis absorption spectrum of powdered materials can be directly obtained by the use of optical waveguide spectroscopy.

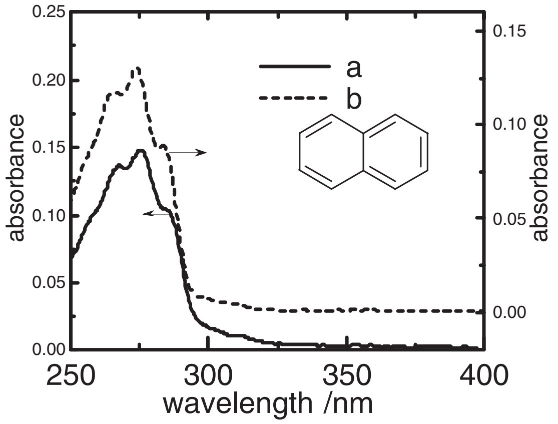


Figure 1. UV–vis absorption spectra of naphthalene. (a) Optical waveguide spectrum of powder. (b) Transmission spectrum of a hexane solution. $c = 8.0 \times 10^{-5}$ M, path length = 1 cm. Arrows indicate the corresponding ordinate.

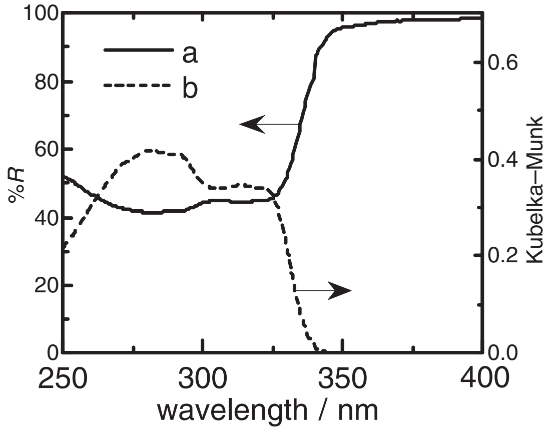


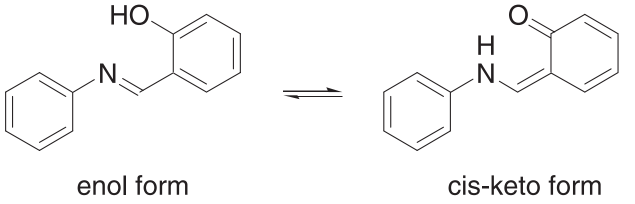
Figure 2. (a) Diffuse reflectance spectrum of naphthalene powder. (b) Kubelka–Munk spectrum from the diffuse reflectance spectrum. Arrows indicate the corresponding ordinate.

An optical waveguide spectrum of naphthalene powder is shown in Figure 1. The spectrum was measured on a SIS-50 optical waveguide spectrometer (System Instruments) using a quartz optical waveguide SIC-960016.[9] A few mg of naphthalene powder as purchased (Kanto Kagaku, the purest grade) was placed on the waveguide. The grain diameter of the sample was 1.0–0.01 mm. The angle of the incident light was 50° from the normal to the surface of the waveguide. The spectrum was obtained as an average of 200 accumulated spectra, for each of which the integration time was set at 50 ms.

The spectrum exhibits a main absorption band with a well-resolved fine structure at 250–300 nm and a weak absorption band at 300–340 nm. The spectrum strikingly resembles the absorption spectrum of a hexane solution (Figure 1) not only in the positions of absorption maximums, but also in the shape of the fine structure.[10,11] Thus, optical waveguide spectroscopy realizes the observation of a true absorption spectrum of powdered materials as they are without any treatment of them.

The advantage of optical waveguide spectroscopy becomes clearer when the spectrum is compared with the diffuse reflectance and the Kubelka–Munk spectrum of the same sample (Figure 2).[12] The diffuse reflectance spectrum does not exhibit a distinct band. The Kubelka–Munk spectrum exhibits a very broad absorption band, the shape of which is far different from that of the absorption band in the optical waveguide spectrum. The large deformation of the absorption band in the Kubelka–Munk spectrum is due to regular reflections, which apparently decrease absorption. The apparent decrease of absorption is larger as the absorbance is larger. As a result, the band between 250 and 300 nm is severely suppressed. The optical waveguide spectrum is, in contrast, free from such a systematic error.

The advantage of optical waveguide spectroscopy is further evident when it is applied to detect a trace amount of colored species in a photochromic crystalline powder of salicylideneaniline (**SA**), which is one of the most well known organic photochromic compounds.[13–17] It has long been assumed that the photochromic crystals of **SA** contain only the enol form and that the yellow color of the crystals is due to this form. However, we recently revealed that the photochromic crystals contain a trace amount of the cis-keto form, a tautomer of the enol form, and that the yellow color of the crystals is due to the cis-keto form.[18] The reason for such an incorrect assumption being accepted for a long time is due to the difficulty in detecting a trace amount colored species in solid materials. However, the detection is easy if optical waveguide spectroscopy is used (Figure 3).[19] The spectrum exhibits a strong absorption band with a well-resolved fine structure at 250–380 nm (band A) and also a weak absorption band at 400–500 nm (band B). The spectrum again strikingly resembles the absorption spectrum of a methanol solution (Figure 3), which exhibits the main absorption band (at 250–380 nm) that is assigned to the enol form and a very weak absorption band (at 400–500 nm, see the inset) that is assigned to the cis-keto form. Accordingly, band A is assigned to the enol form and band B is assigned to the cis-keto form. Thus, by the use of optical waveguide spectroscopy, it has been easily confirmed that a trace amount of the cis-keto form exists in the photochromic crystals of salicylideneaniline.



In summary, optical waveguide spectroscopy is an excellent method for obtaining absorption spectra of powdered materials as they are without any treatment. This method can be applied not only to fine powders but also to larger crystals. Optical waveguide spectroscopy would, therefore, become an essential tool in many areas that require absorption spectra of solid materials.

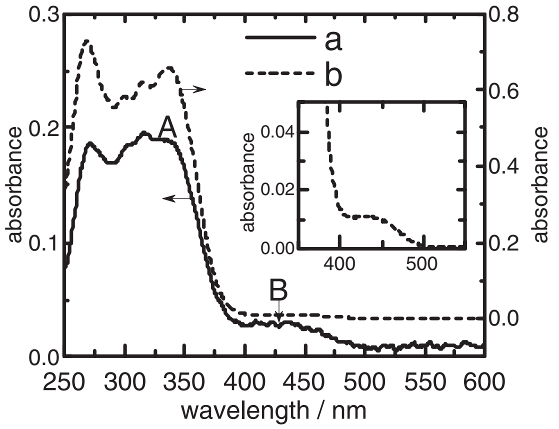


Figure 3. UV–vis absorption spectra of salicylideneaniline. (a) Optical waveguide spectrum of a photochromic crystalline powder. (b) Transmission spectrum of a methanol solution. $c = 5.3 \times 10^{-5}$ M, path length = 1 cm. In the inset, band B is enlarged. Arrows indicate the corresponding ordinate.

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References and Notes

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9 A quartz plate (65 × 20 mm) of thickness 0.2 mm and refractive index 1.46. Each of its edges makes an angle of 60° to the surface of the waveguide. The optical waveguide is transparent in the range between 200 and 1000 nm.
10 Absorption spectra of the hexane solution were measured on a Jasco Ubest50 spectrometer.
11 The remarkable resemblance between the powder and solution spectra suggests that the effect of intermolecular interactions and exciton couplings is negligible in the powder sample.
12 Diffuse UV–vis reflectance spectra were measured on a Jasco V-550 spectrometer equipped with an integrating sphere accessory.
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19 The grain diameter of the sample was 0.1–0.01 mm. The number of accumulation was 100 and the integration time was 20 ms. Other condition of the measurement was the same as that for naphthalene.

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