Direct Visible Spectral Analysis of Solid Samples by Optical Waveguide Spectroscopy due to Adsorbed Sample Molecules after Sublimation

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Visible spectra of solid samples were obtained by optical waveguide (OWG) spectroscopy. The spectra were confirmed to be due not to the powder samples themselves but to molecules sublimed from the solid samples and adsorbed on the waveguide. This result is supported by the observation that no spectrum was obtained from nonsublimed samples.

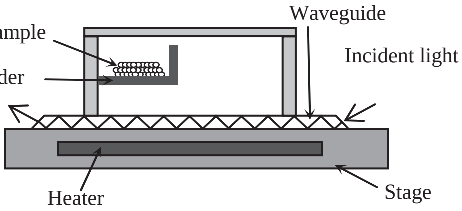
UV–vis spectroscopy provides information on molecular electronic states and is a principal method in materials analysis.[1] Solutions of samples are generally used for quantitative and qualitative analysis.[2] There is strong motivation to develop UV–vis spectrometry for more diverse conditions for use in molecular design, in nanotechnology and microbiotechnology. There are many reports of UV–vis spectral analysis under various conditions by OWG spectroscopy.[3–8] OWG spectroscopy is an internal reflection spectroscopy and detects absorption of the evanescent wave by samples on the waveguide surface.[9] Sensitive and in situ analyses of molecular assembly, such as LB films on an electrode surface, can be performed using OWG spectroscopy.[10–12] We have previously reported OWG methods such as noncontact OWG spectroscopy for analyzing surfaces irrespective of the transparency of the substrate[6,7,13–15] and polarized OWG spectroscopy, which is a powerful tool for the study of molecular orientation.[16]

Many reports exist concerning the sensing of specific molecules dissolved in liquids using OWG spectroscopy.[17] OWG spectroscopy has also been believed to be effective for solid sample analysis. It would be a useful tool in the control of molecular design at the surface, provided that it is possible to analyze molecular behavior at a solid–solid interface. However, OWG spectra cannot always be obtained from solid samples. Questions have arisen concerning the difference between those solid samples which can be detected with OWG spectroscopy and those which cannot.

In this report, we consider the reasons for this difference in direct analysis of solid samples by OWG spectroscopy.

Azobenzene and methylene blue were purchased from Kanto Co., Ltd. and were used without further purification. Absorption spectra were obtained by an OWG spectrophotometer (SIS-50, System Instruments Inc) with a 150-W xenon lamp (Hamamatsu Photonics). A quartz plate (Shin-Etsu Quartz Products, 65 × 20 mm) was used as an optical waveguide, of thickness 200 µm and refractive index 1.46.

To optically analyze only the sublimed molecules, we put an air cell on the waveguide (Scheme 1). The volume of this air cell is 10 mL (length: 50 mm, width: 10 mm, and height: 20 mm). The air cell includes a sample holder over the waveguide to measure the spectrum without putting the sample, of about 30 mg, directly on the waveguide. The air cell was kept at 40 °C. The OWG spectral data were stored at 10-min intervals for adsorption and at 50 ms for desorption.



Scheme 1. Side view of the air cell on the waveguide.

We first put powdered azobenzene directly onto the waveguide. The spectrum, with $\lambda_{\max} = 320\,\text{nm}$, was clearly observed. This spectrum agrees well with that of azobenzene dissolved in methanol.[18] Azobenzene molecules are known to exist as a *trans* state in methanol without UV irradiation. The spectrum obtained is from *trans*-azobenzene molecules when a powdered solid sample was placed on the waveguide.

It is not always possible to obtain the spectra of solid samples by OWG spectroscopy. We suppose that the spectrum obtained originates from molecules that adsorbed from the gas phase. To prove this hypothesis, we developed the air cell. Solid azobenzene was placed on the sample holder in the air cell above the waveguide. At this stage, there is no solid sample on the waveguide. OWG spectra were measured under closed conditions. As a result, a spectrum due to the *trans*-azobenzene was observed. The same spectrum that results from solid azobenzene on the waveguide was observed even though there was no solid sample on the waveguide. The absorbance increased gradually, as shown in Figure 1. The result suggests that the spectrum obtained was based not on the solid samples but on

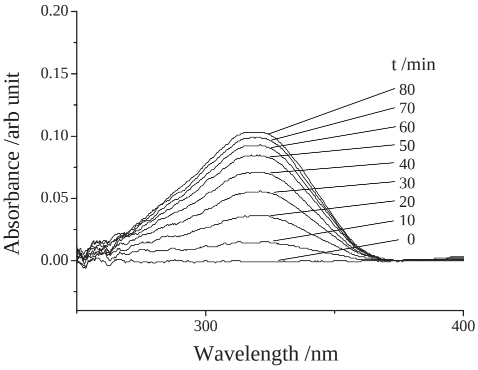


Figure 1. Dynamic change of OWG spectra of azobenzene stored initially in the air cell.

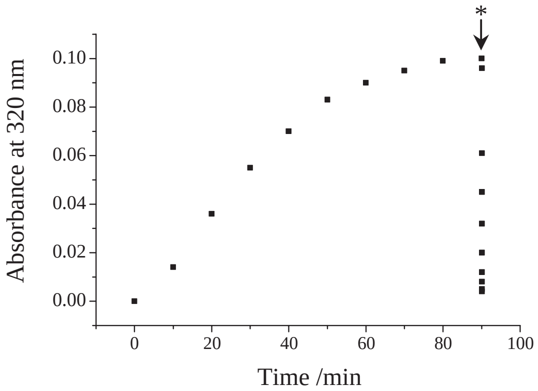


Figure 2. Change in absorbance at 320 nm during adsorption onto the waveguide.

azobenzene molecules that had sublimated and then been adsorbed.

To confirm the effect of sublimation on the spectrum, the same measurement was carried out with methylene blue, which is known not to sublime under ambient conditions. No spectrum was observed when solid methylene blue was placed directly on the waveguide or on the air-cell. This result further indicates that the OWG spectrum obtained when azobenzene is placed directly on the waveguide derives not from the solid-state sample but from sublimated molecules adsorbed on the waveguide.

There should also be adsorption–desorption equilibrium of the samples analyzed here. Solid azobenzene was put in the sample holder, and the temperature of the stage was increased to 80 °C after sufficient adsorption had occurred. As expected, no azobenzene spectrum was detected. These results show that the spectrum observed was due to adsorbed molecules on the waveguide after sublimation when a solid sample was simply placed on the waveguide.

Azobenzene was then placed in the sample holder, and the spectrum change during sublimation was observed. The absorbance at 320 nm was found to increase slowly until it leveled off as seen in Figure 2. This is the same pattern as that of adsorption of gas molecules on the solid surface. Accordingly, the OWG spectra should change when this adsorption equilibrium was shifted. When the sample and the sample holder were removed from the waveguide (see * in Figure 2), an immediate drop of the absorbance was observed. The spectrum vanished completely within 2 s. The adsorbed molecules on the waveguide were all dislocated at once because of the shift in the equilibrium caused by removing the sample holder setup (see Scheme 1). These observations all strongly suggest that the OWG spectra for the solid samples must be based on the sublimed molecules. We, therefore, suggest that no spectra were obtained from solid powder samples, which have no vapor pressure. It is possible to detect visible light absorbance of solid methylene blue when the dye is dissolved in certain solvent and then cast on the waveguide.[16] But there is a big difference in the molecular state of the dyes between powder and cast. Detailed analyses on the effect of sample conditions, such as powder size, pressure, and so on, on the OWG spectra are in progress.

The present study revealed that no spectrum was obtained when nonsublimed samples such as methylene blue were directly placed on the waveguide. Similarly, no spectra was found with a hot waveguide that prevents azobenzene molecules from adsorbing. It is possible to observe absorption spectra for solid powder samples on the waveguide only when they are in a sublimation equilibrium.

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