A study of the dissociation process of oleyl alcohol by two-dimensional Fourier transform near infrared correlation spectroscopy

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Introduction

Recently, there have been a few notable trials to deepen the fundamental understanding of near infrared (NIR) spectra. One of them is to apply generalized two-dimensional (2D) correlation spectroscopy to NIR region.¹ The basic concept of generating 2D infrared (IR) spectra from perturbation-induced time-dependent fluctuation of IR signals was introduced by Noda in 1986.² In 1993, he proposed more generalized 2D correlation spectroscopy to produce 2D correlation spectra from systematic variations of spectra having an arbitrary and complex wave form.³ Now, extension to other areas of spectroscopy, such as Raman and ultrafast time-resolved spectroscopy, has become quite straightforward. The present paper reports about the application of the generalized 2D correlation approach to the analysis of a set of Fourier transform (FT) NIR spectra of oleyl alcohol under temperature variations.

Experimental

The sample of very high purity oleyl alcohol was supplied by Nippon Oil and Fats Co. Ltd. (Amagasaki, Japan) and was used without further purification. The instrumentation and experimental conditions for the FT-NIR measurements and the methods for 2D analysis were the same as those described previously.¹

Results and discussion

Figure 1 exhibits FT-NIR spectra of oleyl alcohol in the pure liquid measured over a temperature range $6.5-90^{\circ}$ C (after density correction).⁴ The temperature-dependent changes in the first (7090 cm⁻¹) and second (10,380 cm⁻¹) overtones of the OH stretching mode of the



Figure 1. Temperature-dependent FT-NIR spectra of oleyl alcohol in the pure liquid [Reproduced from Reference 4 with permission. Copyright (1993) Society for Applied Spectroscopy].

monomeric alcohol show that the hydrogen-bonded species dissociate into monomeric ones with increasing temperature.⁴

Figure 2 show a synchronous 2D FT-NIR correlation spectrum in the 11,500–6000 cm⁻¹ region of oleyl alcohol in the pure liquid.¹ The spectrum represents the temperature-dependent spectral intensity variations of the alcohol between 6.5 and 90°C. There observe two autopeaks around 7090 and 6300 cm⁻¹ in the spectrum. These peaks correspond to the first overtones of the stretching



Figure 2. Synchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 11,500–6000 cm⁻¹ region. [Reproduced from Reference 1 with permission. Copyright (1995) American Chemical Society].

modes of the free OH group of the monomer and hydrogen-bonded OH groups of the linear oligomers. The essentially coincidental behavior of the temperature-dependent intensity changes of the NIR bands at 7090 and 6300 cm⁻¹ is indicated by the appearance of cross peaks at the appropriate spectral coordinate between the autopeaks. There are some more cross peaks in the higher wavenumber region. For example, a strong correlation peak appears between the two bands at 10,380 and 7090 cm⁻¹, indicating that the two bands share the identical temperature-dependent pattern as expected. This result is particularly interesting since such correlation between bands belonging to the same group provides at intriguing possibility of correlating various overtone and fundamental bands to establish unambiguous assignments.

Figure 3(a) shows a synchronous 2D FT-NIR correlation spectrum in the 8000–6000 cm⁻¹ region.¹ The negative cross peaks (indicated by shading) between the bands near 7090 and 6300 cm⁻¹ show that the directions of the peak intensity changes at these wavenumbers are opposite. The result is consistent with the fact that associated alcohols dissociate into monomeric species as the temperature is raised.

Figure 3(b) shows the corresponding asynchronous NIR spectrum.¹ A cross peak near 6840 cm⁻¹ probably corresponds to the OH band due to the dimer.¹ It is revealed from Figure 3(b) that the pattern of the temperature dependence for the peak intensity change at 7090 cm⁻¹ is different from other bands. The signs of the cross peaks indicate that the peak intensity at 7090 cm⁻¹ increases at higher temperature than those at other coordinates. In other words, the disappearance of the polymeric form does not simultaneously result in the formation of the monomeric form, indicating the existence of intermediate species such as the dimer.¹ Therefore, it seems that the chain oligomers dissociate into the dimer first and then the dimer breaks down to the monomer. The results of 2D correlation spectroscopy support the following mechanism for the dissociation of the hydrogen-bonded alcohol;

chain oligomers \rightarrow intermediate species \rightarrow monomer



Figure 3. (a) Synchronous 2D FT-NIR Correlation spectrum of oleyl alcohol in the 8000–6000 cm⁻¹ region; (b) corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region. [Reproduced from Reference 1 with permission. Copyright (1995) American Chemical Society].



Figure 4. Pseudo-three dimensional stacked trace representation of the 2D FT-NIR synchronous correlation spectrum in the 7300–6800 cm⁻¹ region.

Another important feature of the present study is to demonstrate the presence of a band due to the first overtone of a stretching mode of terminal OH groups of chain oligomers and that of two bands arising from the rotational isomerism of the free OH group. It can be seen from Figure 3(a) that the autopeak at 7090 cm⁻¹ is significantly extended into the off-diagonal area of the spectrum, indicating the existence of additional cross peaks obscured by the strong autopeak. Pseudo-three-dimensional stacked-trace representation of the 2D FT-NIR synchronous correlation spectrum in the 7300–6800 cm⁻¹ region shown in Figure 4 also supports the additional band. The additional band probably arises from a band due to free terminal OH groups of the linear oligomers.



Figure 5. Asynchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 7300–6800 cm⁻¹ region. [Reproduced from Reference 1 with permission. Copyright (1995) American Chemical Society].

The existence of the bands due to the rational isomerism became clear from an asynchronous 2D FT-NIR correlation spectrum in the 7300–6800 cm⁻¹ region shown in Figure 5.¹ Figure 5 indicates that there are several different types of spectral responses of oleyl alcohol to the temperature variations.¹ Bands at 6840, 7070, 7090 and 7115 cm⁻¹ are clearly differentiated.¹ The splitting of two bands at 7090 and 7115 cm⁻¹ may be caused by the rational isomerism of the free OH groups. These bands, the band due to the terminal OH groups and those from the rational isornerism, are not observed in the conventional one-dimensional spectra. Therefore, the present study demonstrates the usefulness of generalized 2D correlation spectroscopy in providing spectral information not readily accessible from the conventional spectra.

References

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