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Two-Dimensional Fourier Transform Near-Infrared Correlation Spectroscopy Studies of Temperature-Dependent Spectral Variations of Oleyl Alcohol

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Received: October 3, 1994; In Final Form: December 5, 1994[®]

Generalized two-dimensional (2D) correlation spectroscopy has been applied to the near-infrared (NIR) region for the first time to investigate temperature-dependent spectral variations of *cis*-9-octadecen-1-ol (oleyl alcohol) in the pure liquid state. The 2D correlation spectroscopic analysis has provided spectral information not readily accessible from conventional one-dimensional spectra. For example, the analysis has shown that a band at 7090 cm^{-1} due to the first overtone of an OH stretching mode of the monomeric alcohol consists of two bands arising from the rotational isomerism of the free OH group. The existence of a band due to free terminal OH groups of the linear polymeric species has also been suggested from a synchronous 2D NIR correlation spectrum of the alcohol. An asynchronous 2D NIR spectrum of the alcohol has indicated that the pattern of the temperature dependence for the peak intensity at 7090 cm^{-1} is different from other bands near 6300 cm^{-1} attributed to the polymeric forms of the alcohol. The signs of the cross peaks indicate that the change (increase) of the peak intensity at 7090 cm^{-1} occurs at higher temperature than those peaks at other spectral coordinates. It seems, therefore, that the disappearance of the polymeric form does not simultaneously result in the formation of the monomeric form. The polymeric species dissociate into the intermediate species such as the dimer first, and then the latter breaks down to the monomer. A strong correlation peak appears between two bands at 10 380 and 7090 cm^{-1} assignable to the second and first overtones of the OH stretching mode of the monomeric alcohol, respectively. This observation indicates that the two bands share the identical temperature dependent pattern as expected. The correlation between the bands arising from the same groups of the same species provides an intriguing possibility of correlating various overtone and fundamental bands to establish unambiguous assignments.

Introduction

Near-infrared (NIR) spectroscopy has shown remarkable recent progress, especially in instrumentation and chemometrics.^{1–3} The striking technological innovations in instrumentation are the introduction of the Fourier transform (FT) technique and of acousto-optic tunable filters (AOTF) to the NIR region.^{4–6} As for the advances in chemometrics, new statistical methods such as soft independent modeling of class analogy (SIMCA), partial least squares (PLS) regression, and neural networks are noted.^{2,3,9} This progress in the hardware and software has made the wider and more reliable applications of NIR spectroscopy possible.^{7–9}

One of the most important issues to be addressed in NIR spectroscopy is the need to deepen the fundamental understanding of NIR spectra. There are a few notable trials in this direction. For example, we have been undertaking systematic studies of NIR spectra of basic molecules such as alcohols, fatty acids, and amides by using FT-NIR spectroscopy.^{10–17} Our strategy has been to employ difference spectra for analyzing rather complicated NIR spectra. FT spectroscopy, which gives more precise spectra in both absorbance and wavenumber scales, has been especially profitable for our purpose. Mantsch *et al.*¹⁸ presented a theoretical framework based on the local-mode

model for assigning NIR spectra of larger biomolecules, such as polypeptides. Their detailed assignments were based on the local-mode framework, and the relevance of the assigned spectral features in spectra–structure correlation was discussed. This was, indeed, a new direction for the analysis of NIR spectra.

Another new trial came from Barton *et al.*,^{19,20} who reported two-dimensional (2D) covariance spectra for agricultural products. In their approach a set of randomly ordered spectra are used, and a 2D plot of the correlation coefficient for statistical derivation from the mean value of NIR intensity is constructed. In this type of analysis, however, no attention is paid to the specific order of the spectral changes taking place during the measurement or the value of the controlling variable affecting the spectra.

The sequence of spectral intensity changes often provides very valuable information not to be dismissed. The generalized 2D correlation approach, which takes the order of the data set into account, provides a much more powerful analytical framework widely applicable to various spectral data sets.^{21–25} The purpose of the present paper is to demonstrate the potential of generalized 2D correlation spectroscopy for unravelling NIR spectra. Temperature-dependent spectral variations of *cis*-9-octadecen-1-ol (oleyl alcohol) are taken up as an example.

The basic concept of generating 2D IR spectra from perturbation-induced time-dependent fluctuations of IR signals was

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[®] Abstract published in *Advance ACS Abstracts*, February 1, 1995.

introduced by Noda in 1986.²¹ Unlike the double time-domain FT methods used extensively in NMR, a simple cross-correlation analysis was applied to sinusoidally varying dynamic IR signals to construct a pair of 2D IR correlation spectra.^{22,23} Such dynamic 2D IR spectra were found to be especially useful in providing spectral information not readily accessible from conventional one-dimensional spectra.²⁴

One of the major limitations of the previous approach has been that the wave form of dynamic spectral intensity variations must be a simple sinusoid with a fixed frequency to employ the data analysis formalism. A more generally applicable mathematical formalism has been proposed to produce 2D correlation spectra from systematic variations of spectra having an arbitrary and complex wave form.²⁵ This formalism was found to be applicable to spectral intensity fluctuations as a function of not only time but also of any other physical variables, such as pressure, electrical field strength, and, most importantly, temperature.

The 2D spectra obtained by this method can accentuate useful information often obscured in the original spectral data set. This development opens up the possibility of introducing the versatile capability of 2D correlation analysis to much wider ranges of applications, including complex reaction kinetics, electrochemistry, and photochemistry.^{26,27} Further extension to other areas of spectroscopy, such as Raman and ultrafast time-resolved spectroscopy, has also become quite straightforward. In this study, we apply the generalized 2D correlation approach to the analysis of a set of FT-NIR spectra of oleyl alcohol under temperature variations.

Background

The generalized 2D correlation of temperature-dependent FT-NIR spectra is carried out as follows. Given a NIR spectral intensity variation $A(\nu, T)$ observed in a temperature range between T_{\min} and T_{\max} , the *synchronous* and *asynchronous* 2D NIR correlation intensities, $\phi(\nu_1, \nu_2)$ and $\psi(\nu_1, \nu_2)$, become

$$\phi(\nu_1, \nu_2) + i\psi(\nu_1, \nu_2) = \frac{1}{\pi(T_{\max} - T_{\min})} \int_0^\infty Y_1(\omega) Y_2^*(\omega) d\omega$$

where $Y_1(\omega)$ is the *temperature domain* Fourier transform of $A(\nu_1, T)$ and $Y_2^*(\omega)$ is the *conjugate* of the Fourier transform of $A(\nu_2, T)$.

Choice of the terms *synchronous* and *asynchronous* is somewhat awkward here since the spectral variation is measured in this experiment as function of not *time* but *temperature*.²⁸

Experimental Section

The sample of oleyl alcohol of very high purity (>99.9%) was supplied by Nippon Oil and Fats Co. Ltd. (Amagasaki, Japan) and used without further purification.

All the FT-NIR measurements were performed at a resolution of 8 cm^{-1} with a JEOL JRS 6500N FT-Raman spectrophotometer equipped with a TGS detector. The light source used was a halogen lamp. A total of 300 scans were accumulated. A quartz cell of 1 cm thickness was employed for the NIR measurements, and the equipment used for the temperature control with precision of $\pm 0.1^\circ\text{C}$ was the same as that described previously.¹¹

Results and Discussion

Figure 1 shows FT-NIR spectra in the $11\,500\text{--}6000 \text{ cm}^{-1}$ region of oleyl alcohol in the pure liquid measured over the temperature range $6.5\text{--}90^\circ\text{C}$ (after density correction). The band assignments have been made in our previous paper.¹³

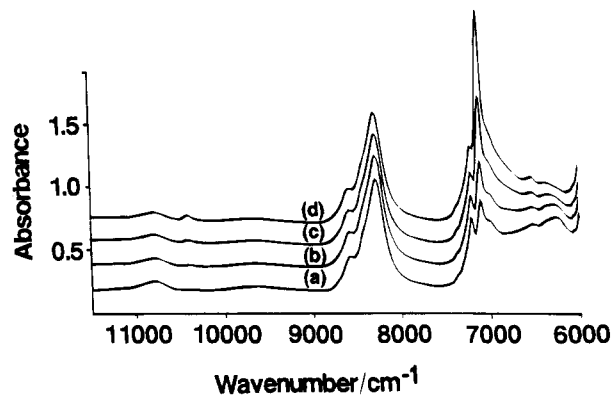


Figure 1. FT-NIR spectra of oleyl alcohol in the pure liquid measured over a temperature range of (a) 6.5 , (b) 30 , (c) 60 (c) and (d) 90°C .

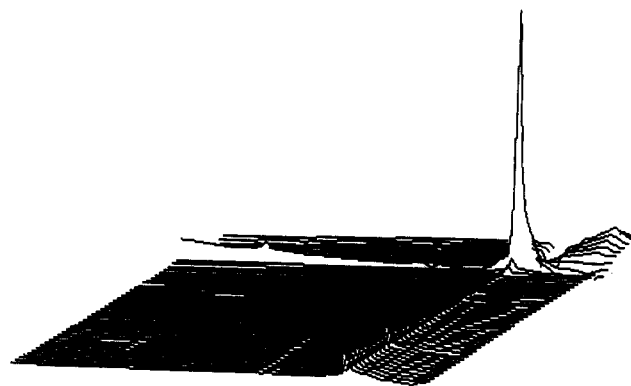


Figure 2. Full view of the pseudo-three-dimensional stacked-trace representation of the 2D FT-NIR synchronous correlation spectrum of oleyl alcohol in the pure liquid.

Accordingly, bands at $10\,753$, $10\,375$, 8555 , and 8254 cm^{-1} are assigned to the third overtones of the CH stretching modes, the second overtone of the OH stretching mode of the monomeric form, the second overtone of the CH stretching mode of the $\text{HC}=\text{CH}$ group, and the second overtones of the CH stretching modes of CH_3 and CH_2 groups, respectively. Among these four bands, only the band at $10\,375 \text{ cm}^{-1}$ shows temperature dependence.^{13,14}

A band at 7090 cm^{-1} is assigned to the first overtone of the OH stretching mode of the monomer. This band heavily overlaps with bands arising from combinations of CH vibrations. A broad feature in the $6600\text{--}6200 \text{ cm}^{-1}$ region is assigned to the first overtone of the OH stretching mode of polymeric forms of the alcohol. The temperature-dependent changes in the first and second overtones of the OH stretching modes of the free and associated alcohols show that the hydrogen-bonded species dissociate into the monomeric species with increasing temperature.^{13,14}

In our previous studies,^{13,14} the difference spectra were calculated by subtracting the spectrum measured at the lowest temperature, 6.5°C , taken as a reference spectrum, from other spectra in order to investigate the temperature-dependent spectral changes in detail. In the present study we employ 2D correlation spectroscopy instead of the difference spectra to analyze the NIR spectra of the alcohol in the pure liquid.

Figure 2 shows the full view of the pseudo three-dimensional stacked-trace representation of the 2D FT-NIR synchronous (strictly speaking *synthermal*) correlation spectrum. The spectrum represents the temperature dependent spectral intensity variations of oleyl alcohol between 6.5 and 90°C in the $11\,500\text{--}6000 \text{ cm}^{-1}$ region. The sharp major autpeak at the diagonal position near 7090 cm^{-1} dominating the synchronous

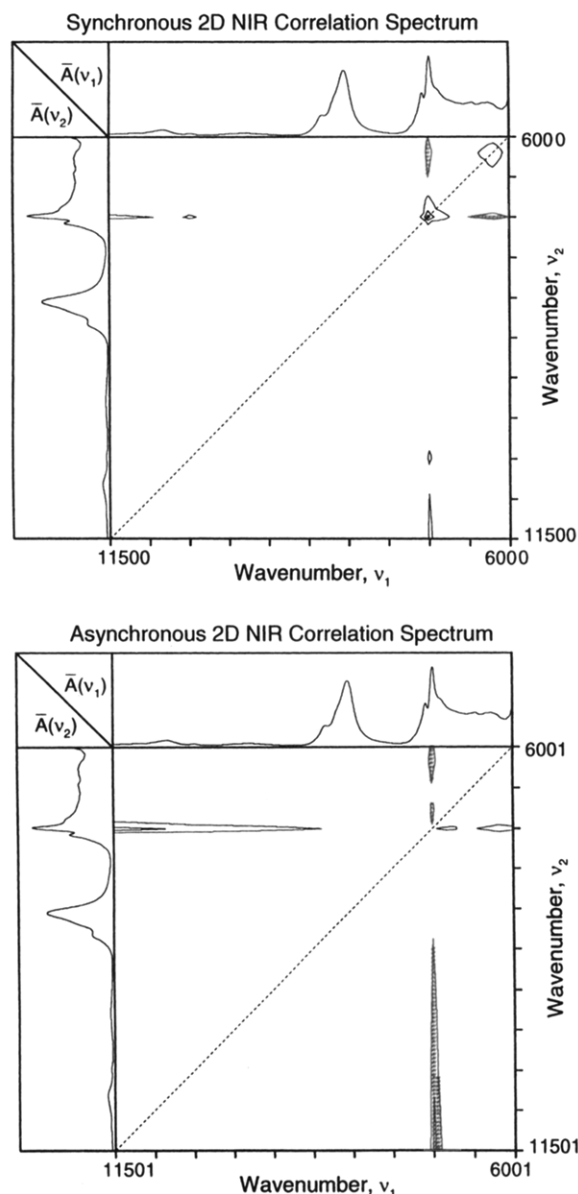


Figure 3. (A, top) Synchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 11500–6000 cm^{-1} region. (B, bottom) Corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

2D NIR spectrum corresponds to the temperature-induced peak-intensity variation of the first overtone of the OH stretching mode of monomeric alcohol.

While such a stacked representation provides the best overall view of a 2D correlation spectrum, it is usually easier to employ contour map representation to observe the detailed peak shapes and positions. We will therefore use the latter representation method. In Figure 3A is shown a synchronous 2D FT-NIR spectrum of oleyl alcohol in the pure liquid in the 11 500–6000 cm^{-1} region. The *reference spectrum* of oleyl alcohol is obtained by averaging a set of NIR spectra over the entire temperature range of the experiment. Two traces of such one-dimensional NIR reference spectrum are placed on top and left side of the 2D contour map to provide the basic feature of the NIR spectrum of the system during the experiment.

One of the shortcomings in using the average spectrum as a reference is that fine features of temperature-dependent variations of individual NIR spectrum are often obscured by such gross averaging operation. It is sometimes possible to use the power spectrum, i.e., $P(\nu) = \phi(\nu, \nu)$, of the temperature-

dependent variations of the spectral intensity instead of the average as the reference spectrum. This approach was found to be not very helpful since the 7090 cm^{-1} peak is disproportionately large, so that the rest of the spectral feature is obscured. The peak had to be actually clipped 20% of the original size to see the rest of spectral features.

The development of an additional autopeak is observed around 6300 cm^{-1} in Figure 3A. The essentially coincidental behavior of the temperature-dependent intensity changes of NIR peaks around 7090 and 6300 cm^{-1} for the alcohol 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. The signs of some cross peaks are positive while others are negative, indicating the existence of complex thermally induced spectral intensity changes, both increases and decreases, occurring at different wavenumbers. More detailed features of these peaks will be studied later with an expanded local view of the 2D NIR spectrum.

Figure 3B shows the corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region. The asynchronous 2D correlation spectrum provides information complementary to the synchronous spectrum. The most obvious feature in this plot is the long streaks of asynchronous peaks all located at the spectral coordinate centered around 7090 cm^{-1} which extend throughout the plot. The development of such peaks indicates that the temperature-dependent behavior of the FT-NIR signal at 7090 cm^{-1} arising from the monomeric OH stretching modes is very different from any other part of the spectrum.

It is often difficult to find out the fine features of a 2D correlation map if too wide a spectral range is represented by a single plot. A somewhat more localized plot like Figure 4A representing the spectral region between 9000 and 11 500 cm^{-1} is much easier to analyze. Here we see more clearly the autopeak at 10 380 cm^{-1} corresponding to the second overtone of the OH stretching mode of the monomeric form.^{13,14} The temperature-induced variations around 9600 cm^{-1} for the second overtone of the OH stretching mode of the polymeric form are too weak to be observable as well-defined 2D NIR peaks. There is, however, an extended tail of a strong autopeak located above 11 500 cm^{-1} for the third overtone of CH stretching modes. Although there is some development of cross peaks between 10 380 cm^{-1} and these higher-wavenumber bands, their thermal dependence patterns belong to essentially different types of behavior as indicated by the asynchronous spectrum discussed below.

The corresponding asynchronous 2D FT-NIR spectrum for the same spectral region is plotted in Figure 4B. The development of asynchronous peaks at 10 380 cm^{-1} which extend in the regions from 9200 to 10 250 cm^{-1} and from 10 450 to above 11 500 cm^{-1} indicates that the pattern of the temperature-dependent peak intensity change of the 10 380 cm^{-1} band for the OH stretching mode of the monomeric form is different from the rest of bands in this spectral region. The signs of cross peaks located at the spectral coordinate $\nu_1 = 10 380 \text{ cm}^{-1}$ are all negative (indicated by the shading) such that most of the thermally induced intensity changes at 10 380 cm^{-1} occur at temperatures higher than those for other bands. The long streak in the 10250–9250 cm^{-1} region of asynchronous peaks shows that bands in this region are unambiguously assigned to the second overtone of the OH stretching modes of the associated forms.

The localized view of the off-diagonal position of a synchronous 2D NIR spectrum shown in Figure 5 compares the

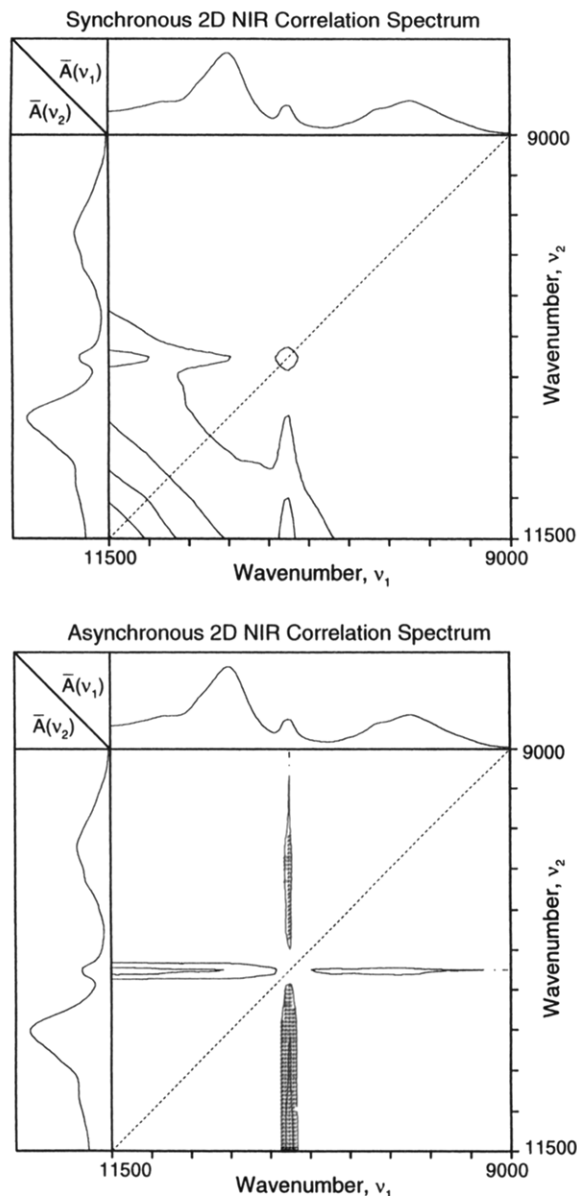


Figure 4. (A, top) Synchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 11500–9000 cm^{-1} region. (B, bottom) Corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

temperature dependence patterns of the peak intensity changes of bands at 10 380 and 7090 cm^{-1} . They are assigned to respectively the second and first overtones of the OH stretching mode of the monomeric form of oleyl alcohol. A strong correlation peak appears between the two bands, indicating that the two bands share the identical temperature-dependent pattern, as expected. No appreciable asynchronicity is observed in this region. This result is particularly interesting since such correlation between bands belonging to the same group provides an intriguing possibility of correlating various overtone and fundamental bands to establish unambiguous assignments.

The expanded view of the synchronous 2D FT-NIR correlation spectra for the lower wavenumber region (Figure 6A) shows the dominant autopeak at 7090 cm^{-1} for the OH stretching mode of the monomer, as well as the peak around 6300 cm^{-1} for the polymeric form. The negative cross peaks (indicated by shading) at off-diagonal position between 7090 and 6300 cm^{-1} show that the directions of the peak intensity change at these wavenumbers are opposite. The result is consistent with the fact that the peak intensity at 7090 cm^{-1} increases with

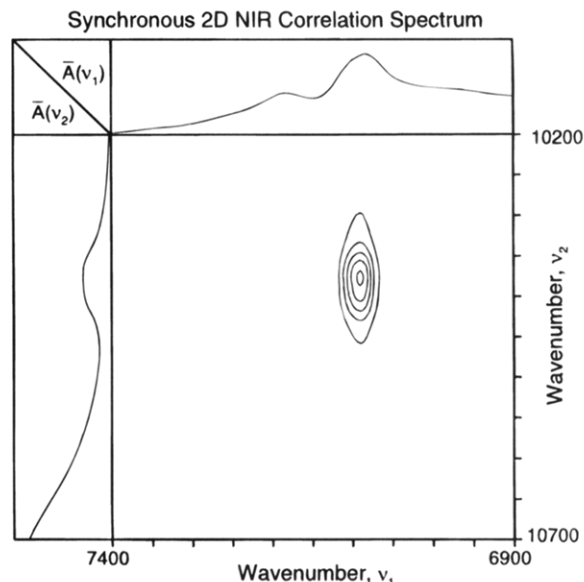


Figure 5. Localized view of the off-diagonal position of a synchronous 2D FT-NIR spectrum of oleyl alcohol.

temperature, while those around 6300 cm^{-1} decrease with temperature.^{13,14} The coordinated appearance and disappearance of monomeric and polymeric forms of OH stretching bands indicated by the cross peaks suggest a shift of population of oleyl alcohol from polymeric to monomeric form as the system temperature is raised.^{13,14}

Interestingly, however, the apparent decrease of the peak intensity of the polymeric form and subsequent increase of the monomeric form observed in this spectral region do not occur at the same temperature. The asynchronous 2D FT-NIR spectrum shown in Figure 6B clearly indicates 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 change (increase) of the peak intensity at 7090 cm^{-1} occurs at higher temperature than those peaks at other spectral coordinates. In other words, the disappearance of the polymeric form does not simultaneously result in the formation of the monomeric form, indicating there may be intermediate species such as the dimer. In our previous paper¹⁴ it was suggested that the predominant species of neat oleyl alcohol are the linear and cyclic polymeric species, such as the tetramer. It is, therefore, very likely that the tetramer dissociates into the dimer first, and then the dimer breaks down to the monomer. It is particularly notable that 2D correlation spectroscopy provides new insight into the mechanism of the dissociation of the hydrogen-bonded alcohol.

The existing species of neat oleyl alcohol can be classified into three types in terms of temperature-dependent behavior: (i) polymeric species—bands due to these species always decrease as temperature is raised; (ii) monomeric species—bands due to this species always increase with temperature; (iii) intermediate species, such as dimer, trimer, and so on—bands due to these species first increase with temperature increase and then their intensities decrease when the temperature is further increased.

The cross peaks near 6840 and 6200 cm^{-1} in the asynchronous 2D NIR correlation spectrum probably correspond to the dimer and polymer bands, respectively (Figure 6B).

A careful study of the spectral region at lower wavenumbers corresponding to the first overtone of OH stretching vibrations also shows interesting features. The synchronous spectrum in the region from 6800 to 7300 cm^{-1} is shown in Figure 7A. The comparison of the temperature-dependent behavior of the

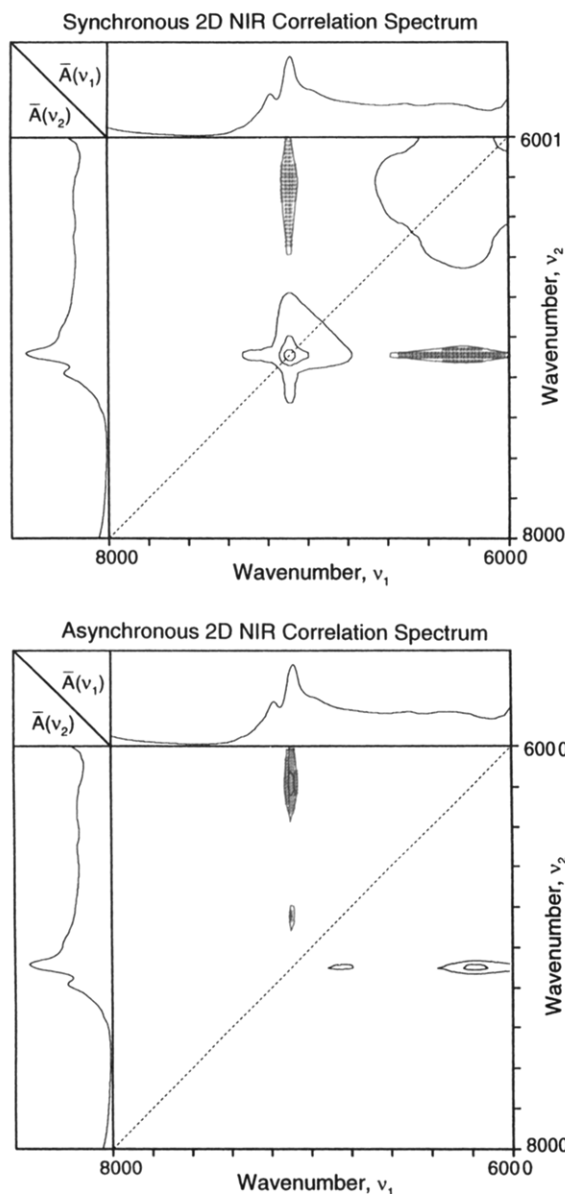


Figure 6. (A, top) Synchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 8000–6000 cm^{-1} region. (B, bottom) Corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

band resulting in the strong autopeak observed at 7090 cm^{-1} to those for other NIR bands has already been discussed. Interestingly, 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. The additional cross peaks probably correspond to a band due to free terminal OH groups of the linear hydrogen-bonded species.¹⁴ In our last study of the alcohol in CCl_4 solutions, the band was observed at the same frequency (7070 cm^{-1}); it was not identified in the conventional 1D spectra but was observed in the difference spectra.¹⁴

The corresponding asynchronous 2D NIR spectrum in Figure 7B reveals there are several different types of spectral responses of oleyl alcohol to the temperature change: bands at 6840, 7070, 7090, and 7115 cm^{-1} are all clearly differentiated. The spectral separation of 7090 and 7115 cm^{-1} bands may be more clearly seen in the expanded view (Figure 8). This splitting may be caused by a rotational isomerism of the free OH group. We recently reported that a band due to the first overtone of an OH stretching mode of the monomeric species of decan-1-ol consists of two bands arising from the rotational isomerism. The

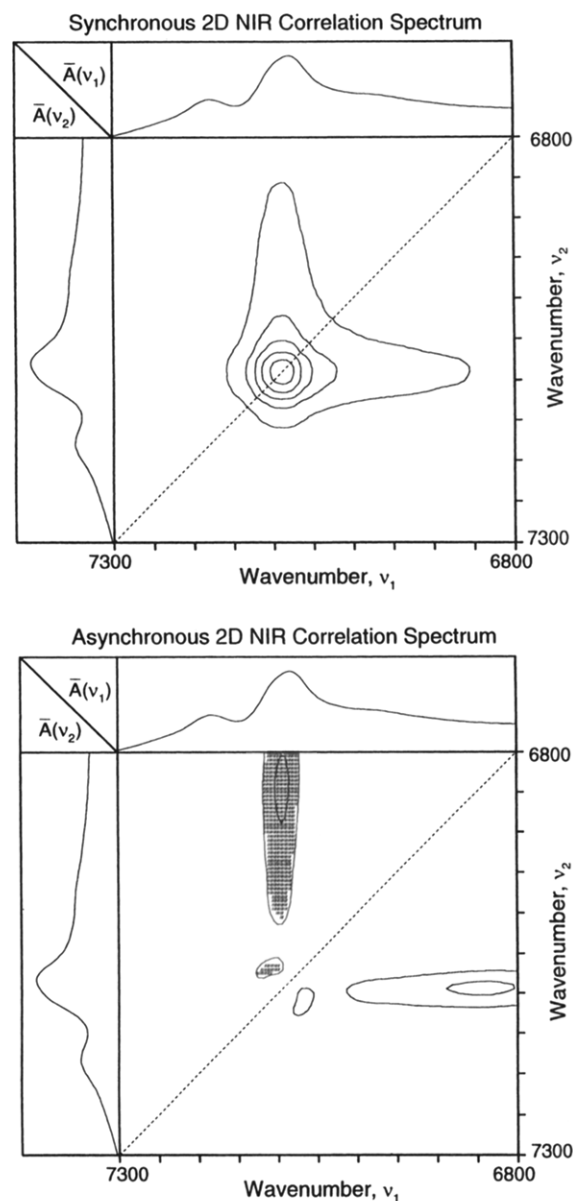


Figure 7. (A, top) Synchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 7300–6800 cm^{-1} region. (B, bottom) Corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

splitting was not clear in the conventional spectra, but it was confirmed in the second derivative and deconvolution of the spectra.¹⁵ The size of the splitting was 25 cm^{-1} and temperature-independent for decan-1-ol.¹⁵

The band at 6840 cm^{-1} may be attributed to the dimer. It is particularly notable that the bands due to the rotational isomers, the free terminal OH groups, and intermediates can be identified separately in the 2D spectra. The peak signs indicate that the NIR band intensity changes around the region below 7000 cm^{-1} occur at a lower temperature compared to that at 7090 or 7115 cm^{-1} . Likewise, the increase of NIR intensity at 7090 or 7115 cm^{-1} occurs at a higher temperature than 7070 cm^{-1} . The temperature-dependent behavior of the band at 7070 cm^{-1} should be complicated because the band intensity increases when the polymeric species dissociate into the dimers, but if the dimer dissociates into the monomer, it decreases. Subtle differences in the temperature dependence patterns of the spectral intensity changes are responsible for the differentiation of these bands by 2D correlation analysis.

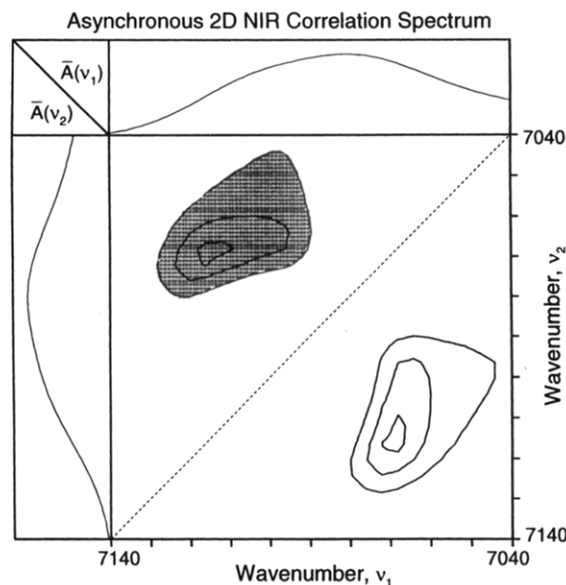


Figure 8. Asynchronous 2D FT-NIR correlation spectrum of oleyl alcohol in the 7140–7040 cm^{-1} region.

Conclusion

NIR spectra are intrinsically very rich in information for studying molecular structure and for making qualitative and quantitative analysis. However, because of their complexity, it is not always easy to extract useful information from the spectra. Therefore, there has long been extensive effort in developing powerful techniques to analyze the NIR spectra. The present study has demonstrated the potential of 2D correlation spectroscopy in exploring complicated NIR spectra.

A set of FT-NIR spectra of oleyl alcohol under a temperature variation has been unravelled by the combination of the synchronous and asynchronous 2D NIR correlation spectra. The existence of bands obscured by other strong bands, for example, the existence of the band due to the terminal OH groups, has been shown by the 2D technique without employing difference spectra, derivative spectra, or deconvolution techniques.

It has been found that the asynchronous 2D spectrum is particularly useful for obtaining information on the mechanism of the dissociation of the hydrogen-bonded alcohol. The signs of cross peaks in the asynchronous spectrum suggest that the peak intensity at 7090 cm^{-1} changes at a higher temperature than those for other bands. It seems, therefore, that the polymeric form does not dissociate directly into the monomeric form; it dissociates into an intermediate species first, and then the latter breaks down to the monomer.

A strong correlation peak appears between the bands at 10 380 and 7090 cm^{-1} due to the second and first overtones of the OH stretching mode of the monomeric alcohol, respectively, and no appreciable asynchronicity is observed. This result illustrates an intriguing possibility of correlating various overtone and fundamental bands to establish unambiguous assignments in the

NIR region. Such an attempt is now being undertaken in our laboratories and will be reported elsewhere soon.

Acknowledgment. The authors thank Prof. M. Iwahashi (Kitasato University) for valuable discussion and Dr. M. Suzuki (Nippon Oil and Fats Co., Ltd.) for useful discussion and donation of the sample.

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- (28) This unfortunate misnomer arises from the historical background. In the early development, 2D correlation spectroscopy was applied almost exclusively to time-dependent fluctuations of spectral signals. To minimize the indiscriminate coinage of new terminology, it was decided to avoid the invention of word like *synthermal* and *asynthermal* 2D correlation spectra.

JP942660U