

# Fourier transform near infrared and Fourier transform infrared studies of oleyl alcohol: dissociation and anharmonicity

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## Introduction

Studies on the hydrogen-bonding and self-association of alcohols in nonpolar solvents have long been a matter of keen interest for many researchers. However, there are still many things to study. For example, some authors have assumed that the position and absorption coefficient of a band due to the terminal OH groups are the same as those for a band due to the monomeric OH. This assumption makes the estimation of thermodynamic parameters simpler, but the results obtained are not reliable.

Fourier-transform (FT) near infrared (NIR) spectroscopy, which gives high-accuracy spectra in terms of both wavenumber and absorbance scales even with low concentrations, enables us to determine the position and molar absorption coefficient of the band due to the free terminal OH groups.<sup>1</sup>

## 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 and FT-infrared (IR) measurements were the same as those described previously.<sup>1</sup>

## Results and discussion

Figure 1 shows difference FT-NIR spectra of oleyl alcohol in  $\text{CCl}_4$  (0.1 M);<sup>1</sup> the difference spectra were calculated by subtracting the spectrum measured at the lowest temperature, 283 K, from the spectra obtained at higher temperatures. It can be seen that a band at  $7104\text{ cm}^{-1}$ , due to the first overtone of the OH stretching mode of the monomer, increases as the temperature increases while bands at  $6640$  and  $6250\text{ cm}^{-1}$  ascribed to the associated forms and that at  $7070\text{ cm}^{-1}$  decrease.<sup>1</sup> There has been no report for this  $7070\text{ cm}^{-1}$  band. Since the frequency of the band at  $7070\text{ cm}^{-1}$  is close to that of the first overtone of the OH stretching vibration of the monomeric form ( $7104\text{ cm}^{-1}$ ) and away from those arising from the associated species (for example,  $6640\text{ cm}^{-1}$ ), this band may be assigned to the first overtone of a stretching mode of the free terminal OH groups of the associated forms.<sup>1</sup>

Figure 2(a), (b) and (c) compare difference FT-NIR spectra of the alcohol in  $\text{CCl}_4$  solutions of 0.21 M, 0.10 M and 0.052 M, respectively, at 303 K and 323 K.<sup>1</sup> It is noted that only when the concentration is lower than 0.10 M, the  $7070\text{ cm}^{-1}$  band increases in a negative direction with temperature. This suggests that at such low concentrations the linear dimer and monomer are predominant. As the concentration is increased, the negative peak at  $7070\text{ cm}^{-1}$  disappears. This means that at the concentrated solutions the alcohol tends to form the aggregates.

The FT-IR measurements also support the above conclusions. Table 1 summarizes anharmonicities of the different OH stretching modes (here the anharmonicities were estimated by calculating the difference between the observed frequency of a band due to the first overtone and the double of the observed frequency of the corresponding OH stretching band). The anharmonicity of the hydrogen-bonded OH groups is 2–2.5 times larger than that of the monomeric OH, while that of the terminal OH groups is very close to the latter.<sup>1</sup>

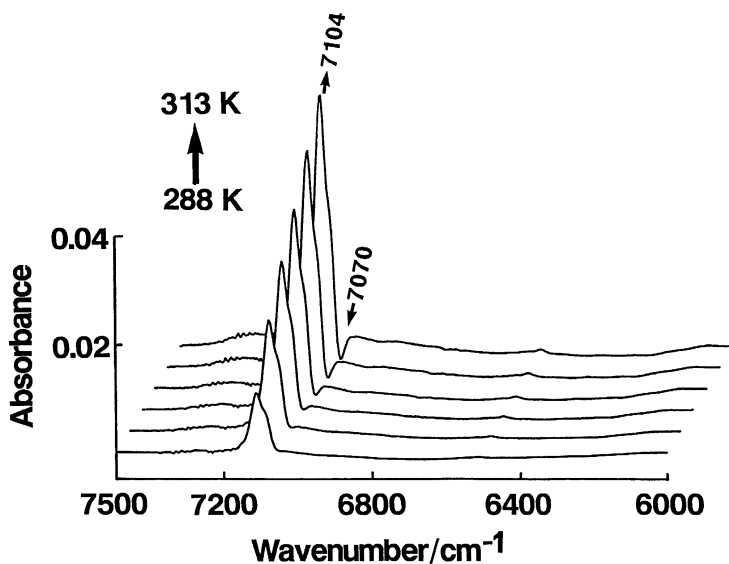


Figure 1. FT-NIR difference spectra of oleyl alcohol in a  $\text{CCl}_4$  solution of 0.10 M over a temperature range of 228–313 K. The spectrum measured at 283 K was taken as a reference spectrum. [Reproduced from Reference 1 with permission. Copyright (1995) Society for Applied Spectroscopy].

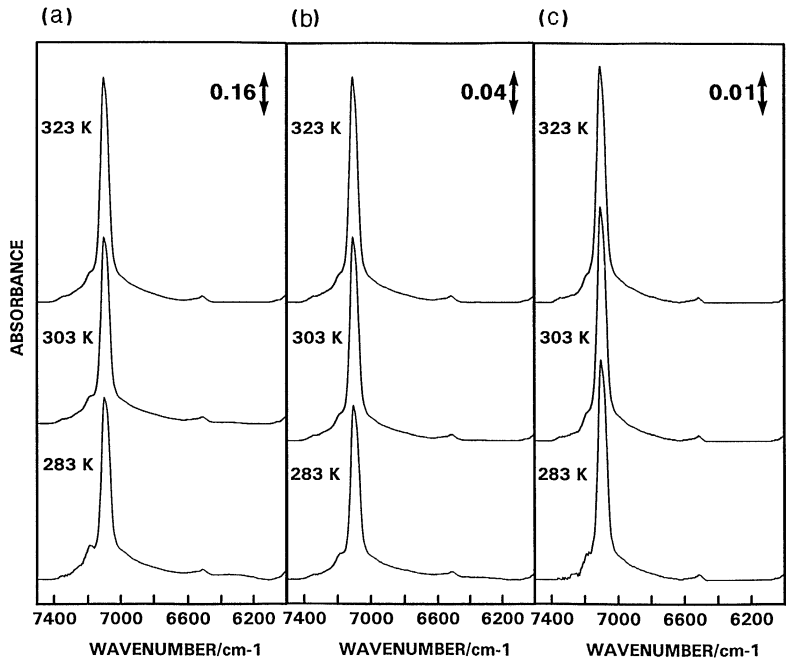


Figure 2. FT-NIR difference spectra of oleyl alcohol in  $\text{CCl}_4$  solutions of (a) 0.21 M, (b) 0.10 M and (c) 0.52 M at 303 K and 323 K, respectively; the difference spectra were obtained by subtracting the spectrum measured at 283 K from the spectra at 303 K for the same solutions respectively. [Reproduced from Reference 1 with permission. Copyright (1995) Society for Applied Spectroscopy].

Table 1. Observed frequencies of bands due to the OH stretching mode and its first overtone for various OH groups of *cis*-9-octadecen-1-ol in the  $\text{CCl}_4$  solution (0.10 M) at 303 K ( $\text{cm}^{-1}$ ).

	Free OH	Terminal OH	Hydrogen-bonded OH	
	$\gamma_1$	$\gamma_2$	(Dimer) $\gamma_3$	(Oligomer) $\gamma_4$
IR region				
$\gamma_{\text{OH}}$	3637	3621	3490	3344
NIR region				
observed	7104	7070	6640	6250
calculated <sup>a</sup>	7274	7242	6980	6688
Difference <sup>b</sup>				
(anharmonicity)	170	172	340	438

<sup>a</sup> $2 \times \gamma_{\text{OH}}$

<sup>b</sup>Difference between the calculated and observed frequencies.

The molar absorption coefficient for the first overtone of the stretching mode of the free terminal OH groups is determined to be  $0.139 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . It is approximately 8% of that of the first overtone of the monomer ( $1.63 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).

## References

1. Y. Liu, H. Maeda, Y. Ozaki, M.A. Czarnecki, M. Suzuki and M. Iwahashi, *Appl. Spectrosc.* **49**, 1661 (1995).