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IV. THE NEAR INFRARED REGION

A. Qualitative and Quantitative Analyses

The region of the near infrared spectrum extends from about 700 nm ($14,000\text{ cm}^{-1}$) near the end of the visible region, to 2500 nm ($4,000\text{ cm}^{-1}$), which is the beginning of the infrared fundamental region. The HF molecule, for example, has its fundamental absorption band at 3962 cm^{-1} . The near infrared spectrum of water is shown in Fig. 12.

The near infrared region is populated with overtone and combination bands of lower frequency fundamentals below $4,000\text{ cm}^{-1}$. These bands are considerably weaker in intensity than fundamental bands. The intensity weakness is an advantage for quantitative analyses, particularly in production processing, because the larger cell thicknesses used can be better controlled, yielding more reproducible intensity measurements. The cells can be made with water-insoluble quartz or sapphire windows for example, which if they are thin enough, can transmit down to about 3000 cm^{-1} . On the negative side, the qualitative information is considerably less extensive than in the fundamental region, as most of the near infrared bands involve summation bands (overtones and combination bands) of CH, OH, and NH stretching vibrations. Binary summation bands are usually the most intense, with tertiary and higher summation bands being progressively weaker. Even so, there is still some useful information to be had about functional groups. Characteristic group frequency charts and tables of these group summation bands can be found in the literature. A very brief selection of these are shown in Table III to serve as some examples.

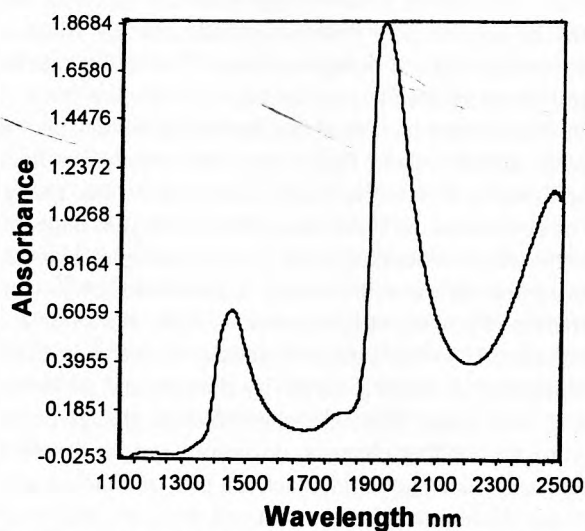


FIGURE 12 The near infrared spectrum of water run in a 0.1-mm cell with bands at 1450 nm ($2 \times \text{H}_2\text{O}$ stretch) and 1950 nm (H_2O stretch + bend).

TABLE III Selected Near Infrared Characteristic Bands

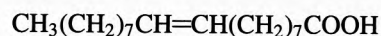
Group	nm	cm^{-1}	Assignment ^a
$-\text{CH}_3$	1680–1760	5950–5680	$2 \times \text{CH}_3$ str.
$-\text{CH}_3$	2240–2360	4465–4235	CH_3 str. + bend
$>\text{C}=\text{CH}_2$	1625–1675	6155–5970	$2 \times =\text{CH}_2$ asym. str.
cis- $\text{CH}=\text{CH}-$	2120–2170	4715–4610	$=\text{CH}$ str. + $\text{C}=\text{C}$ str.
$-\text{C}\equiv\text{C}-\text{H}$	1520–1565	6580–6390	$2 \times \text{C}\equiv\text{C}-\text{H}$ str.
$\text{R}-\text{OH}, \text{H}_2\text{O}^b$	1385–1460	7220–6850	$2 \times \text{OH}$ str.
H_2O^b	1880–1950	5290–5130	H_2O str. + bend
R_2NH	1520–1560	6580–6410	$2 \times \text{NH}$ str.
$\text{R}-\text{SH}$	1960–2020	5100–4950	$2 \times \text{SH}$ str.
$>\text{C}=\text{O}$	1920–1970	5810–5075	$3 \times \text{C}=\text{O}$ str.

^a str, stretch.

^b Varies with changes in hydrogen bonding.

B. Derivative Spectra

In the near infrared region, the bands are not only weaker, they can be broader and more overlapping. For example, the near infrared spectrum of oleic acid



can be seen in Fig. 13. The overtones of the CH_2 group out-of-phase and in-phase stretch bands show clearly at 1723 and 1758 nm. However, the expected weaker bands for the CH_3 out-of-phase stretch overtone and the $=\text{CH}$ stretch overtone, which are expected below 1723 nm, are so broad and weak that they are hard to detect.

For this reason, second derivatives of the spectra are often used, as seen in Fig. 14. Now the strong CH_2 overtone bands at 1726 and 1761 nm are much narrower and better

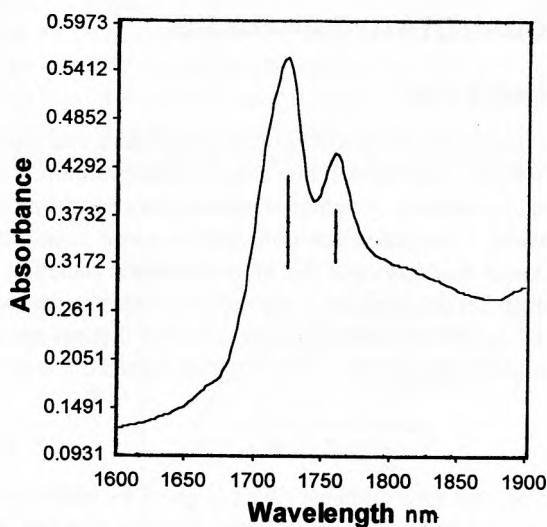


FIGURE 13 The near infrared spectrum of oleic acid run in a 1-mm cell with bands at 1723 nm ($2 \times \text{CH}_2$ out-of-phase stretch) and 1758 nm ($2 \times \text{CH}_2$ in-phase stretch).

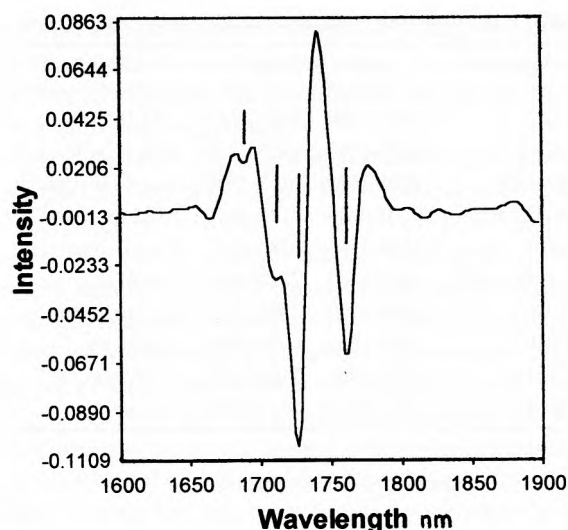


FIGURE 14 The second derivative of the near infrared of oleic acid (Fig. 13). Strong bands are seen at 1726 and 1761 nm ($2 \times \text{CH}_2$ stretch) as seen in Fig. 13 but with bands pointing down. Bands not seen easily in Fig. 13 are seen here at 1711 nm ($2 \times \text{CH}_3$ out-of-phase stretch) for the terminal CH_3 and 1688 nm ($2 \times \text{=CH}$ stretch) for the internal unsaturation. Negative side lobes on the sides of the strong bands are seen pointing up.

resolved, and the weak CH_3 and =CH overtone bands are clearly seen at 1711 and 1688 cm^{-1} , respectively. The second derivative of a typical band has a strong central peak, but it also has a weaker negative side lobe on both sides of the main band that complicates the presentation. However, the advantages are that it gives narrower bands that improve the resolution, it brings out weaker bands, and it also straightens out the background.

V. QUANTITATIVE ANALYSIS

A. Beer's Law

The basic law for spectroscopic quantitative analysis is Beer's law. This shows how sample concentration is related to a measure of radiation intensity in a spectrometer. Consider a sample in solution, held in a cell of uniform thickness that transmits the monochromatic radiation of interest. Let the intensity of the radiation entering the sample be I_0 and the intensity of the radiation that has passed through the sample be I . Then the transmittance T is given by

$$T = I/I_0. \quad (15)$$

The percent transmittance ($\%T$) is given by multiplying the transmittance T by 100. Beer's law is commonly expressed as

$$\log_{10}(I_0/I) = abc. \quad (16)$$

Here (I_0/I) can be recognized as the reciprocal of the transmittance ($1/T$). The quantity b is the cell thickness and c the sample concentration in the solution. The quantity a is called the absorptivity, which is a constant characterizing the capacity of the sample to absorb radiation. Its value varies with the wavelength or frequency of the radiation being measured and with the units used for cell thickness and sample concentration.

Beer's law is more simply expressed as

$$A = abc, \quad (17)$$

where A is called the absorbance, defined as

$$A = \log_{10}(I_0/I) \quad \text{or} \quad A = \log_{10}(1/T). \quad (18)$$

If the cell thickness and the radiation wavelength are held constant, Beer's law states that the concentration is linearly proportional to the absorbance.

B. Beer's Law Deviations

In IR spectroscopy, the concentration range being measured may be large, sometimes ranging from zero to 100%. Under such circumstances, deviations from Beer's law may be observed. If the cell thickness and radiation wavelength are held constant, a plot of concentration versus absorbance should be a straight line if Beer's law holds. Two conditions are implied in the derivation of Beer's law. The first is that the radiation being measured is monochromatic. In an IR spectrometer, especially under low-resolution conditions, what is actually measured is the intensity of a narrow region of the spectrum that may be significantly wide compared with the width of the absorption band being measured. This means that the absorbance deduced is an average absorbance for a finite wavelength section of the absorption band. This can cause deviation from Beer's law. The second condition for linearity is that the sample absorptivity not change with concentration. If the concentration range is large, the sample environment may change. For example, when the concentration is low, the sample is surrounded by solvent, whereas when the concentration is high, the sample is surrounded by other sample molecules. The change in environment can cause absorptivity changes and deviations from Beer's law. When the concentration change causes hydrogen-bonding changes, deviations can be severe. If Beer's law does not hold exactly, a plot of concentration versus absorbance (for constant cell thickness and wavelength) will not be a straight line, but will have a slight curvature. For narrow concentration ranges, such a plot will be nearly linear.