

Theory and principles of near infrared spectroscopy

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History

The history of near infrared (NIR) begins in 1800 with Herschel.¹⁻³ His experiments to find a way to filter heat from a telescope demonstrated that there was light radiation beyond what we know as the visible spectrum. This discovery was largely ignored for the better part of a century and even longer before modern instruments were used to acquire spectra. In the mid-1950s Wilbur Kaye, with Beckman Instruments, published two papers which put NIR spectroscopy on a firm footing.^{4,5}

These manuscripts described the instrument⁴ and the theoretical basis for the spectra in di- and tri-atomic molecules from group theory and selection rules.⁵ The NIR was not viewed as containing relevant structural information. The separation of NIR from mid infrared (MIR) was further enhanced when commercial instruments appeared combining the visible (vis) and NIR from Perkin-Elmer and Cary. The rationale was to get the most from sources and detectors rather than of building an instrument that could be used for the whole vibrational spectral region. The emergence of NIR into the analytical world as an accepted technique began with the work of Karl Norris of the US Department of Agriculture, Agricultural Research Service in the early 1960s.^{6,7} This was followed by the USDA/ARS National NIR Research Project, which developed, into a worldwide network of collaborating laboratories. This research project's efforts culminated in the publication of *Handbook #643* and two AOAC International Official Methods.⁸⁻¹⁰ From this point NIR spectroscopy flourished and expanded well beyond the agricultural realm into pharmaceuticals, industrial, process control, food processing, remote imaging spectroscopy and other diverse applications. The programme of this, the 10th ICNIRS, shows the breadth of the technology in the papers and posters to be presented.

Vibrational spectroscopy

There are many good text books on vibrational spectroscopy and the list in the literature cited reflects both my years in the area and my book shelf.¹¹⁻¹⁶ A soon to be published compendium by Chalmers and Griffiths and a new Edition of Williams and Norris are the most up-to-date references available^{17,18} on vibrational spectroscopy and NIR, respectively. For anyone just beginning to use spectroscopy, any general text will suffice to give you the pertinent information to understand the technology. For NIR, some of the best sources of information and specifics about applications can be found in the Proceedings of these conferences. Several of them are available from NIR Publications.

There are two Laws which govern the basics of vibrational spectroscopy, "Hooke's Law" and the "Franck-Condon Principle". Hooke's Law states that the frequency of a vibration (ν) is equal to the re-

ciprocal of 2π times the speed of light times the square root of the force constant (5×10^5 dynes cm^{-1}) times the sum of the two masses divided by there product for a simple two body harmonic oscillator.

$$\tilde{\nu}(\text{in cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \quad (1)$$

Hooke's Law can be used to calculate the fundamental vibrations for diatomic molecules in the MIR, but the NIR is comprised of combination bands and overtones. If everything were simple, NIR bands could be calculated from combinations of the MIR fundamentals and 2,3, 4, etc. times the fundamental frequency to produces the overtones. However things are not simple and so we need to understand how the Franck–Condon Principle, given below, applies to NIR spectroscopy.

Franck–Condon Principle, a classical interpretation

“When a molecule vibrates, the probability of finding a given atom at a certain point is inversely proportional to its velocity when it is at that point. Therefore the atoms in a vibrating molecule spend most of their time in configurations in which the kinetic energy is low—that is, the configurations in which the potential energy is nearly identical with the total energy, or at the intersection of the vibrational energy level with the potential energy surface of the molecule. Thus the photon is most likely to be absorbed when the nuclei are stationary or are moving slowly. Furthermore, the excitation resulting from the absorption of the photon cannot be transferred immediately to the nuclei. The nuclei will therefore tend to continue moving slowly immediately after the absorption process. Thus in the excited state the nuclear configuration also tends to be close to the intersection of the vibrational energy level with the excited potential energy surface. Therefore transitions tend to take place between vibrational levels in which the nuclear configurations are the same in both states, and they tend to occur when the nuclear kinetic energies are small”.¹⁹

Thus, these small variations give rise to anharmonicity, which causes the combination and overtone bands to appear at imprecise multiples of the fundamentals. The more vigorous the vibration the greater the anharmonicity. One of the best examples is the water molecule. The principle fundamental vibrations of water are shown in Figure 1. The combination band of water, which occurs at 5180 cm^{-1} (1930 nm), is thought to arise from the asymmetrical stretch at 5180 cm^{-1} (2660 nm) and twice a rocking motion vibration at 660 cm^{-1} (15150 nm), i.e., $5180 \text{ cm}^{-1} + 660 \text{ cm}^{-1} + 660 \text{ cm}^{-1} = 5076 \text{ cm}^{-1}$ or (1970) nm. This is 10–40 nm longer in wavelength than we are accustomed to seeing for the water band, the difference is anharmonicity. The same types of calculation can be made for the C–H stretch, N–H stretch, C=O and C–O–H which, along with O–H stretch, comprise the bulk of NIR active vibrational bands.

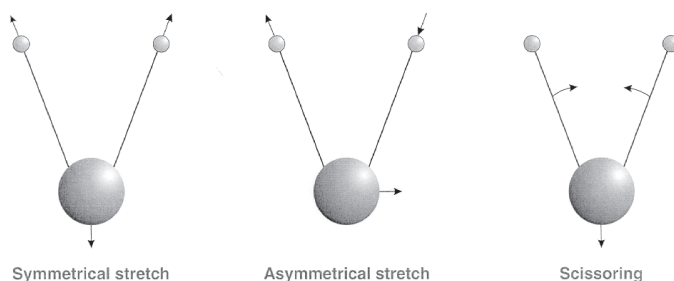


Figure 1. Fundamental vibration modes of water.²⁰

Instrumentation

In my early days of NIR spectroscopy, instruments were not computer controlled and in some ways simpler but harder to use than the modern spectrometers we use today. The first NIR instrument I used was a Beckman DU, which did not even have a recorder to plot the spectrum! For looking at the MIR the Perkin-Elmer Infracord was the first general purpose IR spectrometer. The Cary 14 was the first recording NIR I used. This instrument was the one Karl Norris used in his research combined with a Hewlett-Packard calculator to do the statistics, later replaced by a mini-computer.

In a recent article, Tony Davies detailed the history of the many instrument companies that have produced near infrared instrumentation.²¹ Throughout the 90's the main research instrument was a dispersive monochromator and still is. Only the names have changed. Like all industries, the instrumentation industry for NIR spectroscopy underwent growth, acquisitions and mergers. The figure in Davies' 1999 article shows who became whom and approximately when the changes took place and the table in the article lists the prominent manufacturers of instrumentation both in the near and mid infrared. As the 90s came to an end, the NIR community was still heavily into dispersive instruments and the mid infrared was totally into FT instruments. There are reasons for this difference of perspectives. For many years the agricultural community used NIR to measure compositional analysis of agricultural commodities and were concerned with taking the spectrum of a series of samples to the same exacting specifications. Those in the MIR community were interested in taking the best spectrum of the analyte. These two positions were somewhat mutually exclusive and remain so today. The NIR user is still "model" and "statistically" oriented and the infrared user is still concerned with functional groups resolution and spectral interpretation. In the United States our laboratory has been the only NIR group primarily concerned with interpretation. FT-Raman is quickly bridging this separation. Its "NIR" ease of use and sampling with the information content of mid-infrared satisfies both communities. One additional aspect has also remained constant. In 1990 we were asked to say where we wanted to see technology head, both in those areas we would research and those requiring input from instrument and software makers.²² In an article for the "Spectroscopy Across the Spectrum" meeting, a system of interconnected instrumentation was described (Figure 2). This goal has largely been accomplished due in great measure to local area networks and PC's. Currently in our system we can accomplish this task from any PC to any of our instruments, across spectrometer types, manufacturer or software applications. The modern laboratory of today is pretty much as we predicted in 1990. The "LAN" has replaced the term "HOST" but the rest is as shown in Figure 2. The individual instruments all have their own data station (DS) and multiple experiments can be called up from remote locations. It is important that

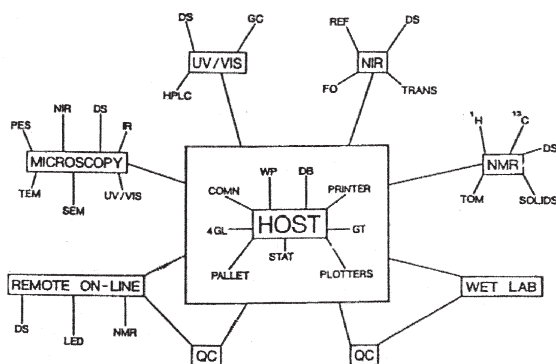


Figure 2. The 21st Century laboratory as predicted in 1990.

data can be moved from one station to another. Today we can even monitor and control experiments from home. The system we currently have in place consists of microscopy (all the way from UV to MIR and NMR), NIR, FT-IR, FT-Raman, UV/VIS, chromatography, mass spectrometry and the reference laboratory data stations. All the peripheral devices found around the "HOST" in Figure 2 can be found somewhere on the "LAN". Some of the "networks" that exist today for NIR instrumentation can contain many NIR instruments. The Grain Inspection Packers Stockyard Administration (GIPSA) Federal Grain Inspection Service (FGIS) maintains over 125 instruments in their network which monitors grain quality all across the United States.²³ While networks come in all sizes and levels of diversity, we have managed to make them functional to serve agriculture. Many of the networks of instruments are in use by regulatory agencies by numerous countries and the results are not published in the literature. However, some of the findings of one such networks in Europe have been published.²⁴⁻²⁶ These authors discuss the network in Belgium and how calibrations are transferred from one instrument to another. In this case, the software used and the procedures followed are those of Shenk and Westerhaus.²⁷

When the 1990's began, dispersive instruments were the principle tools used for NIR research and for spectroscopy in agriculture. Major manufacturers included Foss NIRSystems, Bran+Luebbe, Foss Grainspec and Tecator which eventually became part of Foss. The instruments produced by these companies were the workhorse instruments for agriculture and the instruments that formed numerous forage and grain networks in the US, Europe, Australia and Asia. The instrument has remained unchanged, but the sampling accessories have been greatly augmented. These sampling devices, new to NIR, would be "at home" in visible and traditional infrared laboratories. This is particularly true for fibre optic probes and liquid sample devices. In the 80s our only choice was a ground sample in a small cup in a spinning device. The improvement in signal-to-noise (S/N) allowed non-spinning devices with unground samples to yield the same spectral results. Fibre-optics permitted sampling of bulk containers and in line processes. Small instruments were also to be found from companies like Ocean Optics. Bran+Luebbe introduced an FT-NIR and an acoustic optical tunable filter (AOTF) instrument that gave them perhaps the broadest base of NIR technologies. They were joined by others, Buchi, Buhler, (now one company) and Bomem for FT instruments while Brimrose and Rosemount introduced AOTF instruments. The diode array spectrometer was introduced about midway through the 1990s. The Perten DA 7000 and the Zeiss Corona spectrometers are two instruments that can function in the processing arena with "no moving parts". The Zeiss Corona has recently been mounted in a combine by a major harvesting equipment manufacturer for in-field use. The ATR System of Analytical Spectral Devices also brought another mid-IR technique to NIR.

In the mid 1990's the NIR equipment caught up with Mid-IR in another way. Perkin-Elmer introduced the first solely NIR FT-NIR microscope. Micro-spectroscopy usually thrives on "Information content" which is often lacking in NIR spectra. However, the combination with an FT instrument could provide a unique system for certain purposes. The field of FT instruments has expanded during the last five years. The major manufacturers all have an instrument at this time. The Perkin-Elmer instrument utilises a methane gas internal reference and software, which can create "virtual instruments", easing calibration transfer problems. The Bruker instrument has a sample wheel which permits multiple samples (40 for small cells, others as designed) and since it is possible to use both the internal integrating sphere or the external InGaAs detectors, one can theoretically sequentially obtain both the reflectance and transmittance spectra on the same sample. However, set-up limitations in the software for the transmission system require modifications before this technique can be used. The new Nicolet Antaris instrument offers a modular approach to experiments by replacing sampling modules. As such, these new instruments promise to enhance what we have traditionally done with NIR and open new vistas for research and industrial applications. Along with all these new instruments comes new chemometric software for calibration and model development.

Chemometrics

When I began in NIR spectroscopy, multiple linear regression was the technique of choice to develop models for prediction as well as for kinetic studies. My earliest ventures required “punch cards” and the IBM 1620 computer, a system that took up a large room but today can be replaced by a \$50.00 calculator. In 1996 there were two excellent reviews of chemometrics published.^{28,29} The authors of these reviews examined some 25,000 citations before selecting the 1400 they used. The Brown, *et al.* review, containing over 1200 citations, describes the success of the First International Chemometrics Internet Conference in 1994. For the first time the full papers were available for scientists to read and comment upon over the course of four months. The review covered software, tutorials, books and journal articles on vibrational and magnetic resonance spectroscopy. The second review, by Workman *et al.*, was the first part of a three part series which covered the general techniques of chemometrics but also quantitative analysis and advanced chemometric techniques.^{30,31} Both reviews cited the tremendous advantages and use of partial least squares (PLS) as the best or preferred “whole spectrum” modelling technique. Beyond these similarities, the two reviews then went into different directions. Brown *et al.* described many chemometric applications and gave a thorough listing of those who were publishing in the areas. Workman *et al.* went into more detail on the particular application of the techniques to specific problems with fewer references (about 200). Taken together these reviews are a body of knowledge that anyone should find invaluable.

In many ways chemometrics is similar to the spectroscopy it serves. It is as much an art form as a science. This has been obvious to me each time I am asked the question “which software package is best?” The answer must always depends on the perspective of the authors of the package as to what they emphasised as important and what is included in the software package. The greatest change in chemometrics was initiated in the late 1980s when Galactic Industries Corporation developed the LabCalc software package and the GRAMS software packages that have succeeded it over the years.³² These packages are a bridge for all the different formats of data collection in all the popular spectrometers and chromatographs. Files can be converted to a standard format and handled by the GRAMS package or exported to JCAMP or ASCII and moved to other packages if desired. The other big change was moving all chemometric software packages to the Windows operating system. This too made the moving of data from one package to another easier.

Conclusion

The theory and principles of NIR are not comprised of just the physics and electronics. The theory and principles must include the chemometrics and the reference analysis as part of the total technique. Our use of NIR spectroscopy is expanding into many new applications. I believe, in the near future, we will see sensors utilising multiple regions of the electromagnetic spectrum with embedded computational capabilities, which will greatly enhance our ability to classify, identify, measure and provide assurance of quality. There is a pyramid of growth for any instrumental technology, i.e., after a period the technology is replaced. This will not happen for NIR spectroscopy since its growth has always been dependent on a synergism of technologies, which together provide us with powerful new analytical tools.

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