Yin and Yang in Chemistry Education: The Complementary Nature of FT-IR and NMR Spectroscopies

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Key Words
Aspirin, Chemistry Education, FT-IR, Infrared, NMR, Wintergreen Oil

Introduction

Although the two analytical techniques have fundamental differences, Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopies successfully complement each other in the teaching laboratory. In a demonstration of the two techniques' cooperative abilities, a cornerstone experiment in the undergraduate chemistry laboratory curriculum was conducted and analyzed by Thermo Scientific™ FT-IR and NMR spectrometers. The purpose of the experiment was to synthesize aspirin (acetylsalicylic acid) and wintergreen oil (methyl salicylate) via an esterification reaction. Aspirin was synthesized from the reaction of salicylic acid and acetic anhydride, whereas wintergreen oil was made via the reaction of salicylic acid and methanol (Figure 1).

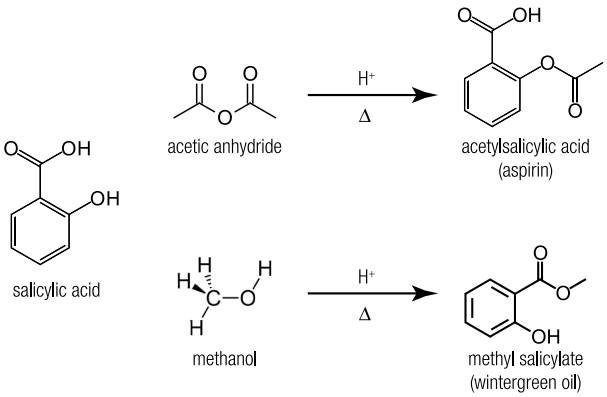

Figure 1: Reaction pathways to aspirin and wintergreen oil

The reactants and products of the experiment were analyzed using a Thermo Scientific™ Nicolet™ iS™5 FT-IR spectrometer and Thermo Scientific™ picoSpin™ 45 and 80 NMR spectrometers. The data acquired from the FT-IR and NMR spectrometers was examined to provide useful information about the atomic structure and ultimately confirm a successful synthesis.

Theory

The theories of FT-IR and NMR spectroscopies are based on the interaction between electromagnetic energy and a molecule of interest. FT-IR spectroscopy is often used to identify functional groups within a molecule and can be used to quantitatively determine concentrations of molecules within a sample. NMR spectroscopy is primarily used to determine a molecule's chemical structure.

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Infrared spectroscopy is based on the interaction between energy from the incident IR light and the covalent bonds within a molecule. In infrared spectroscopy, the frequency of light impinging on the molecule must be identical to the natural frequency of the molecular vibrations. The natural frequency of this resonance is based on a number of factors, including the mass of the atoms in the bond and the bond order.[1] The vibration of the bond must also cause a change in the dipole moment of the molecule in order for the infrared light to be absorbed. The advantage of an FT-IR spectrometer is that all wavelengths of light are measured simultaneously, allowing for a much shorter analysis time compared to traditional dispersive instruments. For this type of analysis to be possible, the light from the source must pass through a precise optical component before it reaches the sample. This optical device is known as an interferometer and is used to generate an interference pattern in the wavelengths of light emitted from the source. The interference pattern is based on the movement of an internal mirror and is later mathematically altered via the Fourier transform function to produce the recognizable FT-IR spectrum.[2]

To collect the spectrum for a sample, the instrument first measures the intensity of each wavelength of light with no sample present in the beam path. This spectrum is referred to as the background. When the sample is inserted into the beam path, some of the infrared light from the source is absorbed by the covalent bond vibrations within the molecule. The instrument collects the sample spectrum and uses a ratio to eliminate the background spectrum from the equation, leaving behind a spectrum that is unique to the sample components (Figure 2). Much like chemical shift correlations in NMR spectroscopy determine the chemical structure of a molecule, characteristic infrared light absorption frequencies in infrared spectroscopy determine chemical functional groups present within a molecule.[3]

NMR spectroscopy revolves around the interaction between energy from the incident radio frequency and the nuclei of the atoms in a molecule. When the nucleus, which is a spinning particle, contains unpaired protons or neutrons, the spinning positive charge creates a magnetic field. Nuclei with unpaired protons and neutrons, therefore, are said to be magnetically active. The unpaired proton in hydrogen, for example, makes it a commonly studied atom by NMR spectroscopy.

In the absence of an applied external magnetic field, the magnetic field vectors from the nuclear spins of the hydrogen atoms are abundant and random. When an external magnetic field is present, however, the magnetic field vectors align themselves with or against the field of the external magnet (Figure 3).[4] Once the magnetic field vectors are aligned, a radio frequency pulse is used to excite these nuclei to a higher energy state, causing their magnetic fields vectors to point away from their z-axis alignment and process about the x,y-plane (Figure 4).

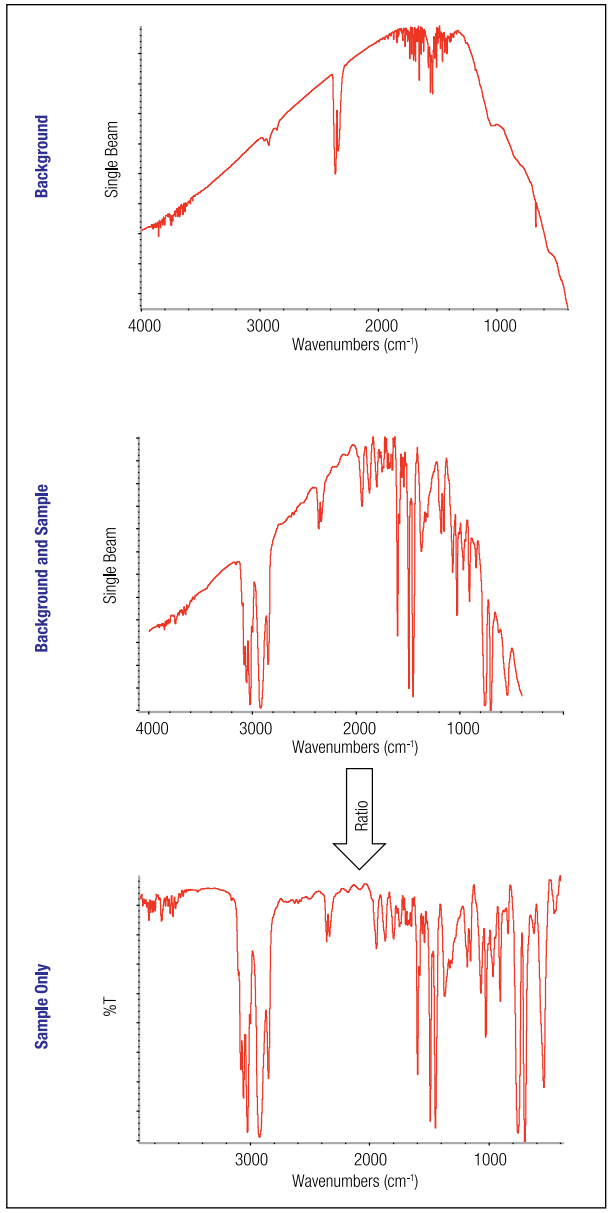

Figure 2: Sample spectrum calculated by the ratio of 'Background and Sample' to 'Background' spectra

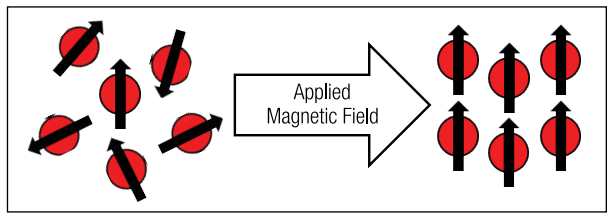

Figure 3: Magnetic vector orientation in absence and presence of applied magnetic field

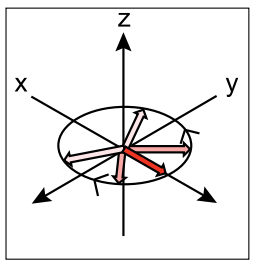

Figure 4: Total magnetic field vector immediately after radio frequency pulse

When the radio frequency pulse is turned off, the magnetic fields vectors from the spinning hydrogen nuclei begin to relax back toward their z-axis equilibrium state. This procession and relaxation causes a fluctuation in the magnetic field of the overall system, which generates an electric current in a receiver coil. The electrical current, or signal, is then detected and converted from a time domain function into a frequency domain function by the mathematical process known as a Fourier transform.[5] This final mathematical conversion ultimately produces the recognizable NMR spectrum.

If all protons in a molecule reside in the same magnetic field environment, there would be no separation in the NMR spectrum. Spectral separation results from protons residing in different electronic environments. Small, local magnetic fields are generated in a molecule by the rotation of sigma bond, π bond and lone pair electrons of the nearby atoms. These local magnetic fields influence the applied magnetic field for a nearby proton, causing it to absorb a different wavelength of the radio frequency pulse. This phenomenon is referred to as shielding and is what produces the distinct spectral separation used to interpret chemical structures in NMR spectroscopy (Figure 5).

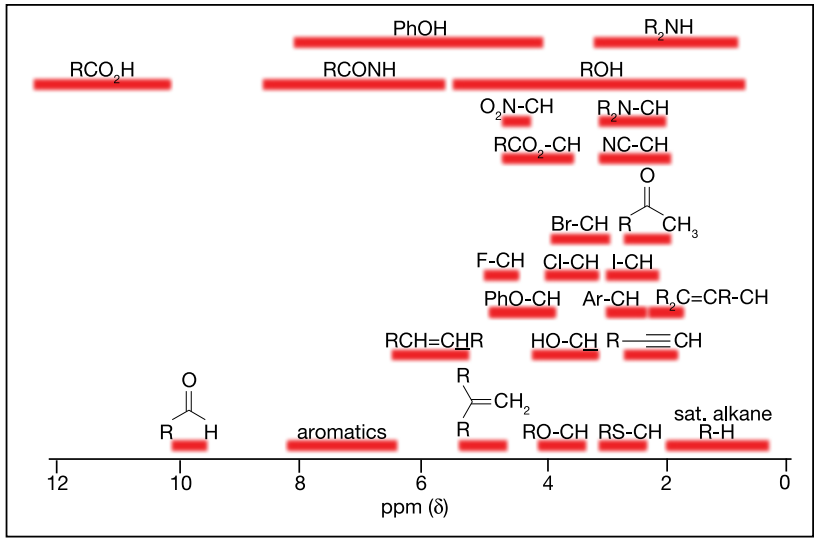

Figure 5: Typical chemical shift ranges in ^{1}H NMR spectroscopy

Experiment

The synthesis of aspirin and wintergreen oil were both driven by an acid-catalyzed esterification reaction. Aspirin was synthesized from salicylic acid and acetic anhydride while wintergreen oil was synthesized from salicylic acid and methanol.[6,7] Both reactions were catalyzed with concentrated sulfuric acid.

The IR spectra were collected using a Nicolet iS5 FT-IR spectrometer with an iD5 single bounce ATR accessory equipped with a diamond laminate crystal. The IR spectra were collected from 4000 to 600 cm^{-1}, with 10 scans per spectrum and 4.00 cm^{-1} resolution. The NMR spectra were collected using picoSpin 45 and 80 NMR spectrometers. The spectrometers were 45/82 MHz pulsed, Fourier transform ^{1}H NMR permanent magnet instruments equipped with a capillary cartridge probe. All spectra were acquired using a 90° excitation pulse, 750 ms acquisition time and 8 second recycle delay. Each final spectrum resulted from an average of co-added scans; 16 scans for neat samples and 64 scans for dissolved solids. Data was processed in the MestReNova™ NMR software using a standard set of processing parameters, including zero filling, phase correction, peak picking and integration.

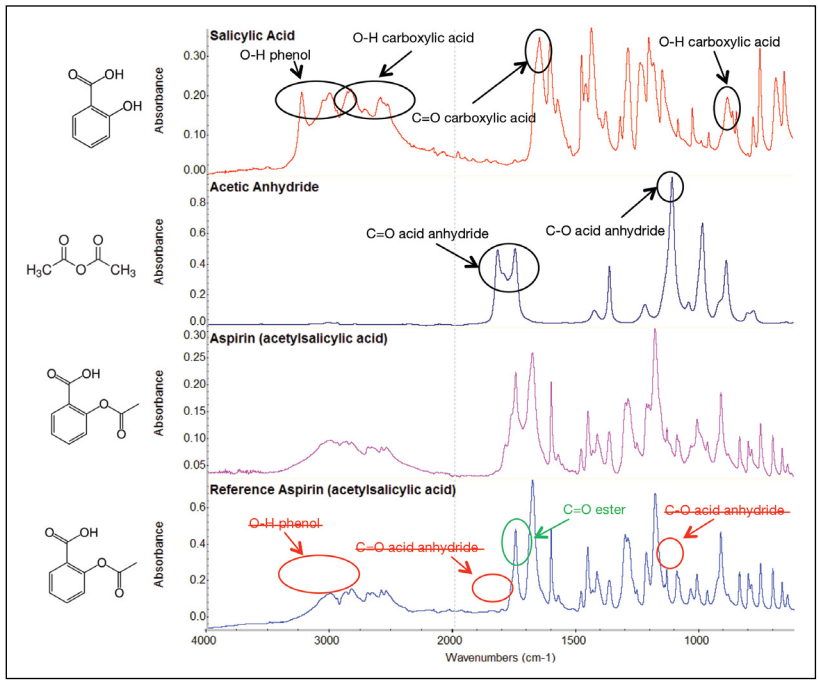

Figure 6: IR spectra acquired from aspirin synthesis

Results and Discussion

FT-IR spectroscopy was used to identify the functional groups present in the reactants and products while NMR spectroscopy was used to determine the organic framework of the molecules. First, the IR spectra for the aspirin synthesis were acquired (Figure 6). From the top of the spectra stack to the bottom, the salicylic acid reactant, acetic anhydride reactant, experimentally synthesized aspirin and the reference aspirin spectra are shown.

The salicylic acid starting material has two unique functional groups: a carboxylic acid and a phenol. The O-H phenol (3230–3000 cm^{-1}), O-H carboxylic acid (3000–2500 cm^{-1}, 881 cm^{-1}) and the C=O carboxylic acid (1652 cm^{-1}) absorbing bands are all labeled in the top spectrum. In the acetic anhydride reactant, the C=O acid anhydride (1822 cm^{-1}, 1751 cm^{-1}) and C-O acid anhydride (1113 cm^{-1}) absorbing bands are also labeled. The product, aspirin, has an ester functional group that was not present in either of the reactants. The addition of this C=O ester stretching band (1749 cm^{-1}), labeled green in the bottom spectrum, provides evidence that a new functional group has been formed. In aspirin, the ester functional group replaces the phenol group from the salicylic acid reactant. Therefore, the O-H phenol peak that was present in the salicylic acid spectrum (3230–3000 cm^{-1}) is labeled red and no longer present in the aspirin spectrum. Furthermore, the C=O acid anhydride (1822 cm^{-1}, 1751 cm^{-1}) and C-O acid anhydride (1113 cm^{-1}) absorbing bands from the acetic anhydride reacting material are also no longer seen in the aspirin spectrum, as aspirin does not contain an acid anhydride functional group.

The spectrum of the experimentally synthesized aspirin (pink) shows signs of product impurities. For example, there is evidence of residual acetic anhydride in the synthesized aspirin, as the C=O acetic anhydride stretching bands (1822 cm^{-1}, 1751 cm^{-1}) appear to be broadening the ester peak located at 1749 cm^{-1}. The majority of the synthesized aspirin spectrum, however, closely resembles the pure, reference aspirin spectrum.

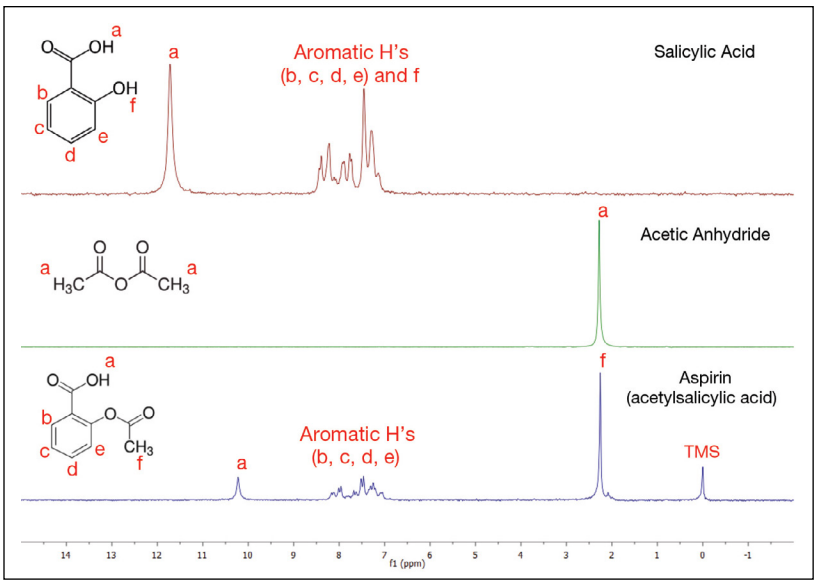

Figure 7: picoSpin 45 NMR spectra acquired from aspirin synthesis

A successful synthesis of aspirin can be further confirmed by combining the information obtained from the IR spectra with that of the NMR spectra (Figure 7). The salicylic acid NMR spectrum shows the carboxylic acid hydrogen (a) downfield with a chemical shift of 11.75 ppm. The presence of this peak confirms the IR evidence that a carboxylic acid functional group is present in salicylic acid. The other five hydrogen atoms in salicylic acid all have similar chemical shifts between 7 and 8.5 ppm. The multitude of peaks in that chemical shift region show evidence of an aromatic ring as well as the phenol function group that was seen in the IR spectrum. The acetic anhydride spectrum is located in the middle of Figure 7. Acetic anhydride is a symmetric molecule with six identical protons, which are found on the methyl groups and give rise to a single peak at 2.25 ppm. This single peak further supports the information obtained from the IR spectrum of acetic anhydride. In NMR spectroscopy, hydrogens that are on the alpha-carbon of a carbonyl functional group (O=C-C-**H**) have chemical shifts in the range of 2.1–2.6 ppm.[7] The presence of the peak at 2.25 ppm in the acetic anhydride spectrum confirms that the structure of the reactant has only methyl groups adjacent to the acid anhydride functional group.

The NMR spectrum of synthesized aspirin is located at the bottom of Figure 7. The peak near 10.5 ppm represents the hydrogen from the carboxylic acid functional group, which can be confirmed by the IR spectrum of aspirin (O-H carboxylic acid band at 3000–2500 cm^{-1}). Once again, the peak at 2.25 ppm is indicative of hydrogens that are on the alpha-carbon of a carbonyl functional group. Finally, the cluster of peaks between 6.5 and 8.5 ppm suggests that aromatic hydrogens are present in the molecule. The substitution pattern (e.g., ortho, meta, or para) can be derived from examination of an aromatic species and can be determined by measuring the coupling constant of the aromatic region. In the case of both salicylic acid and aspirin, both molecules are ortho-substituted; the typical J-coupling of ortho-substituted molecules is ~7–9 Hz[1].

The IR spectra for the wintergreen oil synthesis were also collected (Figure 8). From the top of the spectra stack to the bottom, the salicylic acid reactant, methanol reactant, experimentally synthesized wintergreen oil and the reference wintergreen oil spectra are shown. Once again, the same three functional groups can be seen in the salicylic acid starting material spectrum. In the methanol spectrum, the O-H hydroxyl (3327 cm^{-1}) and the C-O alcohol (1023 cm^{-1}) absorbing bands are easily visible. The sp^3 hybridized C-H stretching (2944, 2832 cm^{-1}) is visible in the methanol spectrum because it is not covered up by a broad absorbing feature in the same region. The wintergreen oil reference spectrum located at the bottom of Figure 8 once again shows the presence of the new C=O ester stretching band (1674 cm^{-1}). The O-H carboxylic acid (3000–2500 cm^{-1}, 881 cm^{-1}) and the C=O carboxylic acid (1652 cm^{-1}) stretching bands seen in the salicylic acid reactant are no longer present in the wintergreen oil spectrum.

The synthesized wintergreen oil spectrum (pink), indicates that a significant amount of impurities were present in the product. First, there is evidence for residual methanol in the wintergreen oil product, as the broad O-H alcohol peak from methanol carried over into the wintergreen oil spectrum. Had the wintergreen oil been allowed additional drying time, this peak would have likely decreased to zero. A methanol impurity can also be seen at 1023 cm^{-1}, where the C-O alcohol band from methanol carried over and significantly increased the peak intensities in that region. Finally, additional broadening features can be seen in the spectrum region of 1300–900 cm^{-1}, indicating that salicylic acid impurity is also present.

Again, the functional group information obtained from the IR spectra can be combined with the structural information acquired from either the picoSpin 45 or picoSpin 80 NMR data. The picoSpin 80 NMR spectrometer provides increased resolution and sensitivity when compared to the picoSpin 45 NMR spectrometer. This enhanced capability can be seen in the aspirin spectrum collected on the picoSpin 80 (Figure 9). The increased resolution of the picoSpin 80 is most prominent in the aromatic region from 6.5 to 8.5 ppm. When compared to the same region on the picoSpin 45, the peaks in the picoSpin 80 spectrum are sharper and more defined. Moreover, the expanded aromatic region shown at the top of the picoSpin 80 spectrum highlights the observable first and second order coupling.

The main reason for using NMR spectroscopy is for structural elucidation, which requires combining the splitting patterns with the relative amounts of protons. The integration of the peak areas provides the relative number of hydrogen atoms present within a molecule. The peak labeled ‘a’ has an area of approximately one,

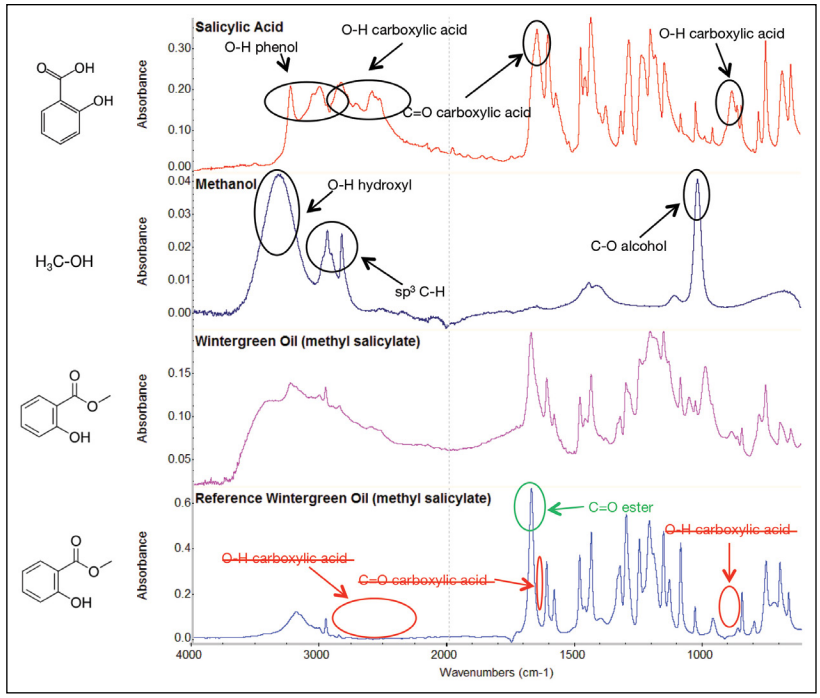

Figure 8: IR spectra acquired from wintergreen oil synthesis

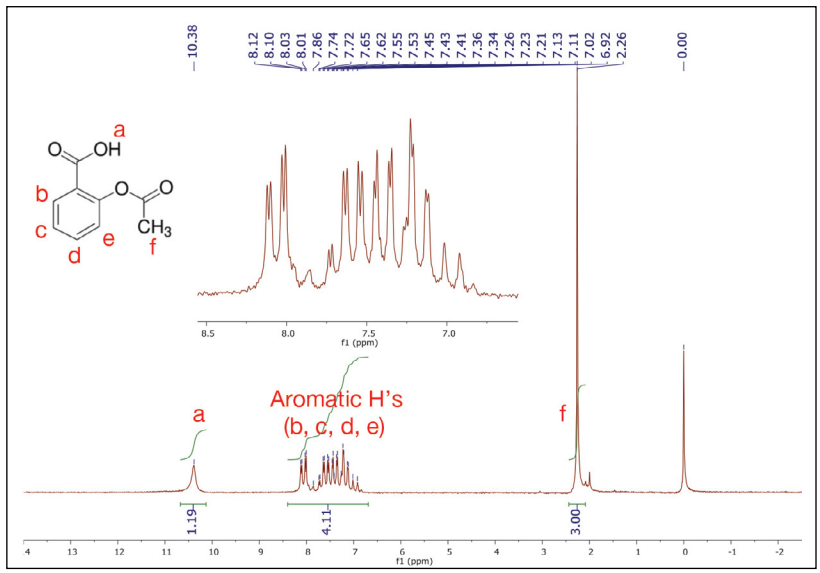

Figure 9: picoSpin 80 NMR spectrum of aspirin

which corresponds to the one hydrogen on the carboxylic acid functional group. The aromatic peaks (b,c,d,e) have a combined integration value of four, which corresponds to the four aromatic hydrogens. Likewise, the peak labeled ‘f’ has an integration value of three, which represents the three hydrogens on the methyl group attached to the ester functional group.

Conclusion

FT-IR and NMR spectroscopies can provide complementary chemical information about a given molecule. FT-IR spectroscopy can be used to successfully define the presence and absence of functional groups while NMR spectroscopy is best used to identify the organic structure. In the undergraduate laboratory curriculum, Thermo Scientific FT-IR and NMR spectrometers not only provide useful molecular information regarding the identity and characterization of molecules, but can also be effectively used in conjunction with one another to teach students about the differences and similarities between these powerful analytical techniques.

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