Spectroscopy analysis techniques

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Nuclear Magnetic Resonance spectroscopy is an extremely powerful and useful tool in performing experiments on the nuclei of atoms. NMR is defined by The American Heritage Dictionary as " The absorption of electromagnetic radiation of a specific frequency by an atomic nucleus that is placed in a strong magnetic field, used especially in spectroscopic studies of molecular structure and in medicine to measure rates of metabolism." NMR is used to study magnetic nuclei, such as the nucleus of a hydrogen, carbon, or nitrogen atom. NMR isn't used in only laboratory research, but it is also used in the field of medical work, in the form of a Magnetic Resonance Imaging (MRI) device.

Infrared (IR) Spectroscopy is another type of spectroscopy is used to analyze samples. On the electromagnetic spectrum, the frequencies used in IR fall in-between the frequencies used in NMR and the frequencies used in Ultraviolet-visible spectroscopy (UV-Vis). IR involves molecular excitation (vibration) of a sample caused by bonds stretching and bending. IR is not only used by those working in science fields, but also by those working in forensics and telecommunications. IR technology is also used a variety of everyday items, from microwaves to remote controls.

Mass Spectroscopy (MS) is another type of spectroscopy that involves detecting positively charged cations. This is important in understanding the difference between MS and the other two types of spectroscopy (NMR and IR), because MS doesn't use electromagnetic radiation causing excitation that gives a readable signal. MS measures the mass-to-charge ratio (m/z) of ions. MS is used in many things, including the verification and analyzation of a structure, trace-gas analysis, and regional sample identification (due to different areas of the earth containing different ratios of elements). However, MS is not very effective nor useful in analyzing small, minute samples, because it destroys them during analyzation.

The purpose of these labs is to give us an introduction to spectroscopy and the techniques used in spectroscopy. Three different types (NMR, IR, and MS) of spectroscopy are demonstrated in these labs.

The theory behind the NMR is that pulse of energy from a magnetic field can excite the nuclei of an atom and affect its spin. NMR involves placing a sample inside an instrument that has a magnetic field and shooting an energy pulse through the sample. This energy is roughly around the same frequency that a TV or a radio would use on the electromagnetic spectrum. Nuclear excitation occurs when these energy waves hit the sample and effect the spin of the nuclei. Depending on the type of sample used, the pulse will be absorbed by the sample to a certain extent.

Chemical shift is a phenomenon that is a result of the shielding effect and the density of the electrons in the molecules. According to the Merriam-Webster dictionary, chemical shift is, “ the characteristic displacement of the magnetic resonance frequency of a sample nucleus from that of a reference nucleus that provides the basis for generating and interpreting nuclear magnetic resonance and magnetic resonance imaging data.” The reference structure generally used in NMR is tetramethylsilane, due to the fact that it is volatile, soluble, only has a limited ability to react chemically, and shows up as a single peak at 0 ppm on an NMR plot.

The theory for IR involves using frequencies in the electromagnetic spectrum from around 800 nm to around 1, 000, 000 nm. A sample is shot with energy of the above frequency, causing the bonds to become excited and vibrate, resulting in bond stretching and bond bending. There are three factors that affect the position of the IR peak on the plot. First, the mass of the atom affects the position because a heavier atom will vibrate at a lower frequency than a lighter atom will. Second, the stiffness of the bonds is a key factor, as the stronger a bond is, the harder it will be for the frequency to make it vibrate. Therefore, a stiffer bond will vibrate at a much higher frequency than will a less stiff bond. Finally, the change in dipole moment of the molecule affects the position, because to be able to see the resulting IR peak in a plot, a molecule must have a change in its dipole moment. This dipole moment is caused by the molecule stretching or bending.

The theory for MS involves passing an electron beam through a sample being analyzed. This electron beam removes one electron from the sample, thus forming a cation. The cation is very unstable and is known as a “ radical cation” of the sample. Due to its instability, fragmentation occurs, starting with the weakest bonds of the molecule fragmenting. Then the machine that is used in mass spectroscopy records the relative abundances of the different ions, and a graph containing the relative abundance (y-axis) versus the mass to charge ratio (on the x-axis, m/z) is made. When you look at the graph, you will notice that some peaks are very tall, while others are short. The peak that is at 100% abundance is considered the base peak, and is used to see how frequently a specific fragment of the molecules has been lost during MS. Finally, the peak that corresponds to the formula mass of compounds is used as the “ M+” peak. By using this peak, you can put together the fragments from what you see in the spectrum graph. Different elements will have different isotopes, and each isotope has different relative abundances. These known abundances are then used in analyzing the unknown compound.

The procedure for NMR spectroscopy is rather complicated. A machine that creates a magnetic field is used to hold the sample being studied. This machine has a coil of wire inside, which is kept very cold at 5 Kelvin. A current is ran through this wire, then turned off, but keeps on flowing inside the wire because it is superconductive. A superconductive substance loses heat extremely slowly. Due to the coil of wire being circular, magnetic lines of flux come out of the coil. Samples of the substance being studied are placed in a small, 5 mL glass tube, which is then carefully placed into the center of the area where the magnetic field is located. It is important to note that before handling the tube, one must cleanse their fingers and the outside of the glass tube with a cleaning wipe to make sure that no oils or contaminants affect the NMR results. The machine used in this process has liquid nitrogen and helium inside it to keep it super cold. The sample, held in the magnetic field, is spun at a fast rate, so as to even out the sample, and makeup for discrepancies in the glass tube. The magnetic field then sends a pulse through the sample and the characteristics of how the sample absorbs the pulse are recorded on a computer attached to the machine generating the magnetic field. From these results, you can see the patterns that can be used to analyze a substance. The plot of the absorptions peaks are on the x-axis and the plot of the intensity of the peak is the y-axis. Plotted together, you can find the analyzation of the sample graphed on the x- and y-axis.

The procedure used in IR is much simpler than the procedure used in NMR. First, a background scan is done with the IR machine. The background scan is performed to give the user information about other substances present, such as atmospheric H2O and CO2, so that their presence may be taken into account when one is analyzing the IR results. Secondly, the sample to be tested is crushed to a fine powder in a marble pestle and mortar. Then, this powder is placed between two salt plates and the salt plates are placed into a holder in the IR machine. Salt is used because it is transparent to IR light (thus and the beams pass directly through it), it is much cheaper than other substances that also are transparent to IR light, and with the sample in place inside the IR machine, a beam of IR light is shot through the sample. It is important to note that one conducting this test should be wearing gloves when handling the salt plates, so that the salt places don’t dissolve due to any liquids present. A detector behind the sample measures any change in the heat of the sample, and the data gathered is relayed back to a computer. Next the information from the background spectrum scan is subtracted from the scan with the sample. From this data, a plot is derived, with wavenumbers (in cm-1) on the x-axis and the percentage of transmittance on the y-axis. This information is then used to analyze the sample.

Mass Spectroscopy is conducted with a very straight forward procedure which involves an electron beam machine and a detector. In a low resolution, dated model, a sample is injected into the machine with a syringe and shot with an electron beam created by heat. Then the ions are sent through several slits, and down an analyzer tube. This machine has a magnetic field throughout its body, and the ion finally gets through the tube, into a collector, and a reading is given. With this data, a graph is created as stated beforehand in the mass spectroscopy theory section. Then you can compare the possibilities of the molar mass by comparing the M+ peak mass to a chart in a book or online and figure out what each fragment is, based on the fragment peaks on the graph.

Based on the NMR, IR, and MS data, the molecular structure of the sample is:

From the NMR calculations, one can see that there are two possible choices of chemical structures that align with the graph. Neither solution has any blatantly obvious errors that don’t agree with the graph. However, the first chemical structure seems to agree with the data presented on the graph more than the second one does, as the numbers in the first more closely align with the graph numbers. The broad, 1H exchanges around 10 show the presence of OH, while the two peaks next to each other show that there must be two methylene groups there.

From the sample calculations page, one can see exactly what parts of $C_3H_5BrO_2$ align with what parts of the graph. The different peaks on the graph correspond with $C_3H_5BrO_2$ molecule. At 3067 cm-1, the broad stretch is a O-H stretch. At 2670 cm-1, the sharp stretch is a C-H stretch. At 2571 cm-1, the sharp stretch is also a C-H stretch. At 1717 cm-1, the strong stretch is a C= O stretch. At 1432 cm-1, the sharp bend is a -C-H bend. At 1395 cm-1, the sharp bend is also a -C-H bend. At 1265 cm-1, the strong stretch is a $-CH_2-Br$ stretch.

From the data and sample calculations page for MS, one can see how the sample, when passed through an electron wave, fragments into different ions. The tallest peak, at 73, is shown to represent the molecular cation without the -Br, while the peak at 152 (M+ peak) is used to determine the mass of the entire molecule. The peak at 107 is from -COOH fragmentation, and the peak at 135 is from -OH fragmentation. You should notice, however, that on the graph in the data sheet, there appears two peaks only 2 m/z (mass to charge ratio) apart at 107, 152, and 135. This is due to the fact that each different isotope has a different relative percent abundance. The relative abundance of the 79Bt is 100% and that of 81Br is 98%. The means that roughly 1/2 of the molecule fragments will have a 79Br and the other half will have a 81Br. Thus, those peaks previously mentioned are double because they have either a 81Br or a 79Br. However, at 73, the peak is not double. This is because at 73, the -Br has fragmented off, and 73 is how much the molecule weighs with the -Br gone.

In conclusion, spectroscopy is a very useful and powerful tool used in many different fields of study today. Spectroscopy is a term used to describe several different types of analyzing done using the electromagnetic spectrum. In these labs, one is exposed to three different types of spectroscopy, these being Nuclear Magnetic Resonance (NMR), Infrared (IR), and Mass Spectroscopy (MS). Nuclear Magnetic Resonance is used not only to analyze samples, but it is also used to analyze humans via Magnetic Resonance Imaging (MRI). Interestingly, MRI isn’t called NMR, because the word “ nuclear” tends to invoke a sense of fear on patients. Infrared spectroscopy is also used to analyze samples, and is often used by forensic specialists to examine evidence from crime scenes. Mass Spectroscopy is totally different than the other two methods because it doesn’t used electromagnetic radiation. Instead, it involves passing the sample through an electron beam, which then fragments the sample, and a graph of the fragmentation is created. Mass Spectroscopy is useful as a powerful analytical tool, yet it is not very useful in studying very small samples because it causes them to break up (fragment) and thus would destroy the sample.

Spectroscopy is an amazing tool that God has allowed us to discover and use to help mankind in many fields of study. Overall, I believe that spectroscopy is a pretty spiffy way to find out information regarding different samples of various chemical compounds, and I am grateful to Him for allowing us to use such cool methods.

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