Spectroscopy

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Abstract

The structure and composition of a molecule can provide useful information for chemists to learn about mechanisms and reactions. However, it is impossible to physically see the atoms and bonds in a compound. In order to determine what the molecule is and get an idea of its structure, scientists use various forms of spectroscopy.

This project demonstrates some of the basic molecule vibrations that cause the various results seen in a spectroscopy spectrum. VPython was used to create the atoms and bonds and simulate their bends and stretches, which can be seen in infrared spectroscopy (IR).

1 Background

In chemistry, spectroscopy is often used to identify a molecule in order to determine unknown compounds and impurities in samples. There are different types of spectroscopy that one can use. Each has its own advantages and disadvantages, which depend on the main end goal of the chemist.

1.1 Infrared Spectroscopy

One type is *infrared spectroscopy* (IR), often used to analyze samples with covalent bonds. This uses infrared radiation, with long wavelengths and lower frequencies, to analyze a compounds functional groups. Peaks and bands in an IR spectrum represent absorbed wavenumbers, or the resonant frequency at which the absorbed energy matches the transition energy of the bond or functional group vibrating. When the bonds are disturbed, they vibrate

in quantized modes, bending and stretching, giving off quantized energy in packets.

There are different ranges of infrared on the electromagnetic spectrum: *near*-, *mid*-, and *far*-infrared, all relative to the visible spectrum. High energy *near*-IR can excite overtone or harmonic vibrations. *Mid*-infrared, one of the most commonly utilized regions, can be used to analyze fundamental vibrations and their rotational vibrational structure. The *far*-infrared is very low energy, and can be used for rotational spectroscopy.

In all of the above, the absorption of energy given off by bond stretches and bends can be seen in an IR spectrum, shown in the figure. The x-axis is the *wavenumber*, typically given in inverse centimeters. Higher energy bonds appear with higher wavenumbers, which are found decreasing from left to right. The determination of a peak's position in an IR spectrum is determined by the strength of the bond, the mass of the atoms involved, and the type of vibrational mode. The y-axis is the *percent transmittance*, showing where the absorption occurs. The intensity of the absorption depends on the change in the local dipole, or the distribution of charge between two atoms. Due to background noise and imperfections in the machine, a spectrum will almost never have an instance of total transmittance between absorption peaks. Instead, smaller and weaker peaks will exist, creating a baseline to which the more intense peaks and bands can be compared and considered to be of significance.

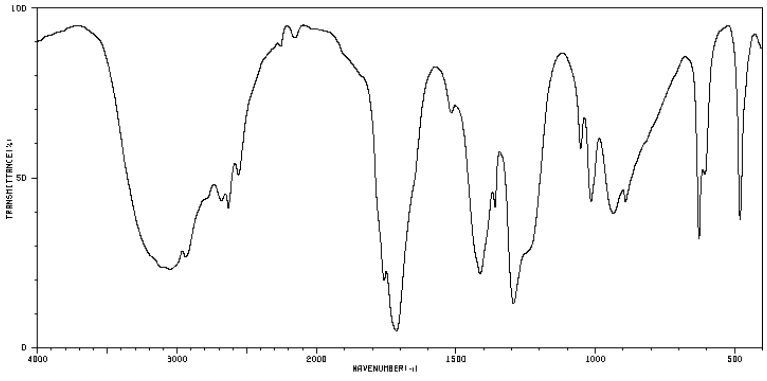

Figure 1: IR spectrum of carboxylic acid.

IR is fairly sensitive to change in composition. This is due to the understanding that bonds between atoms are not fixed, but behave as springs,

able to move and stretch and bend. According to Hooke's Law, a spring has a force constant κ. Based on this constant and the masses of the atoms participating in the bond, the wavenumber ($\bar{v}$) of the resulting absorption peak can change drastically. Given below is the general equation for determining a baseline wavenumber of a bond, with m and M representing the masses of the two atoms involved in the bond [1]. The two constants are the spring force, κ, and the speed of light, c.

$$\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{\kappa(m+M)}{mM}}$$

A typical C-H bond will occur around 3090cm^{-1}. In the equation below, m_H is used for the smaller atom, the hydrogen, and M stands for the larger carbon's mass.

$$\bar{v_{\mathrm{H}}} = \frac{1}{2\pi c}\sqrt{\frac{\kappa(m_{\mathrm{H}}+M)}{m_{\mathrm{H}}M}}$$

One can replace the typical hydrogen, which has one proton, with a deuterium, a heavier isotope of hydrogen, with a proton and a neutron, represented by D in C-D. The m_H is now replaced with the new mass, m_D.

$$\bar{v_{\mathrm{D}}} = \frac{1}{2\pi c}\sqrt{\frac{\kappa(m_{\mathrm{D}}+M)}{m_{\mathrm{D}}M}}$$

Since the addition between the atoms has little effect compared to multiplication when the , the relationship between hydrogen and deuterium can be approximated by assuming the numerators are about the same within the square root ($(m_{\mathrm{H}}+M) \approx (m_{\mathrm{D}}+M)$). After further simplifying the approximate ratio between them, one finds that the relationship between their wavenumbers is reliant on the square root of their masses.

$$\bar{v_{\mathrm{D}}} = \bar{v_{\mathrm{H}}}\sqrt{\frac{m_{\mathrm{H}}}{m_{\mathrm{D}}}}$$

Since the mass of the deuterium is about twice that of hydrogen, the wavenumber of a C-D bond would be proportional to the of $\sqrt{\frac{1}{2}}$ of that of a C-H bond, around 2185cm^{-1}.

Not included in the equation is the third element in determining the wavenumber of bond, which comes from the *vibrational mode*. There are six

main vibrational modes categorized either as stretches(symmetric or asymmetric) or bends(scissor, rock, wag, or twist). Stretches refer to any movement along the atomic bond. Bends are any other movement that does not occur along the bond. In order for a bond to be *IR active*, which means it has the ability to appear on a spectrum, it must not be part of a symmetrical diatomic molecule. This is due to the fact that diatomic molecules have one bond and no permanent dipole, and therefore one single vibration [2]. However, asymmetrical diatomic molecules and polyatomic molecules experience the various vibrational modes. My project in VPython was done to demonstrate the six normal vibrational modes on a carbene (CH_2) molecule, making a simple three-atom system. The code used to create the movements can be seen in section 2.

The majority of the peaks that can be analyzed individually will be a result of stretches, as these are higher in energy and consequently have higher wavenumbers. These fall in the *group frequency* region, where different bonds and functional groups can be identified [3]. A significant part of a spectrum that must also be taken into consideration is the fingerprint region for mid-IR, typically considered to be anything below about $1500cm^{-1}$. In this region, many different bond stretches and most of the bends overlap, making it extremely difficult to identify individual peaks. However, together they make a unique pattern; every molecule has a distinct fingerprint region. This can be used to compare very complex yet similar compounds that may otherwise have very similar spectra.

Unfortunately, IR can only provide qualitative, but not quantitative, information such as how many bonds are present. However, it is a quick, reliable, and cost efficient technique to analyze a sample, which is why it is widely used in research and industry in both organic and inorganic chemistry. They are a great way to test for impurities in a product, as they are fairly sensitive.

1.2 Nuclear Magnetic Resonance Spectroscopy

A type of quantitative spectroscopy commonly used is *nuclear magnetic resonance* (NMR). It utilizes the magnetic properties of certain atomic nuclei, applicable to any nucleus with nuclear spin, meaning an odd number of electrons and protons. In the absence of a magnetic field, nuclear magnetic poles are randomly oriented throughout the molecule. After a magnetic field is applied, the spins will align either with the field at a lower energy or against

the field at a higher energy. The energy difference between these spin states of proton p is given in the next equation [1].

$$\Delta\epsilon_{\mathrm{p}} = \hbar\gamma_{\mathrm{H}}\mathbf{B_p}$$

In the above equation, $\hbar$ represents Planck's constant. $\mathbf{B_p}$ refers to the magnitude of the actual magnetic field at this proton, not that applied. This is due to shielding effects of the compound, always making the actual magnitude less than that of the magnitude of the applied magnetic field [4]. Finally, the constant γ_{H} is the gyromagnetic ratio, or the fundamental constant of a proton. As can be deduced from the equation, when there is no magnetic field, there is no energy difference between spin states. As a greater magnetic field is applied, the energy difference is directly proportional to the magnitude of the field. This can be seen in the graph below in figure 2.

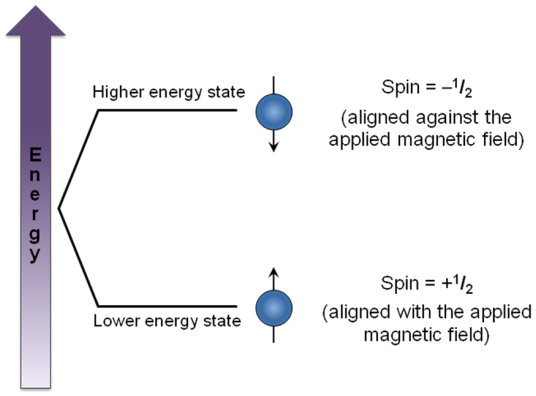

Figure 2: Relative energies of spin states in an applied magnetic field.

There are different types of NMR that can be utilized. One common method to help with determining a small organic molecules structure is proton NMR (^{1}H-NMR). A spectrum for proton NMR can be seen in figure 3. Evaluating an NMR spectrum means one has to take into account unique proton environments (symmetry), chemical shift, multiplicity, and integration.

The x-axis of an NMR graph contains the first property of *chemical shift*, which is given relative to *tetramethylsilane*, or TMS. This is a highly shielded, and unreactive molecule that has a very low frequency. It has one, high intensity peak at around 0ppm. The chemical shift, δ, is measured in ppm, or

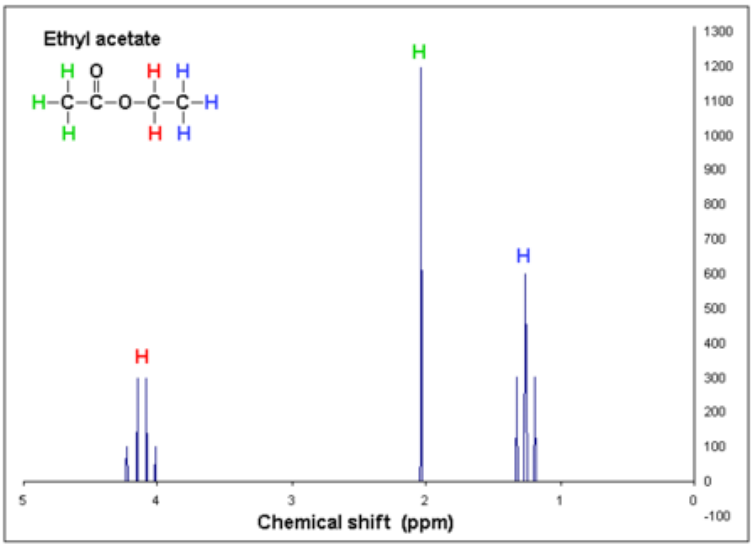

Figure 3: ^{1}H-NMR spectrum for ethyl acetate.

parts per million, and is measured relative to this peak for TMS. For proton NMR, most resonance peaks will occur between 0ppm and 12ppm. The higher the chemical shift value (and therefore higher frequency), the more deshielded a proton group is. This means that there are electron withdrawing groups or structures, such as aromatic rings and π-bonds in double or triple bonds, that decrease electron density around a proton. More shielded protons will be upfield, closer to TMS. There will also be a peak on the spectrum for the solvent used. The most common is deuterated chloroform, $CDCl_3$, which has a known chemical shift of 7.26ppm.

The second property of multiplicity has to do with the *spin-spin splitting* and is dependent on the number of protons on adjacent carbons. If there are n adjacent protons, then the multiplicity will usually be $n+1$ splittings of the peak. This is due to whether the adjacent protons are aligned with or against the applied magnetic field, or some combination of both. Having more spins aligned with the magnetic field will have the splitting peak more downfield. The more spins aligned against the field there are, the more upfield the splitting peak will be. If a signal experiences splitting, it will have a J-coupling constant. This is measured in Hertz (Hz), and is the difference between the splitting peaks themselves within the signal. Two groups with the same coupling constant are said to be *coupled* to each other, or are

adjacent groups. The anisotropic effect can change the expected multiplicity. This involves protons in special structures such as aromatic rings and π-bonds that create their own magnetic field.

The last significant property of an NMR spectrum is *integration*. This is the number of protons represented in the signal. For a methyl group, or —CH_3, has an integration of 3 for the three hydrogens. In practice, the numbers are not typically exact. The first reason is that the integration values are a simplified ratio. If there is a ratio of groups with the expected proton group integrations to be 2:4:2, then they will initially be shown as 1:2:1. Also, the integration values will not be exact whole numbers, and will be to be rounded up or down.

There are different types of NMR that can be used, depending on the compounds being evaluated. Carbon NMR (^{13}C-NMR) can also be used for larger hydrocarbon chains. It has the advantage of no splitting, so it gives a cleaner spectrum. However, it is much less sensitive than proton NMR, and thus needs a more concentrated sample. For some larger, more complex compounds, phosphorous NMR (^{31}P-NMR) gives one singlet with a unique chemical shift dedicated to a specific molecule. It has a large chemical shift range, and shows sharp peaks. However, it does not contribute much to the structure of the molecule. Rather it is used to determine a large, complex compound's identity.

NMR is very useful to identify organic compounds and their structures. However, it is not the best test for determining impurities in a sample. While there are some commonly known impurity shifts, they can mix with the desired compound and cause confusion. Also, the spectrometers themselves are very expensive, and thus the machines are not commonly found outside of universities.

2 VPython RTICA

Due to little to no background in programming at the beginning of this course, VPython was used to create the RTICA example of the six vibrational modes of carbene mentioned previously. The central carbon was used to set the initial frame. Off of this, the hydrogens were positioned relative to the carbon's frame.

```
fcarbon = frame()
fhydrogen1 = frame(frame=fcarbon, pos=(3,3,0))
```

```
fhydrogen2 = frame(frame=fcarbon, pos=(-3,3,0))
```

The atoms themselves were represented by colored sphere objects, with white spheres for the hydrogens and red for the central carbon.

```
carbon = sphere(frame=fcarbon, pos=(0,0,0), radius=1,
color=color.red)
hydrogen1 = sphere(frame=fhydrogen1, pos=(0,0,0), radius=0.7,
color=color.white)
hydrogen2 = sphere(frame=fhydrogen2, pos=(0,0,0), radius=0.7,
color=color.white)
```

Finally, the bonds were made using a gray helix object. This was chosen over a simple cylinder or rod to better show why the bonds behaved the way they did when they stretch and bend. The end positions for these helix bonds were defined according to the carbon frame and then the position of the hydrogen.

```
bond1 = helix(frame=fcarbon, pos=carbon.pos,
axis=(fhydrogen1.pos.x,fhydrogen1.pos.y,fhydrogen1.pos.z),
coils=10, thickness=0.1, radius=0.5)
bond2 = helix(frame=fcarbon, pos=carbon.pos,
axis=(fhydrogen2.pos.x,fhydrogen2.pos.y,fhydrogen2.pos.z),
coils=10, thickness=0.1, radius=0.5)
```

To make the atoms move, an *infinite while loop* was implemented. The t is used at the time variable, initialized to 0. The br is used as a constant to change how much the hydrogens would move. Within the while loop, the *rate(50)* sets the speed of the animation so that it does not go too fast or too slow. The time t is continuously incremented. As t increases, the position of the hydrogens changes depending on the movement. To keep repetitive motion, a *sin()* function was used. In the code below, the *symmetric stretch* is modeled, stretching the carbon-hydrogen bonds in phase with one another. The only difference was the direction of the movement, with each going to opposite sides. For the *symmetric stretch* model, the movements would be exactly π out of phase, with one stretched out and the other pressed in.

```
t=0
br=1
while 1:
     rate(50)
     t=t+0.1
     fhydrogen1.pos=(3+br*sin(t),3+br*sin(t),0)
     bond1.axis=(fhydrogen1.pos.x,fhydrogen1.pos.y,fhydrogen1.pos.z)
     fhydrogen2.pos=(-3-br*sin(t),3+br*sin(t),0)
     bond2.axis=(fhydrogen2.pos.x,fhydrogen2.pos.y,fhydrogen2.pos.z)
```

Similar code was constructed for the various bending models. While the movements are generally the same, they happened along different axis in each mode. The scissoring and wagging models were done in phase due to symmetry, as demonstrated by the symmetric stretch. Therefore, the final two bends, rocking and twisting, were created by adjusting one side to be π out of phase with the other, resulting in asymmetrical vibrations.

References

[1] Loudon, Marc G.*Organic Chemistry*. Greenwood Village: Roberts and Company Publishers, 2009.

[2] "Number of Vibrational Modes for a Molecule." *Chemistry LibreTexts*. N.p., 21 July 2016. Web. 22 Nov. 2016.

[3] Reusch, William. "Infrared Spectroscopy." Infrared Spectroscopy. Michigan State University, 5 May 2013. Web. 14 Dec. 2016.

[4] Reich, Hans J. "5.2 Chemical Shift." 5.2 Chemical Shift. University of Wisconsin, 22 Mar. 2016. Web. 22 Nov. 2016.