Chapter 12.4: Molecular Spectroscopy

Introduction: Basic Quantum Mechanics for Molecules.

So far, we have focused on the interactions of individual atoms with electromagnetic radiation. But light is also a very powerful tool for both determining the identity and measuring important properties of larger atomic assemblies - molecules. Molecules, in the simplest sense, are groupings of atoms that are held together in very specific arrangements to form compounds that typically have properties that are quite different from the elements that make them up. The unique properties of molecules derive largely from how the electrons from the individual atoms work together to form a more stable arrangement than that of the free atoms. In other words, there must be an energetic advantage for atoms to group themselves together into these well-defined arrangements over existing solely as separate, unconnected atoms.

The energy holding atoms together as molecules can be thought of as a balancing act between the attractive forces of differently charged objects with the repulsive forces of like charged objects. We know that a positive charge is attracted by a negative charge while two positive charges repel each other. Therefore, when a negatively charged electron is placed between two positively charged nuclei, as shown in figure 12.4.1, each nucleus is strongly attracted to the negatively charged electron. The net result of this attraction is that the two nuclei are pulled together by the electron that they share in common. The two nuclei are drawn towards each other until the repulsive force between these like charged nuclei becomes too great to allow them to approach each other any closer. The result is that the unit of the two nuclei and the electron form a tightly bound trio that is lower in energy than if they were simply free atoms – the driving force for making a molecule. In a molecule made up of many atoms, there can be a large number of these types of interactions holding the entire assembly together in a carefully balanced network.

Knowledge of the behavior of the electrons in molecules, therefore, is the key to understanding molecular properties, including how they interact with light. The electrons, in turn, can be best understood by the same quantum mechanical ideas that we developed in section 12.2 for individual atoms.

Consider, for a moment, the simplest of all molecules – hydrogen (H₂). From quantum mechanics, we know that the electrons in the two hydrogen

![Figure 12.4.1. Electron-nuclear attractions and nuclear-nuclear repulsions in the hydrogen atom (JTS).](image)

![Figure 12.4.2. Waves of two individual hydrogen atoms (left) can add together constructively to reinforce each other (top) or destructively to cancel each other where they overlap (bottom) to form the hydrogen molecule, H₂.](image)
atoms can be considered solely as waves – we call these wave descriptions of electrons in atoms orbitals – each orbital of an atom is similar to a different standing wave possibility in the jump rope analogy presented in Figure 12.2.5. When two electron waves or orbitals are brought together, they can overlap to add together as any normal waves do – constructively or destructively. If we start with two completely isolated hydrogen atoms that are far apart from each other and bring them together, the electron waves will begin to overlap, shown in Figure 12.4.2. When the waves overlap they add constructively or destructively to form a new composite wave. What this means to molecule formation is that, if the waves add constructively, the electron will spend more of its time between the two nuclei (the place where the waves reinforce each other), pulling the nuclei towards each other to hold the atoms of the molecule together by a chemical bond. If the waves add destructively, the electrons are pushed away from the space between the two nuclei – exposing the two nuclei to their mutually repulsive like-charges and forcing them apart – called an antibonding arrangement or orbital (usually denoted with an asterisk “*” next to the name of the new waves). It is called antibonding since it pushes the atoms away from each other and is the conceptual opposite of the bonding arrangement. These two types of bonding environments are shown in Figure 12.4.3. When these atomic waves, or orbitals, are added together, the resulting new waves are no longer just atomic orbitals but extend their wave features over more than one atom and are, therefore, called molecular orbitals.

Energetically, the two possible arrangements, bonding and antibonding molecular orbitals, play the defining role in determining how molecules behave and even what molecules can form in the first place. The bonding arrangement where the waves reinforce each other and draw the atoms closer together is lower in energy than when they destructively add, causing the nuclei to repel each other. This is shown in Figure 12.4.4 where the waves for the two H atom electrons are shown at each side of the diagram and the waves (orbitals) for the figure 12.4.3. Graphic depiction of the addition of the orbitals (waves shown as spheres) of two hydrogen atoms to form the hydrogen molecule (H₂). The top shows the bonding molecular orbital where the electron resides more between the two atoms; the bottom shows the antibonding arrangement where the electrons spend more of its time away from the space between the nuclei, leading to an arrangement where the atoms repel each other (www.uniquefueltechnology.com/jet_tech.html).

Figure 12.4.4. The electron waves of two hydrogen atoms can come together to form a bonding (lower energy) or an antibonding (higher energy) arrangement.
newly formed H₂ molecule are in the middle of the diagram. Since each hydrogen atom has just one
electron, the hydrogen molecule (H₂) contains a total of two electrons. These two electrons
completely occupy the lowest bonding molecular orbital in the H₂ molecule – quantum mechanics
dictates that each molecular orbital can contain a maximum of only two electrons. Notice that the
two electrons in the H₂ molecule, in the center of Figure 12.4.3, lie lower in energy than where they
started in the two isolated hydrogen atoms (at the sides of the Figure).

As can be imagined, there are many ways and orientations in which atoms can come together
forming chemical bonding and antibonding arrangements to produce molecules. Quantum
mechanics, however, defines the rules as to exactly how this can happen and what types of new
molecular orbitals can be formed. In the very simple H₂ molecule, there are only two possibilities –
the two molecular orbitals shown in Figure 12.4.3 and 12.3.4 – bonding (σ) and antibonding
(σ*) orbitals. Each of these molecular orbitals has its own unique energy
level – quantized exactly as the
energy levels in atoms and can have
only certain allowed, fixed energy
levels. As molecules become more
complex, the same basic ideas hold
true except that there are many more
possibilities of how the atomic waves
(orbitals) can add together, giving rise
many molecular orbitals, each with
their own quantized energy levels.
Electrons fill these possible molecular
orbitals from lowest energy to highest
energy, just as a drinking glass fills
with water from the bottom to the top.
In Figure 12.4.4, the two electrons in
H₂ fill the lowest energy bonding
molecular orbital, the H₂ molecule’s ground state (labeled σ – “b” for bonding). Even going to a
slightly more complex molecule, such as carbon monoxide (CO) significantly increases the
complexity of the types and number of molecular orbitals that can be formed, as illustrated in Figure
12.4.5 – but the process of
forming new
molecular
orbitals and
filling them
with electrons
is identical to
that used for
H₂. In CO, the
total number of
electrons also
fills the
molecular

\[ \begin{align*}
\text{CO} \\
\end{align*} \]

Figure 12.4.5. Molecular orbital diagram for the carbon monoxide molecule (www.meta-
synthesis.com/webbook/39_diatomics/diatomics.html).

\[ \begin{align*}
\text{Excitation of an electron from the ground state to an excited state}
\end{align*} \]

Figure 12.4.6. Excitation of an electron from the ground state to an excited state
in H₂ by the absorption of a photon (JTS).
bonding orbitals formed from the individual atomic waves (orbitals) from lowest energy to higher energy.

Just as in atoms, electrons in the bonding orbitals of a molecule can absorb a photon of light and become excited to a higher energy level, as shown in Figure 12.4.6 for H₂. This idea is the basis of much of molecular spectroscopy — molecules with electrons in quantized energy levels (molecular orbitals) can absorb or emit light to move between these levels. By measuring the wavelength and intensity of these transitions, we can learn important information about the presence and quantity of specific molecules contained within an unknown sample.

**Ultraviolet-Visible Spectroscopy (UV-visible)**

The part of the electromagnetic spectrum encompassing the ultraviolet and visible regions (between about 150 and 750 nm) contains just the right amount of energy to typically move electrons between energy levels within molecules. For this reason, UV-visible spectrometry is often referred to as electronic spectroscopy. Electrons are excited from a lower level, most often the ground state, to a higher-level energy through the absorption of a photon, shown in Figure 12.4.7. Similarly, molecules may emit a photon when they fall down from a higher energy level to a lower one, as in atomic emission and fluorescence spectroscopy. Usually, in UV-visible spectroscopy, electrons move between only a few orbitals — most often between the highest energy...
molecular orbitals occupied with electrons (labeled “bonding” in Figure 12.4.7) and the lowest energy unoccupied (empty) molecular orbitals (labeled as “antibonding”).

When photons shine on a molecule with an energy that exactly matches the difference between two energy levels within the molecule, the photon can be absorbed. A spectrometer measures the wavelength of the light where this absorption occurs along with how much light is absorbed. These measurements provide useful information for the identification of the molecule. The UV-visible spectra for some common organic molecules are shown in Figure 12.4.8 and for the anti-psychotic drug Solian in Figure 12.4.9. The wavelengths and intensities of the peaks in the spectrum tell what and how much of the chemical is in the sample.

Organic molecules, such as those made by living organisms or the vast majority of the drugs on the market today, are often considered, spectroscopically, as composed of a collection of special components, called functional groups. For example, some organic molecules contain an OH group attached to the molecular framework, such as CH3CH2OH (ethanol). The presence of this OH group imparts certain chemical and physical properties to the molecule (collectively called alcohols). Other organic molecules may contain a bromine atom or a C=O unit as a functional group that provides other chemical features of importance. There are several dozen of these special functional groups that are routinely encountered in organic chemistry. When present, these functional groups give their own special “signatures” in spectroscopy and provide “handles” into the identification of an unknown substance. For example, organic bromide compounds absorb light at around 205 nm while a C=O group may absorb at 290 nm. Identifying the presence of these functional groups in a molecule through spectroscopy helps determine the molecule’s identity. Additionally, measuring the amount of light absorbed by these functional groups gives the amount of the substance present, information that is needed in drug assays.

Visible spectroscopy is particularly important in forensic settings in quantifying the color of an object, such as a paint chip, clothing, tinted glass, and many other forms of colored evidence. It is one thing to say that an object appears red, but something far more useful forensically to say that the object absorbs light at 510 nm, separating it from another red object that absorbs at 525 nm. Our eyes perceive color as the wavelength of light scattered or reflected from an object – but not absorbed by the object. When white light shines on an object, molecules within it may absorb some of the wavelengths of the light – effectively removing these wavelengths from the beam. The remainder of the wavelengths pass through the object unchanged and can be reflected into our eyes to be perceived as color. For example, if white light shines on a leaf, pigment molecules in the leaf absorb the red and blue light but not the green wavelengths.

**Figure 12.4.10.** Absorption of blue and red light from the sun but not green light makes the leaf appear green to our eyes (http://zebu.uoregon.edu/2000/ph102/docs19.html).

![Figure 12.4.11](image-url). When white light passes through a substance, it can absorb certain characteristic wavelengths of the light. The light not absorbed will pass through to be perceived as color.
The green light is then reflected off of the leaf’s surface and we perceive the color of the leaf as green. The color perceived is the **complimentary color** of that which is absorbed. For example, using Figure 12.4.11, if green light is absorbed by an object, the complimentary color of green (opposite green on the color wheel) - red - will be the observed color of the object [Note: this conceptual process is different than when mixing paints or inks to make colors, see Chapter 14]. Obviously, this information has important uses in forensic science in the identification/matching of paint samples, clothing, and pigments – anything that appears colored. Pigments, dyes and other color absorbing materials will be presented in more detail in Chapter 14, but the color analysis of these important forensic forms of evidence relies on UV-visible spectroscopy.

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**The Master’s Touch….or Someone Else’s?**

In the world of fine art, the history of a painting or sculpture is critically important. Spectroscopy can be used not only to separate a fake from the real thing, but it can also be used to see where and how people have “touched up” the work to enhance its value, aesthetic appeal or repair damage.

For example, the painting shown below, entitled “The Virgin and Child”, was painted by Dirck Bouts (1410/1420 - 1475). The photograph, shown at left, displays the way the painting appears under normal visible light illumination. Using Ultraviolet illumination, however, dark spots are easily seen on the woman’s face (right). These spots come from places where the painting has been retouched. Knowing this can help restorers return the work to its original state.


**Infrared Spectroscopy (IR)**

Infrared spectroscopy, unlike most of the other forms of spectroscopy that we’ve discussed, does not deal with the transitions of electrons between large energy levels within atoms or molecules. Infrared light, with longer wavelengths and less energy than visible light, does not contain enough energy to cause these types of transitions to occur. Instead, infrared radiation can excite only specific vibrations within the molecule that are also quantized.

Molecules are held together by bonds between the atoms, as presented previously. In a very simple sense, these bonds may be considered as similar to tiny springs attached at their ends to the two bonded atoms. These atoms can then vibrate through the spring’s action both towards and away from each other. The amount of energy needed to cause these types of vibrations to occur depends
upon how strong the spring, or actually the chemical bond, is – the stronger the bond, the more energy needed to cause the vibration to occur. This is similar to comparing the energy needed to compress a very weak spring from a watch with a spring from a truck’s suspension – it’s relatively easy to move the weak spring but very difficult to compress or expand the truck spring (Figure 12.4.12). The strength of a chemical bond depends upon a number of factors, such as the identity of the two atoms involved, the number of electrons they share between them, what bonding connections there are to other atoms in the molecule, the 3-dimensional shape of the molecule, and a variety of other factors. These factors all go to make different chemical bonds vibrate across a wide range of allowed energies.

Vibrational energies in molecules are quantized just as electronic levels are quantized. Since vibrational energies are small with respect to the electronic energy levels, however, each electronic level contains a number of quantized vibrational energy levels, as shown in Figure 12.4.13. If a photon of light has exactly the right amount of energy to excite the molecule to a higher-energy vibration, then the photon will be absorbed.

As it turns out, quantum mechanics dictates what types of vibrations are allowed for a molecule and what energy is required to cause a vibration to occur. Beside receiving the right energy, in order for a vibration to be “allowed” (and absorb light energy), there must also be a change in the electronic “center of charge” of the molecule when the vibration occurs – something like a change in the “center of gravity” for an object but with relation to the density of charge instead. For example, consider the common molecule, carbon dioxide (CO₂). CO₂ is a linear molecule, Figure 12.4.14, that has three possible ways in which it can vibrate. The first vibration, called a symmetric stretch (Figure 12.4.14a), has the two outer oxygen
atoms moving in and out at the same time – both move in together and both move out together. When this happens, there is no change in the electronic center of gravity of the molecule and so it does not absorb infrared light. The second vibration, Figure 12.4.12b, is called an asymmetric stretch – one oxygen atom moves in closer to the central carbon atom while at the same instant the other oxygen atom moves farther away. There is a change in the electronic center of gravity for this vibration so that infrared light is absorbed. The final vibration, Figure 12.4.14c, is actually made up of two vibrations that are exactly the same but simply rotated by 90° (only one is shown). This type of vibration, called a bending mode, also can absorb infrared light. Thus, two out of the three different vibrations possible for CO₂ can absorb IR light. As expected, the infrared spectrum for CO₂ shows just two absorptions – one for each of the “allowed” vibrations of the molecule.

CO₂ is indeed a very simple molecule but serves to illustrate the way vibrational spectroscopy works at the molecular level. Most molecules of interest are much more complicated, containing dozens or even hundreds of atoms held together in complex shapes that influence how they can vibrate and absorb infrared light. This results in very complicated spectra. But it is this very complexity that makes infrared spectroscopy so useful in identifying compounds – each compound gives rise to a unique spectrum all its own, such as that shown in Figure 12.4.16 for n-propanol – a simple organic alcohol. This complexity works something like a fingerprint - if a fingerprint contained only one or two lines, it wouldn’t be very useful, but since it contains

![Carbon Dioxide - Infrared Absorption](www.elmhurst.edu/~chm/vchembook/globalwarming5.html)

![Figure 12.4.15.](www.elmhurst.edu/~chm/vchembook/globalwarming5.html)

![Figure 12.4.16.](www.chemguide.co.uk/analysis/ir/fingerprint.html#top)
hundreds of lines with many features it is very useful in identifying a person. Infrared spectroscopy

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500-3300 cm⁻¹</td>
<td>N-H stretch</td>
</tr>
<tr>
<td>3500-3200 cm⁻¹</td>
<td>O-H stretch</td>
</tr>
<tr>
<td>3100-3000 cm⁻¹</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>3000-2850 cm⁻¹</td>
<td>C-H stretch</td>
</tr>
<tr>
<td>1760-1665 cm⁻¹</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1680-1640 cm⁻¹</td>
<td>C=C stretch</td>
</tr>
</tbody>
</table>

Table 12.4.1. Table correlating a few selected infrared absorption frequencies with organic functional groups (http://orgchem.colorado.edu/hndbsupport/irtutor/tutorial.html).

is similar in that its complexity allows us to distinguish one compound from another.

Some combinations of atoms are so common in organic chemistry and give rise to infrared absorptions at specific wavelengths that they are diagnostic of the presence or absence of these groups (functional groups). For example finding an IR absorption at 1700 cm⁻¹ is a very strong indicator that a C=O group is present in the molecule – eliminating all possible molecules except those that contain this grouping. Table 12.4.1 shows just a few infrared absorptions that are diagnostic for specific organic functional groups.

The region of the infrared spectrum, from about 500 to 1500 cm⁻¹, is usually very complicated, and is referred to as the fingerprint region. This region is especially important since even small modifications in the structure of a compound will result in noticeable changes in the absorptions in this region. For example, shown in Figure 12.4.16 are the IR spectra for two isomers of C₃H₈O. While parts of the spectra are very similar, the fingerprint region for each isomer is quite different, allowing us to quickly and easily distinguish between the two compounds.

**Forensic Applications of Infrared Spectroscopy:** Infrared spectroscopy is a very important tool for forensic chemical analysis. A few of its key uses include:

- **Alcohol Analysis** – Many current breath-alcohol analyzers are based upon measuring the infrared wavelengths absorbed by ethyl alcohol – the amount of absorption provides a direct measurement of the amount of alcohol in someone’s breath leading to a breath-alcohol concentration (BAC) determination (Chapter 13). One manufacturer of such an analyzer reports that “IR photometry represents the most significant advancement in IR breath

**Strange Conventions?**

In infrared spectroscopy, the spectra are not usually shown in plots of light absorbed or emitted versus the wavelength (λ), as in other forms of spectroscopy. Instead, the wavelength is plotted as 1/λ (wavelength in cm) and is labeled reciprocal centimeters (cm⁻¹):

\[
\text{cm}^{-1} = \frac{1}{\lambda}
\]

Also, typical IR spectra do not plot the amount of light absorbed by the sample but rather plot the percent of light that passes through the sample – called percent transmittance.

(don’t blame me, I didn’t make this up!)

Figure 12.4.17. An infrared-based alcohol breath analysis instrument for field use.

test_7110_evidential.jsp)
analysis in 20 years ……[the] technology is virtually non-sensitive to any potentially interfering substance in the breath of a subject.” (Figure 12.4.17)

- **Identification and Verification of Unknown Compounds** – IR spectra provide key analytical data for the identification and verification of unknown compounds by comparing the measured spectra of the unknown with databases containing the spectra of tens of thousands of known compounds. This can be accomplished very rapidly through computer-based searching techniques. The method provides a rapid identification for drugs, poisons, pollutants, and other types of organic samples;

- **Fiber Analysis** – Today, many fibers are made of polymers of organic compounds. IR spectroscopy provides the best method for identifying the chemical composition of these polymeric materials;

- **Paint and Ink Analysis** – Individual layers of paint can be analyzed by IR spectroscopy to identify the pigments, dyes, and binders in the sample through comparison with known reference samples. Similarly, inks, dyes and other similar materials can be identified using IR.

**Microwave, Terahertz, X-ray, and Related Spectroscopies**

Other forms of molecular spectroscopy are gaining application in specialized areas of forensic analysis.

Microwave spectroscopy primarily measures the rotation energies that are present in each vibrational level of a molecule. These rotational energy levels, although quantized, are very close together and require even less energy to excite than infrared vibrational activity, Figure 12.4.13. Thus far, however, microwave spectroscopy has not made much of an impact in forensic analysis.

Also at the long wavelength end of the spectrum is terahertz radiation (usually between 0.1 and 10 mm). The main application of terahertz spectroscopy has been in imaging people for the detection of concealed weapons, such as at airports, border crossings and similar security situations, as shown in Figure 12.4.18. Terahertz radiation can easily pass through clothing, wood, plastic, fog, mist, and ceramics, among others. They are blocked, however, by metal, water, and certain chemicals of particular interest, such as explosives. Terahertz radiation has been able to “see” inside sealed envelopes, packages, and through clothing to not only detect but also to help identify the contents. There is still a great deal of work needed to make this technology practical, including addressing public concern about “invasion of privacy” rights.

Finally, X-rays have also been used to identify materials if interest. This technique has already been presented in detail in Chapter 8.