All molecules are constantly vibrating, and can absorb energy from an incoming photon to increase their vibrations. The two types of vibrational spectroscopy are infrared spectroscopy and Raman spectroscopy. Vibrational spectroscopy is the science of measuring exactly which wavelengths of light are absorbed by a molecule. This technique could be used identify an unknown molecule by comparing its absorption to that of other molecules. Or vibrational spectroscopy could be used to gain further understanding of the physical properties of a known molecule.

Introduction

Molecular vibration can be modeled by balls attached by springs. Displacing an atom from its most stable position requires energy proportional to the displacement. IR spectroscopy can be used to characterize a molecule is the energy of its vibrations falls in the infrared range. Alternatively, higher energy light can be absorbed, the re-emitted at a different wavelength and/or in a different direction; this leads to Raman spectroscopy. So a molecule can absorb radiation to change bond lengths or positions with respect to the other atoms in the molecule. From the number, frequency, and intensity of these absorptions or emissions we can gain insight into the composition of the sample being measured. The number of different absorptions is indicative of the number of different atoms and shape of the molecule. The frequency or wavelength absorbed is indicative of the energy of the bonds and vibrations. And the intensity of the absorptions is related to the concentration of the analyte.

Vibrational Modes

The different possible vibrations are called vibrational modes. Vibrational modes are determined by all the different ways the atoms in the molecule can move with respect to each other, called the vibrational degrees of freedom. Vibrational degrees of freedom differ from the total degrees of freedom in that translation (movement through space) and rotation do not contribute to the vibrational degrees of freedom.

To find the number of vibrational modes one must first know the point group of the molecule. From there, the point group’s character table will list all of the possible symmetry operations for the molecule. Each symmetry operation will leave some atoms in the molecule in place and/or move other atoms in the molecule. Count up the number of atoms that do not move for each symmetry operation, and multiply that number by the symmetry operation’s contribution. This gives the total representation of atomic motion. From there, the vibrational modes can be found by reducing the total representation, according to the equation:

\[ n = \frac{1}{h} \sum X_R X_I N \]

where \( n \) is the number of modes with that symmetry, \( h \) is the total number of symmetry operations, \( X_I \) is the number of irreducible representations (the value calculated above), \( X_R \) is the number of reducible representations (the entry in the character table), and \( N \) is the number of identical symmetry operations. Finally, subtracting the rotational modes and translational modes from the reduced representation gives the number of vibrational modes.
Infrared Spectroscopy

A vibrational mode will be observed in an infrared spectrum if it leads to a change in the molecular dipole moment. Compared to Raman spectroscopy, the infrared photon is completely absorbed and its energy is transferred to the vibration of the molecule, not re-emitted.\(^4\)

Different bonds have different energies associated with them, and require different amounts of energy to stretch or bend. In general, the stronger the bond, the more energy required to deform it. So very weak bonds will only be deformed by low energy radiation, and strong bonds will only be deformed by high energy radiation. This leads to characteristic frequencies where only certain vibrations are absorbed. For example, C-H bonds are typically the only bonds observed in the range from \(2960-2850 \text{ cm}^{-1}\). So if an absorption is present at that frequency, it can be assumed that it is due to a C-H bond.\(^1\)
Raman Spectroscopy

A vibrational mode will be observed in Raman spectroscopy if it leads to a change in the polarizability of the electron cloud of a molecule. \(^4\)

If a photon has energy that is significantly higher than the energy of the vibrational states, it may either be deflected without any change in energy, or it may interact with the molecule and either take energy from it or give energy to it. \(^2\)

When the photon is absorbed and re-emitted in a different direction, it is called Rayleigh scattering, and this is strongly dependent on the wavelength of the incoming light. When there is a change in the energy of the photon, it is called Stokes scattering or anti-Stokes scattering, depending on whether energy is absorbed or lost by the molecule. This change in the behavior of the incoming photons can be measured, and will provide information about the concentration and chemical properties of the analyte. \(^3\)


References


Outside Links

- [http://www2.ess.ucla.edu/~schauble/m...vibrations.htm](http://www2.ess.ucla.edu/~schauble/m...vibrations.htm)
- [http://www.ch.embnet.org/MD_tutorial/](http://www.ch.embnet.org/MD_tutorial/)
- [http://en.wikipedia.org/wiki/Molecular_vibration](http://en.wikipedia.org/wiki/Molecular_vibration)
Problems

1. Why is it that the symmetric stretch of carbon dioxide (CO\textsubscript{2}) is IR inactive, while the symmetric stretch of carbonyl sulfide (COS) is IR active?

A: Because the symmetric stretch of CO\textsubscript{2} does not lead to a change in the dipole moment of the molecule, but the symmetric stretch of COS does.

2. How many vibrational modes are IR and Raman active for C\textsubscript{20}?

A: 17 IR active modes, 29 Raman Active modes.

3. Are there any differences between the vibrational spectrums of H\textsubscript{2}O, H\textsubscript{2}S, and H\textsubscript{2}Se?

A: Although they have the same number of atoms, the same point group, and the same number of vibrational modes, the frequencies at which the vibrational modes occur will be different.