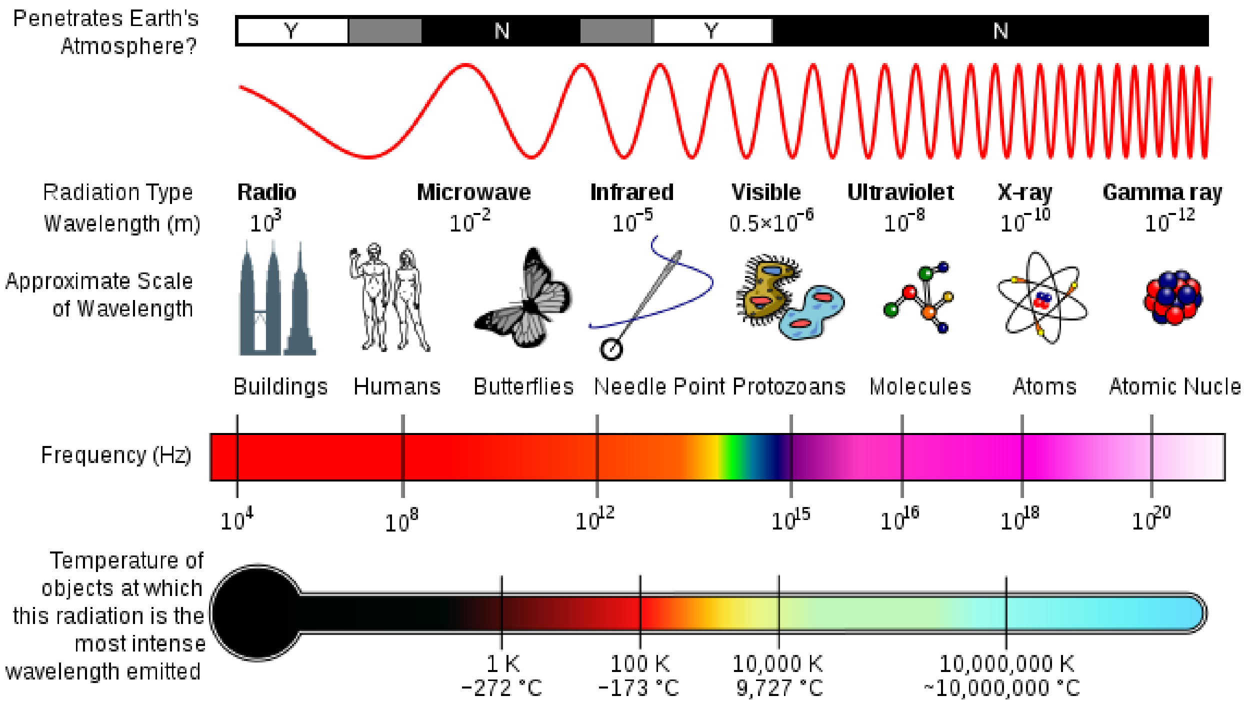
IARPA MORGOTH'S CROWN: Introduction to Infrared Spectroscopy

Contents

Introduction to Infrared Spectroscopy

The fundamental concept underlying infrared spectroscopy is that molecules have quantized vibrational modes, and that absorbing specific amounts of energy in the form of infrared photons can excite these vibrational modes. To back up even a little further, visible light exists in a very small region of the electromagnetic spectrum. Electromagnetic radiation has properties both of a wave (such as interference and diffraction) and a particle. Recognition of this particle/wave duality was one of the key advances of quantum mechanics. According to the wave description, EM radiation ranges from radio frequency waves with wavelengths on the order of tens to hundreds of meters, down to x-rays and gamma rays with wavelengths of picometers (where pico is a metric prefix which stands for 10-12). The infrared band is located at slightly longer wavelengths than visible light. It is further subdivided into bands such as short wave infrared (SWIR), mid wave infrared (MWIR), and long wave infrared (LWIR), which roughly correspond to different operational uses and or detector types. According to the particle description, all EM radiation is composed of little indivisible packets of energy called photons. The energy in a particular photon is proportional to its wavelength according to the relation E = hc/λ, where h is a constant called Plank's constant, and c is the speed of light.



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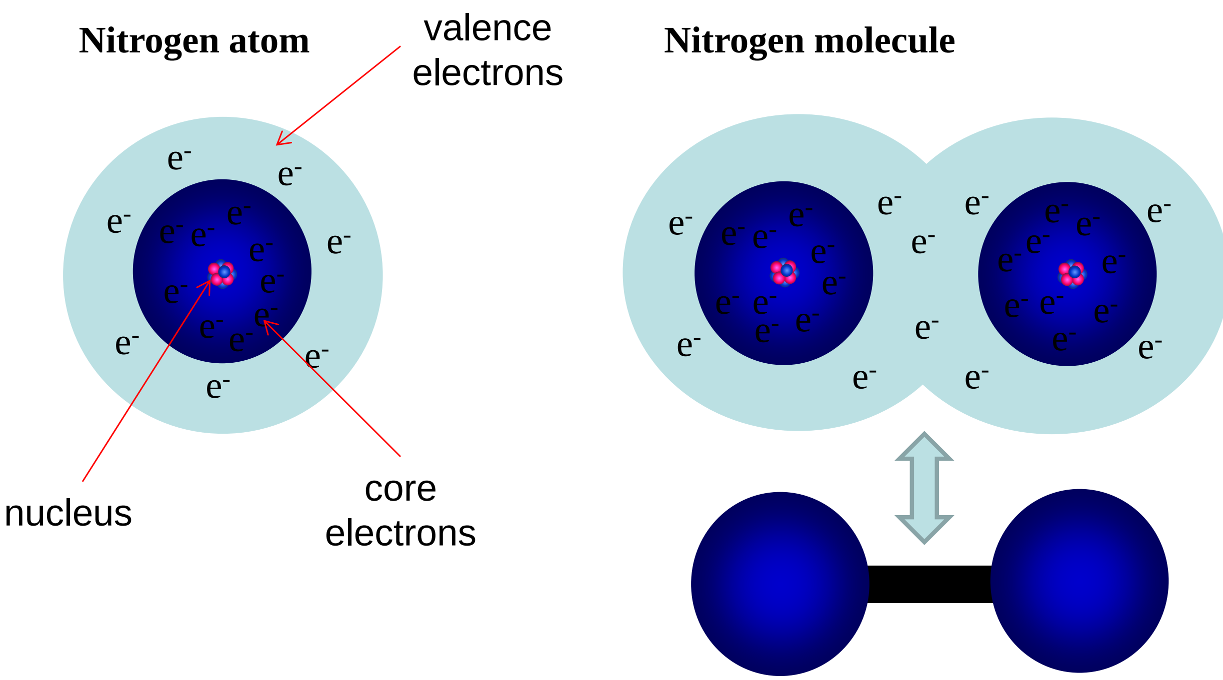
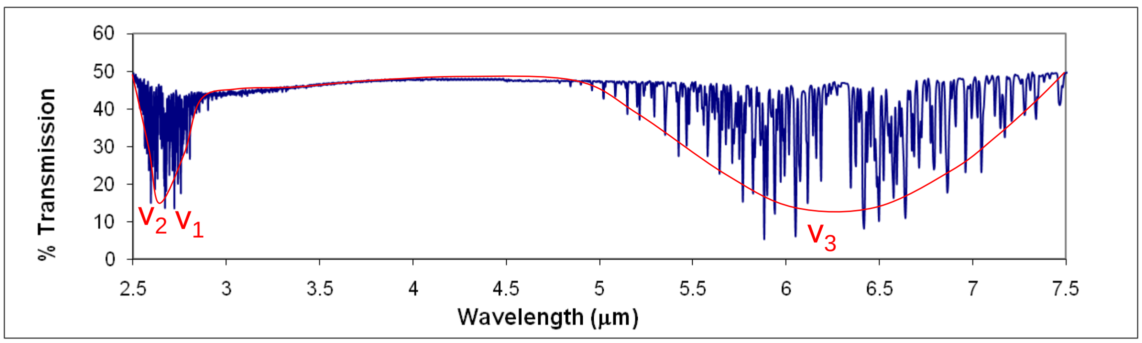
The basic constituent of matter is the atom, which is composed of a core of protons and neutrons, and surrounded by a cloud of electrons (which have a negative charge that balances out the positive charge of the protons in the nucleus). Molecules are formed by one or more atoms sharing their outer (or valence) electrons to form a chemical bond. Chemists often represent molecules by balls that represent the individual atomic nuclei joined by sticks that represent the chemical bonds (called a ball and stick model).

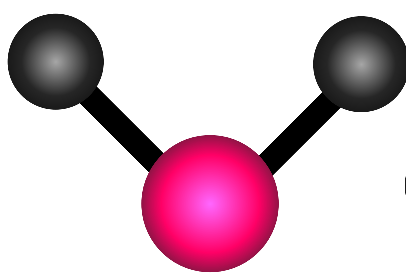


In the vibrational ground state, the positions between the atomic nuclei are fixed at a location that represents an energy minimum between attractive and repulsive forces. However, molecules can absorb energy to excite vibrational modes, which correspond to oscillatory changes in the relative position of atomic nuclei in the molecule. Quantum mechanics dictates that vibrational modes have specific energy levels, and that the molecule can only accept energy increments corresponding to the difference in energy between two vibrational states. Quantum mechanics is not a concept that really has an analog in the macroscopic world we live in. The idea that a molecule can only absorb particular amounts of energy corresponding to vibrational modes would be like if you could only put certain increments of gas into your car, such as the amount to get you from your home to work, or work to the store. If you tried to put in the amount of gas that would get you from your home to 2 miles short of work, your car simply wouldn't accept it. But quantum mechanics is a reality at the atomic and molecular level, and many experiments have been done to prove it.   There are a number of "rules" that quantum mechanics establishes for vibrational excitation. One is that a molecule will have 3N-6 normal (or independent) vibrational modes, where N is the number of atomic nuclei. So for example, a water molecule with one oxygen and two hydrogen atoms will have 3 normal modes. These correspond to the symmetric stretch at 2734 nm, the asymmetric stretch at 2662 nm, and the bend at 6270 nm. If you

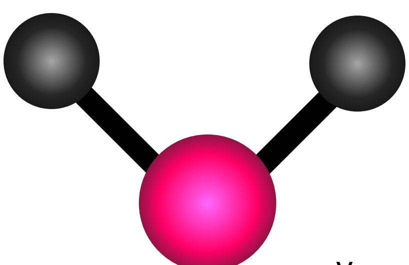
shine a broadband source of infrared light through a sample of water, and then measure the spectrum of the light that emerges on the other side, the amount of light that “gets through” is substantially reduced at the wavelengths corresponding to the normal modes. The actual peaks in the absorption spectrum are broadened (as opposed to the infinitely narrow peaks you would expect from quantum mechanics) due to the fact that rotations of the molecule are quantized as well, but very close together in energy, so this vibrational “peak” is formed from a combination of overlapping rotational lines excited at the same time as the vibration. These rotational lines form the “fine structure” that you see in the gas phase transmission IR spectra of “small” gases such as CO2, H2O, CH4, etc. Larger gas phase molecules such as acetone do still have rotational lines, but these lines become so numerous and densely packed that at room temperature Doppler broadening causes them to blur together. It is this underlying rotational structure (resolvable or unresolvable) that makes vibrational lines significantly broader than the sharp rotational transitions.

Vibrational spectrum of water:

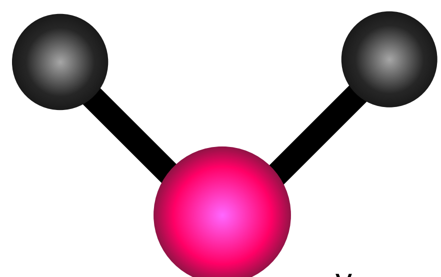




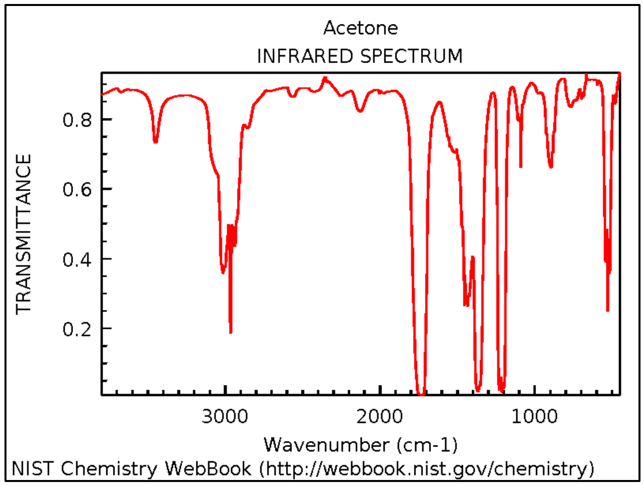
v_2



v_1



v_3



Larger molecules have more complicated vibrational spectra. This molecule has 15 atoms, and therefore 3N-6 = 39 vibrational modes. Some of the modes (located at higher energy or shorter wavelength) correspond to localized excitation of a particular bond stretch or bend. Other modes (located at lower energy or longer wavelength) correspond to overall stretching or breathing modes of the entire molecule. The mid wave infrared (MWIR) region of the IR spectrum is called the "functional group region", since particular modes here are indicative of certain chemical bond types being present in a molecule, such as an OH stretch, which appears as the strong peak indicated by the red arrow. The long wave infrared (LWIR) region of the IR spectrum is called the "fingerprint" region, since the whole-molecule modes here are very specific to a particular molecule. Additional information can be found in the short wave infrared (SWIR) region, where photons have enough energy to excite overtone and combination vibrational modes. Overall, the IR spectrum of a molecule provides a "chemical fingerprint" that can be used to identify a particular compound.