# OBSERVABLE PROPERTIES OF BONDED ATOM PAIRS

When we talk about the properties of a particular chemical bond, we are really discussing the relationship between two adjacent atoms that are part of the molecule. Diatomic molecules are of course the easiest to study, and the information we derive from them helps us interpret various kinds of experiments we carry out on more complicated molecules.

> *It is important to bear in mind that the exact properties of a specific kind of bond will be determined in part by the nature of the other bonds in the molecule; thus the energy and length of the C–H bond will be somewhat dependent on what other atoms are connected to the carbon atom. Similarly, the C-H bond length can vary by as much a 4 percent between different molecules. For this reason, the values listed in tables of bond energy and bond length are usually averages taken over a variety of compounds that contain a specific atom pair..*

In some cases, such as C—O and C—C, the variations can be much greater, approaching 20 percent. In these cases, the values fall into groups which we interpret as representative of single- and multiple bonds: double, and triple.

Potential energy curves
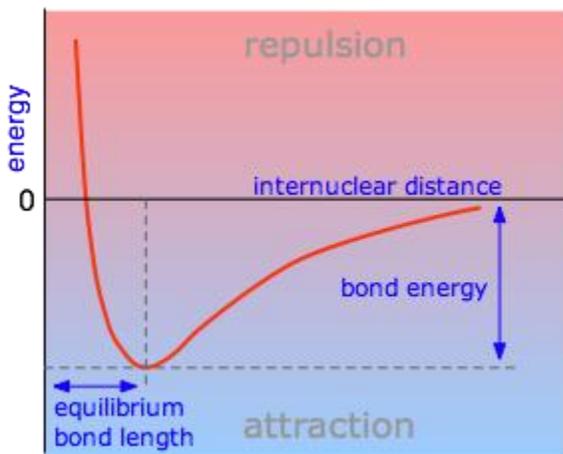
The energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning "no interaction". At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. Plots that illustrate this relationship are known as Morse curves, and they are quite useful in defining certain properties of a chemical bond.

The inter nuclear distance at which the potential energy minimum occurs defines the bond length. This is more correctly known as the equilibrium bond length, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length.

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of RT, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H_2.

The weak attraction between argon atoms does not allow Ar2 to exist as a molecule, but it does give rise to the van Der Waals force that holds argon atoms together in its liquid and solid forms.

> *Potential energy and kinetic energy Quantum theory tells us that an electron in an atom possesses kinetic energy K as well as potential energy P, so the total energy E is always the sum of the two: E = P + K. The relation between them is surprisingly simple: K = –0.5 P. This means that when a chemical bond forms (an exothermic process with ΔE < 0), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy–ΔE has half the magnitude of the fall in potential energy.*
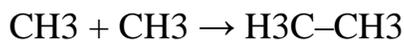
Bond energies

The bond energy is the amount of work that must be done to pull two atoms completely apart; in other words, it is the same as the depth of the "well" in the potential energy curve shown above. This is almost, but not quite the same as the bond dissociation energy actually required to break the chemical bond; the difference is the very small zero-point energy. This relationship will be clarified below in the section on bond vibrational frequencies.

How bond energies are measured

Bond energies are usually determined indirectly from thermodynamic data, but there are two main experimental ways of measuring them directly:

> **1. The direct thermochemical method** involves separating the two atoms by an electrical discharge or some other means, and then measuring the heat given off when they recombine. Thus the energy of the C—C single bond can be estimated from the heat of the recombination reaction between methyl radicals, yielding ethane:
>
> $$CH3 + CH3 \rightarrow H3C{-}CH3$$
>
> Although this method is simple in principle, it is not easy to carry out experimentally. The highly reactive components must be prepared in high purity and in a stream of moving gas.
>
> **2. The spectroscopic method** is based on the principle that absorption of light whose wavelength corresponds to the bond energy will often lead to the breaking of the bond and dissociation of the molecule. For some bonds, this light falls into the green and blue regions of the spectrum, but for most bonds ultraviolet light is required. The experiment is carried out by observing the absorption of light by the substance being studied as the wavelength is decreased.

When the wavelength is sufficiently small to break the bond, a characteristic change in the absorption pattern is observed.

Spectroscopy is quite easily carried out and can yield highly precise results, but this method is only applicable to a relatively small number of simple molecules. The major problem is that the light must first be absorbed by the molecule, and relatively few molecules happen to absorb light of a wavelength that corresponds to a bond energy.

Experiments carried out on diatomic molecules such as O2 and CS yield unambiguous values of bond energy, but for more complex molecules there are complications. For example, the heat given off in the CH3 combination reaction written above will also include a small component that represents the differences in the energies of the C-H bonds in methyl and in ethane. These can be corrected for by experimental data on reactions such as

$$CH3 + H \rightarrow CH4$$

$$CH2 + H \rightarrow CH3$$

By assembling a large amount of experimental information of this kind, a consistent set of average bond energies can be obtained (see table below.) The energies of double bonds are greater than those of single bonds, and those of triple bonds are higher still.

Use of bond energies in estimating heats of reaction

One can often get a very good idea of how much heat will be absorbed or given off in a reaction by simply finding the difference in the total bond energies contained in the reactants and products. The strength of an individual bond such as O–H depends to some extent on its environment in a molecule (that is, in this example, on what other atom is connected to the oxygen atom), but tables of "average" energies of the various common bond types are widely available and can provide useful estimates of the quantity of heat absorbed or released in many chemical reaction.

Single Bonds

H	C	N	O	F	Si	P	S	Cl	Br	I	
436	415	390	464	569	395	320	340	432	370	295	H
	345	290	350	439	360	265	260	330	275	240	C
		160	200	270	—	210	—	200	245	—	N
			140	185	370	350	—	205	—	200	O
				160	540	489	285	255	235	—	F
					230	215	225	359	290	215	Si
						215	230	330	270	215	P
							215	250	215	—	S
								243	220	210	Cl
									190	180	Br
										150	I

Multiple Bonds

C=C, 611	C=N, 615	C=O, 741	N=N, 418	O=O, 498
C≡C, 837	C≡N, 891	C≡O, 1080	N≡N, 946	

The bond energy units in the above table are kilojoules per mole.

As an example, consider the reaction of chlorine with methane to produce dichloromethane and hydrogen chloride:

$$CH_4(g) + 2\ Cl_2(g) \rightarrow CH_2Cl_2(g) + 2\ HCl(g)$$
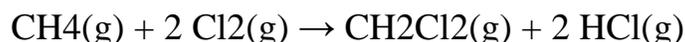
In this reaction, two C–Cl bonds and two H–Cl bonds are broken, and two new C–Cl and H–Cl bonds are formed.

The net change associated with the reaction is

$$2(C–H) + 2(Cl–Cl) – 2(C–Cl) – 2(H–Cl) = (830 + 486 – 660 – 864) \text{ kJ}$$

which comes to –208 kJ per mole of methane; this agrees quite well with the observed heat of reaction, which is –202 kJ/mol.

Bond lengths and angles

The length of a chemical bond the distance between the centers of the two bonded atoms (theinternuclear distance.) Bond lengths have traditionally been expressed in Ångstrom units, but picometers are now preferred (1Å = 10-8 cm = 100 pm.) Bond lengths are typically in the range 1-2 Å or

bond	Ave. Length	Ave. Energy/kJ mol^{-1}
H—H	74 pm	432
H—C	109 pm	415
H—N	101	390
H—O	96	460
H—Cl	127	428
H—Br	141	362
C—C	154	345
C=C	133	615
C≡C	120	835
N≡N	110	942
Cl—Cl	199	240
Br—Br	228	190
I—I	267	149

100-200 pm. Even though the bond is vibrating, equilibrium bond lengths can be
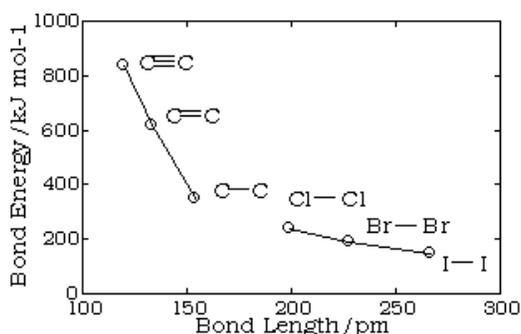
determined experimentally to within ±1 pm.

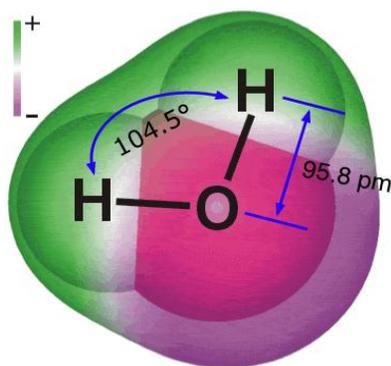Bond lengths depend mainly on the sizes of the atoms, and secondarily on the bond strengths, the stronger bonds tending to be shorter. Bonds involving hydrogen can be quite short; The shortest bond of all, H–H, is only 74 pm.

Multiply-bonded atoms are closer together than singly-bonded ones; this is a major criterion for experimentally determining the multiplicity of a bond. This trend is clearly evident in the above plot which depicts the sequence of carbon-carbon single, double, and triple bonds.

The most common method of measuring bond lengths in solids is by analysis of the diffraction or scattering of X-rays when they pass through the regularly-spaced atoms in the crystal. For gaseous molecules, neutron- or electron-diffraction can also be used.
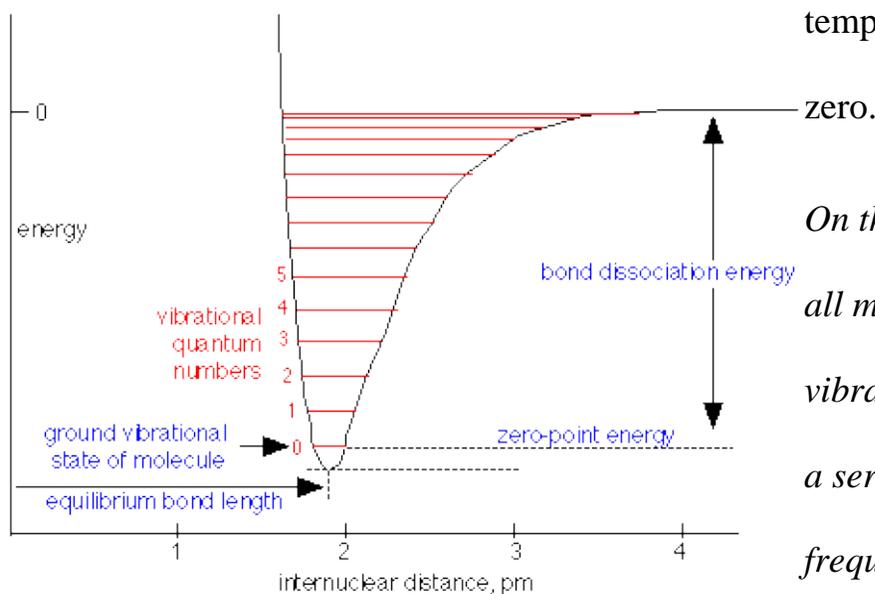

The complete structure of a molecule requires a specification of the coordinates of each of its atoms in three-dimensional space. This data can then be used by computer programs to construct visualizations of the molecule as discussed above. One such visualization of the water molecule, with bond distances and the HOH bond angle superimposed on a space-filling model, is shown here. (It is taken from an excellent reference source on water). The colors show the results of calculations that depict the way in which electron charge is distributed around the three nuclei.

Bond stretching and infrared absorption

When an atom is displaced from its equilibrium position in a molecule, it is subject to a restoring force which increases with the displacement. A spring follows the same law (Hooke's law); a chemical bond is therefore formally similar to a spring that has weights (atoms) attached to its two ends. A mechanical system of this kind possesses a natural vibrational frequency which depends on the masses of the weights and the stiffness of the spring. These vibrations are initiated by the thermal energy of the surroundings; chemically-bonded atoms are never at rest at temperatures above absolute zero.

*On the atomic scale in which all motions are quantized, a vibrating system can possess a series of vibrational frequencies, or states. These are depicted by the horizontal lines in the potential energy curve shown here. Notice that the very bottom of the curve does not correspond to an allowed state because at this point the positions of the atoms are precisely specified, which would violate the uncertainty principle. The lowest-allowed, or ground vibrational state is the one denoted by 0, and it is normally the only state that is significantly*

populated in most molecules at room temperature. In order to jump to a higher state, the molecule must absorb a photon whose energy is equal to the distance between the two states.

For ordinary chemical bonds, the energy differences between these natural vibrational frequencies correspond to those of infrared light. Each wavelength of infrared light that excites the vibrational motion of a particular bond will be absorbed by the molecule. In general, the stronger the bond and the lighter the atoms it connects, the higher will be its natural stretching frequency and the shorter the wavelength of light absorbed by it. Studies on a wide variety of molecules have made it possible to determine the wavelengths absorbed by each kind of bond. By plotting the degree of absorption as a function of wavelength, one obtains the infrared spectrum of the molecule which allows one to "see" what kinds of bonds are present.

Infrared spectrum of alcohol The low points in the plot below indicate the frequencies of infrared light that are absorbed by ethanol (ethyl alcohol), CH_3CH_2OH. Notice how stretching frequencies involving hydrogen are higher, reflecting the smaller mass of that atom. Only the most prominent absorption bands are noted here.
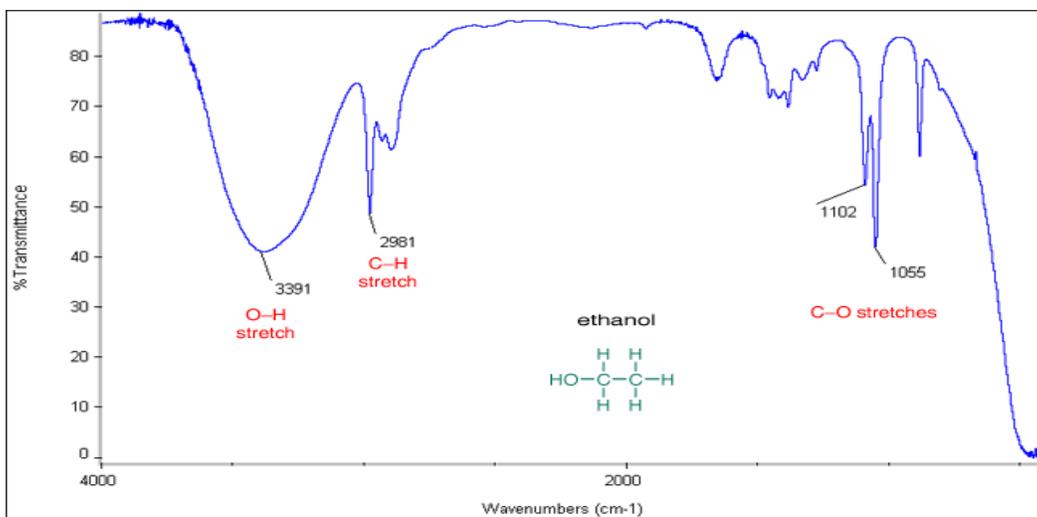
Actual infrared spectra are complicated by the presence of more complex motions (stretches involving more than two atoms, wagging, etc.), and absorption to higher quantum states (overtones), so infrared spectra can become quite complex. This is not necessarily a disadvantage, however, because such spectra can serve as a "fingerprint" that is unique to a particular molecule and can be helpful in identifying it. Largely for this reason, infrared spectrometers are standard equipment in most chemistry laboratories.
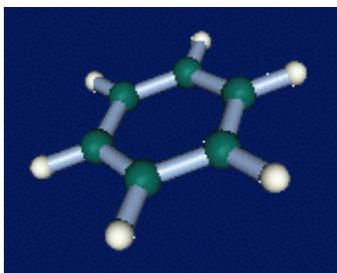

Some vibrational modes of benzene

Infrared absorption and global warming

The aspect of bond stretching and bending frequencies that impacts our lives most directly is the way that some of the gases of the atmosphere absorb infrared light and thus affect the heat balance of the Earth. Owing to their symmetrical shapes, the principal atmospheric components N2 and O2 do not absorb infrared light, but the minor components water vapor and carbon dioxide are strong absorbers, especially in the long-wavelength region of the infrared. Absorption of infrared light by a gas causes its temperature to rise, so any source of infrared light will tend to warm the atmosphere; this phenomenon is known as the greenhouse effect.

The incoming radiation from the Sun (which contains relatively little long-wave infrared light) passes freely through the atmosphere and is absorbed by the Earth's surface, warming it up and causing it to re-emit some of this energy as long-wavelength infrared. Most of the latter is absorbed by the H2O and CO2 , the major greenhouse gas is in the unpolluted atmosphere, effectively trapping the radiation as heat. Thus the atmosphere is heated by the Earth, rather than by direct sunlight. Without the "greenhouse gases" in the atmosphere, the Earth's heat would be radiated away into space, and our planet would be too cold for life.

Radiation balance of the Earth *In order to maintain a constant average temperature, the quantity of radiation (sunlight) absorbed by the surface*

must be exactly balanced by the quantity of long-wavelength infrared

emitted by the surface and atmosphere and radiated back into space.
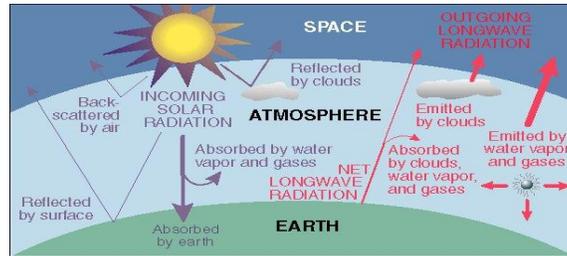
Atmospheric gases that absorb this infrared light (depicted in red on the

right part of this diagram) partially block this emission and become warmer,

raising the Earth's temperature. This diagram is from the U. of Oregon Web

page referenced below.

Since the beginning of the Industrial Revolution in the 19th century, huge quantities of additional greenhouse gases have been accumulating in the atmosphere. Carbon dioxide from fossil fuel combustion has been the principal source, but intensive agriculture also contributes significant quantities of methane (CH_4) and nitrous oxide (N_2O) which are also efficient far-infrared absorbers. The measurable increase in these gases is believed by many to be responsible for the increase in the average temperature of the Earth that has been noted over the past 50 years—a trend that could initiate widespread flooding and other disasters if it continues.