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Some amazing playrooms of chemistry

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Some Amazing Playrooms of Chemistry

Christien Strydom

As often the case with humanity, we get so used to that which is before us, that we forget to appreciate it. I hope to rekindle in my fellow chemists in the audience the awareness of our amazing playing fields and to introduce non-chemists to some wonderful concepts in a chemist's world.

Contents

1. *Chemists' toys*

A chemist's world is made up of atoms, molecules, electrons, bonds, reactions and related matter. To get an idea of what these "toys" are, we start with the theories of Democritus, who lived between 460 and 360 B.C.. He was a philosopher/scientist who theorized that all matter was made of indivisible particles. His theory was based on logical reasoning as philosophers or scientists in his living days believed one could reach the truth by pure logical reasoning.

Democritus

http://chemsite.lsrhs.net/AtomicTheory/democritus.html

Aristotle (384 BC – 322 BC) was also a Greek philosopher, a student of Plato and teacher of Alexander the Great. He wrote on diverse subjects, including physics, metaphysics, poetry, logic, politics, government, ethics, biology and zoology.

Aristotle's theory was that these "indivisible particles" of Democritus consist of four basic elements: Fire, which is hot and dry; Earth, which is cold and dry; Air, which is hot and wet and Water, which is cold and wet! Each of the four earthly elements has its natural place; the earth at the centre of the universe, then water, then air, then fire. When they are out of their natural place they have natural motion towards that place; so bodies sink in water, air bubbles rise up, rain falls, flames rise in the air.

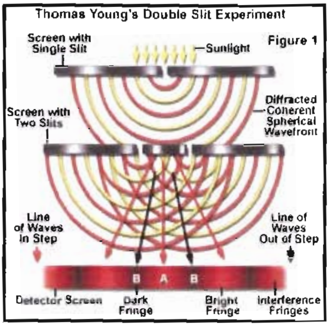
Aristotle

http://en.wikipedia.org/wiki/Aristotle

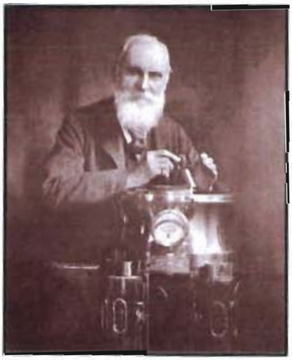
Thomas Young (1773 – 1829), an English physicist, performed experiments to investigate the wave-like nature of light. His double slit experiment to show interference patterns of light became a cornerstone in later theoretical developments of the properties of light and energy. Sunlight is sent through a small hole to obtain a diffracted coherent wave, which is then passed through two small slits. Bright and dark areas show up on a detector screen as constructive and destructive interference occur.

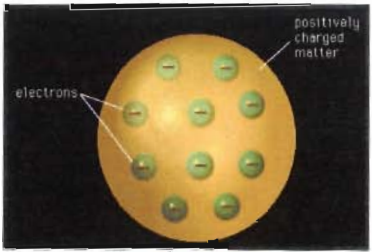

Thomas Young

Thomas Young
http://micro.magnet.fsu.edu/primer/java/interference/doubleslit/index.html



William Thomson (1824 – 1937) envisioned the atom as a sphere with a uniformly distributed positive charge and embedded within it enough electrons to neutralize the positive charge. Later he inherited the title as Lord Kelvin for his work regarding the temperature scale.


Lord Kelvin
http://phys.strath.ac.uk/images/history



Thomson's atomic structure

Ernest Rutherford (1871 – 1937) refined Thomson's model of the atom as a uniformly distributed substance after his famous gold-foil experiments. When only a few of the alpha particles in a beam directed at a gold foil were scattered by large angles after striking the foil, Rutherford knew that *the atom's mass must be concentrated in a tiny, dense nucleus. He thus envisioned an atom to have a small nucleus with most of the mass concentrated in it and much lower mass electrons moving around the nucleus. He received the Nobel Prize for Chemistry in 1908.*

Ernest Rutherford
http://nobelprize.org/nobel_prizes/chemistry/laureates/1908/rutherford-bio.html

From the early 1900's onwards giant steps were made in the development of the theories behind atomic structure, with the likes of brilliant scientists such as Max Planck (1858 – 1947), Albert Einstein (1879 - 1955), Niels Bohr (1885 – 1962), Louis de Broglie (1892 – 1987) and Werner Heisenberg (1901 - 1976) at the forefront. Planck studied black body radiation in 1897 and discovered that at very short wavelengths it did not obey the known laws at that time. In trying to understand this, Planck ran into an "ultraviolet catastrophe". A black body would give off an infinite amount of energy at the ultraviolet end of the spectrum. That was impossible! In what he called "an act of desperation", Planck proposed that, contrary to classical wave theory, matter emits and absorbs radiation in tiny discrete packets or bundles called "quanta" — not continuously, "as should be the case". Initially Planck was not comfortable with this explanation and expected the idea to be disproved. Instead quantum theory, which gained Planck the Nobel Prize for Physics in 1918, was used by Albert Einstein to explain (1905) the photoelectric effect and by Niels Bohr in 1913 to propose a model of the atom with quantified electronic states. Louis de Broglie proposed in his doctoral thesis that not only are waves particles BUT particles are also waves.
http://www.electro-optical.com/bb_rad/mplanck.htm

Max Planck and Einstein

Bohr published a model of the atomic structure in 1913, introducing the theory that electrons travel in orbits around the atom's nucleus, with the outer orbits containing more electrons than the inner ones. An electron can also drop from an outer orbit to an inner one, emitting a discrete amount of energy, called a photon. He received the Nobel Prize for Physics in 1922 for developing the Copenhagen interpretation of quantum mechanics. http://www.internet-encyclopedia..org/ index.php/ Manchester

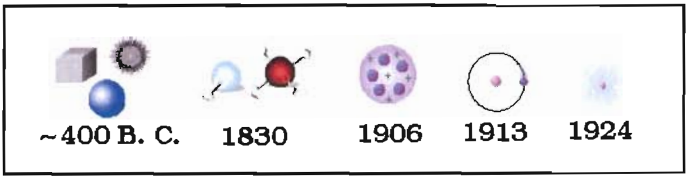
Niels Bohr

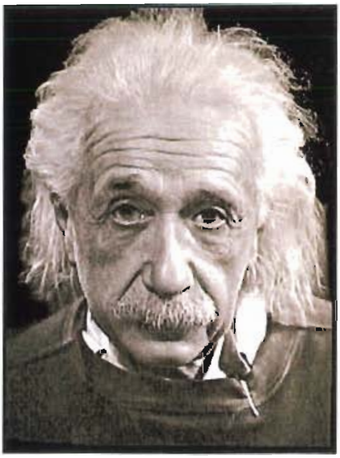
One of Bohr's most famous students was Werner Heisenberg. His uncertainty principle of 1927 states that the determination of both the position and momentum of a particle contains errors, the product of these being not less than a known constant. He received the Nobel Prize for physics in 1932. Nuclear fission was discovered in Germany in 1938. Heisenberg remained in Germany during World War II, working under the Nazi regime, where he was involved in Germany's nuclear weapon program, the extent of which was a subject of controversy in the science community.

Werner Heisenberg

http://www.internet-encyclopedia.org/index.php/Werner_Heisenberg

Schematically the developments thus far can be summarized as in the following figure:



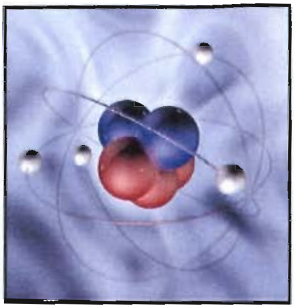


Albert Einstein (1879 - 1955), a physicist and mathematician made major contributions to the development of quantum mechanics, statistical mechanics and cosmology, and is regarded as the most important physicist of the 20th century. In 1921 he received the Nobel Prize for Physics. A unit used in photochemistry was named after him. An einstein is equal to Avogadro's number times the energy of one photon of light. The chemical element Einsteinium is also named in his memory.

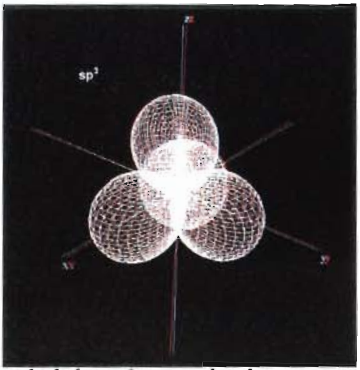
Albert Einstein

http://www.internet-encyclopedia.org/index.php/Albert_Einstein

To understand some of the research that we are involved in, we need to consider the description of an atom in more detail.



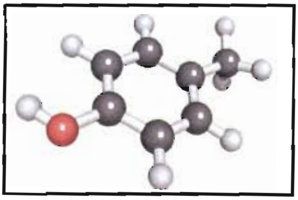
In the nucleus are protons and neutrons, and electrons move around it in specific areas we call orbitals. However, as was indicated, these "orbitals" are not all spherical, but have different shapes in the three dimensional space. Some of these orbitals for a carbon atom are shown in the next figure.



A grain of sand is a thing, but an atom cannot be pictured as a thing. We need to view subatomic particles as tendencies or probabilities to be in a certain area of space. On the subatomic level mass and energy cannot be separated, the one becomes the other. Consider the p-orbitals of a carbon atom. The electron clouds or electron densities are determined as standing waves and present the potential or probability of finding an electron (energy) in a specific space around the nucleus. Electron clouds are mathematical concepts only – it cannot as such be measured – but give us the means of calculating the energy of an electron.

Adrenalin

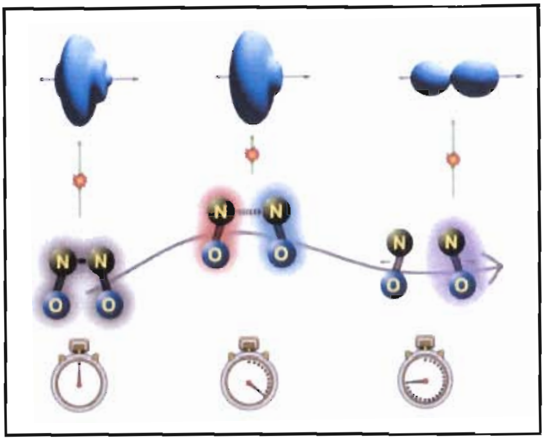
The Uncertainty principle of Heisenberg states that we cannot know both the position and momentum of a particle with absolute precision. The presentation of the chemical adrenalin indicates how we view the three dimensional space occupation of a molecule. To indicate the different atoms and bonds in molecules we usually use the ball-and-stick method as for kresol in the next figure.



Kresol

Chemical reactions occur when bonds break and form. Consider the reaction;

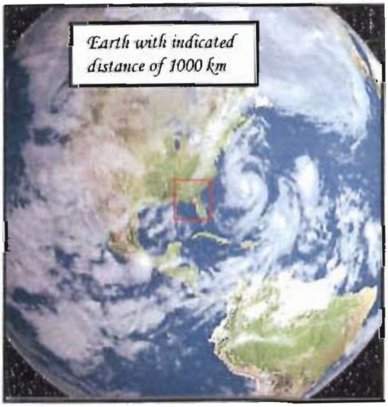
$$N_2O_2\,(g) \rightarrow 2\,NO\,(g)$$



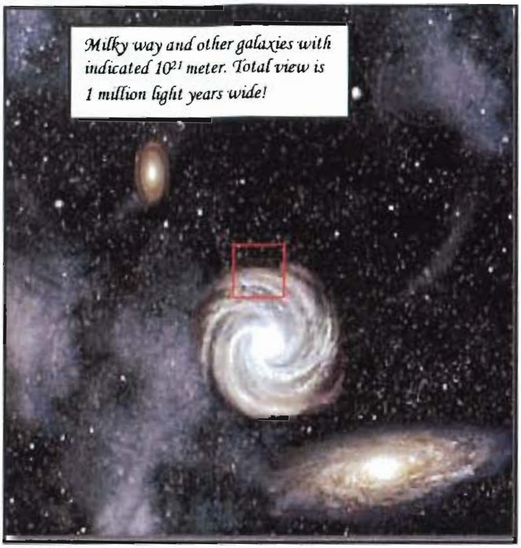
Essentially, a chemist's toys are these molecules. We study how, when, under what conditions, which, how fast or slow, with what implications, etc. these reactions occur. We also use all kinds of tools, instruments, apparatus and laboratories.

2. *Size of chemists' playrooms*

To give an idea of the incredible small particles that are the essence of a chemist's work, we can start out going the opposite direction by considering a leaf and increasing our distance from it in orders of 10. At a distance of 1 (10^0) meter from the leaf we will see a bunch of leaves, at a distance of 10 meter we will see the foilage, at a 100 meter distance a bush and surroundings. Increasing the order to 3, that is 10^3 or 1 kilometer we can jump with a parachute to the leaf, at 10^4 m or 10 km large aircraft carriers travel and cities are visible. From 10^5 m (100 km) large areas or small countries are visible and at 1000 km the typical picture would be that from a satellite. At 10^7 m or 10 000 km, most of the earth will be visible and at a 100 000 km the whole earth as a ball.



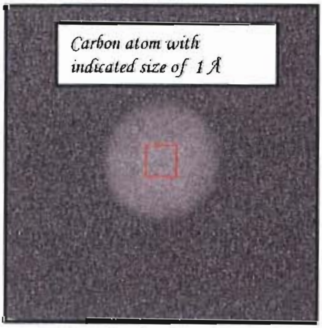
At 1 million km from the leaf, the earth as a small ball with the moon moving around it can be perceived and at 10^{12} m (1 000 million km) the orbits of Mercury, Venus, Mars and Jupiter can also be followed. At a distance of 10^{13} m from the leaf our solar system fits into our view. A distance of 10^{16} m above the leaf relates to *approximately one light year, thus the distance light would travel at its speed of 3 x 10^8 m/s in one year! At this distance the sun would look like a distant lightbulb.*


Milky way and other galaxies with indicated 10^{21} meter. Total view is 1 million light years wide!

From 10^{19} m (1000 light years) the milky way fills our view and at 10^{22} m or a million light years, galaxies appear in our view. 10 million light years from our initial perceived leaf, the galaxies appear as small spots in our view and large "empty" spaces meet our eye. And still we can go further, revealing the incredible immensity of the universe.

Returning to our leaf let's start in the same way to travel into the smaller distance domain. Consider again the bunch of leaves at 10^0 m, that is 1 meter. At a distance of 10^{-1} m or 100 cm, the detail on the leaf becomes visible, at 10^{-2} m or 10 cm, structures are even clearer and at 10^{-3} m or 1 cm, cellular structures fill our view. At 10^{-4} m the cellular structures can be differentiated from one another, even more so at 10^5 m and 10^6 m or 1 micometer, where the nucleus inside the cells may be perceived.

Chromosomes become visible at 10^{-7} m, DNA at 10^{-8} m and at 10^{-9} m or 10 Angstrom large blocks of molecules are seen. Finally we have reached the realm of chemistry! Similar to our view at 10^8 m above the leaf, within a distance of 1 Å (10^{-10} m) an atom such as carbon is perceived with the electrons as a "cloud" around the still invisible nucleus. Carbon atoms form the basis of our living world.


Carbon atom with indicated size of 1 Å

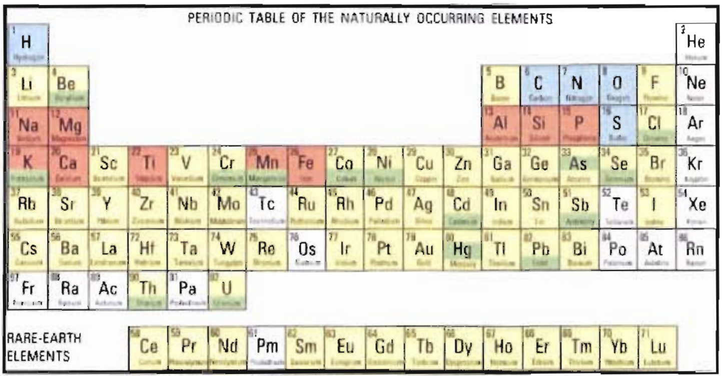
The resemblance between the micro- and micro cosmos is amazing! At 10^{-12} m, we have travelled inside the enormous space between the electrons and the nucleus and the nucleus is perceived as a small ball in the middle, revealing more detail at 10^{-14} m. At 1 femtometer (10^{-15} m) we have travelled into field of scientific imagination as we should observe protons.

3. *My chemical playrooms*

Chemistry is an extremely diverse field including huge industrial set-ups, such as SASOL's coal-to-fuel plants, and small ultra-clean laserchemistry rooms. It gives me pleasure to shortly describe how I entertain myself in these two chemical playrooms.

Coal gasifiaction

Coal is a compact black or dark brown carbonaceous rock consisting of layers of partially decomposed plant and vegetable matter.



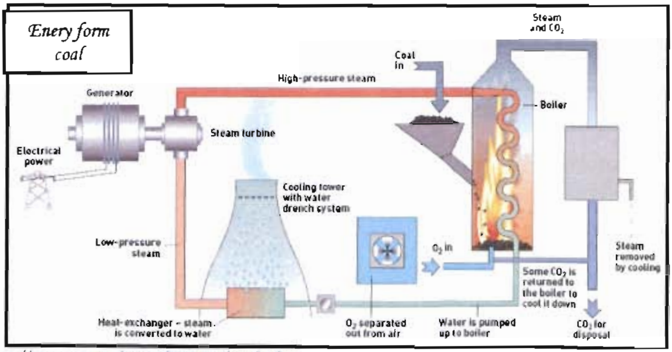
PERIODIC TABLE OF THE NATURALLY OCCURRING ELEMENTS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												
RARE-EARTH ELEMENTS			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	

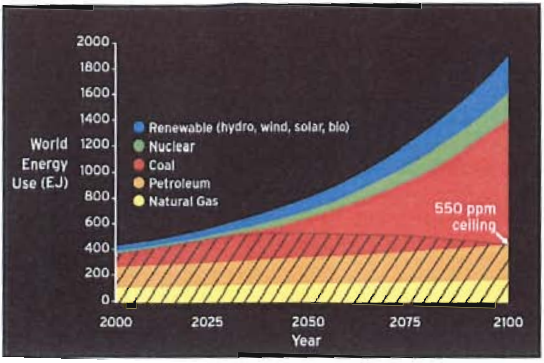
http://pubs.usgs.gov/circ/c1143/html/fig9.html

The 76 elements found in coal are highlighted by colours with regard to their general abundance in coal: blue, major elements (generally more than 1.0 percent present); red, minor elements (generally greater than or equal to 0.01 percent); and yellow, trace elements (generally less than 0.001 percent). Clearly it is a very complex material.

During burning or combustion of coal, energy is released by the reaction between carbon in coal and oxygen. This forms the basis of the energy production processes.



http://www.ntnu.no/gemini/2006-01e/sweden.htm

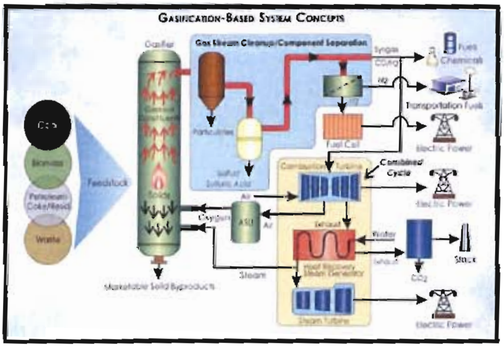


Although extremely important to sustain the world's economy with energy, it is a process during which enormous amounts of "black gold" are burnt away. Predictions are that the use of coal as energy source will increase in the future. www.harvardmagazine.com/lib/06mj/images

SASOL is the world's leader in beneficiation of coal to produce various needed chemical substances. They produce petrol, diesel and other chemicals profitably from coal and natural gas using Fischer-Tropsch synthesis.

Our interest is specifically in what happens during the gasification process of coal. For instance, how does silica, which is a solid at all the operating temperatures, happens to show up in fumes that eventually accumulate outside the reactor?

http://www.beritaiptek.com/zberita-beritaiptek-2007-03-20-Optimalisasi-Pemanfaatan-Batubara-Melalui-Proses-Gasifikasi-(2-Habis).shtml



Our aim is to answer questions such as the following: Can it be that Silica (SiO_2) is reduced to SiO, then oxidized back to SiO_2 in the gas phase, which condenses as soon as it forms? SiO is known to be volatile at the operating temperatures. Tomeczek, J. and Palugniok, H. (2002) Fuel, 81, 1251-1258. *Do the conditions inside the system drive these reactions or are there other species involved? How can we control or reduce the process? These molecules behave as humans – some "like" each other and some not, and sometimes they change their "minds" – especially if the environment gets cold or hot! Our very small playmates certainly can at times entertain us in unpredictable behaviour.*

Femtochemistry

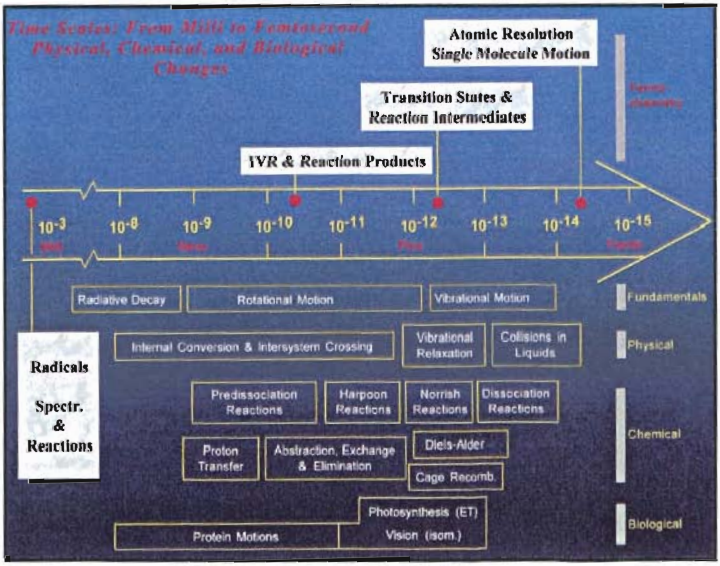
Femtochemistry is in essence a branch of photochemistry, where photons or beams of light are used to investigate or induce reactions. In comparison to activation by means of heat, the fact that light is being absorbed in order to activate a molecule, allows for the selectivity of activation and also the ability to initiate reactions even at low temperatures and in all phases.

To get an idea of the size of this chemical playroom, we consider the size of small molecules and compare that to the "size" of photons or packets of light. Small molecules or the parts of molecules that we would like to use are approximately 2 to 10 Å in diameter. A photon of light travels at the speed of light, 3 x 10^8 m/s or 3 x 10^{18} Å/s. Associating the wavelength of light with the "size" of a photon, the blue light photon has a diameter of approximately 4000 Å. The time it takes a blue light photon to pass a point in space is thus roughly:

$$\boxed{t = \frac{d}{v} = \frac{4000}{3x10^{18}} = 10^{-15} s}$$

An electron moves with a speed of approximately 10^{16} Å/s, thus approximately 10Å in 10^{15} s. This gives the maximum interaction time between a photon and a bond in a molecule as in the order of 10^{-15} s. For us to follow and to control the processes we thus need to be able to work in this extremely small time domain. 10^{16} s is seen as the lower limit of chemical processes. Turro, N.J., Modern Molecular Photochemistry, University Science Books, 1991, p.6

Femtosecond resolution (10^{-15} seconds) is the ultimate achievement for studying the dynamics of chemical bond formation and breakage on an atomic level. The movement and thus dynamic characteristics of nuclei can be followed. The time scales for chemical, physical and biological changes are summarized very well by Ahmed Zewai (1946 -), who recieved the Nobel Prize in 1999 for his studies of the transition states of chemical reactions using femtosecond spectroscopy.



Zewail, A.H., J. Phys. Chem. A,(2000), 104 (24), 5660 -5694

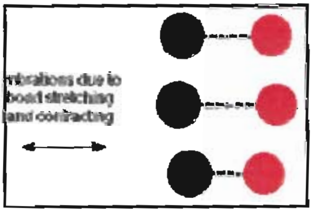
Ahmed H Zewail
http://nobelprize.org/nobel_prizes/chemistry/laureates/1999/

One of the reasons for Zewail's achievements to use a femtosecond laser to study and induce reactions, lies in the incredible short timespans that his research asks for. As described earlier Heisenberg received the Nobel prize for his work regarding the uncertainty in simultaneously determining the position and momentum of a particle, such as an electron. Heisenberg's uncertainty principle states that it is not possible to exactly know the position and energy of an electron. As explained, this is the reason behind using electron clouds to show possible (probable) positions of electrons around a nucleus.

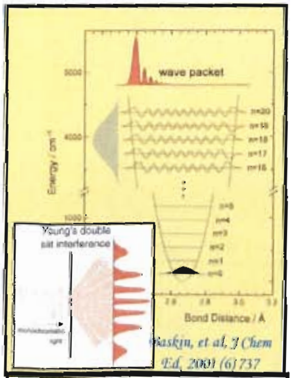
$$\Delta p\Delta x \geq \frac{h}{2\pi}$$

$$\Delta E\Delta t \geq \frac{h}{2\pi}$$

As we would like to measure and influence reactions within femtoseconds, the uncertainty in time measurement is needed to be less than say a femtosecond; thus $\Delta t \approx 10^{-15}$s. The atoms and bonds in molecules vibrate like balls connected with springs and our aim is to activate one of these bonds (springs). A bond absorbs energy by taking up a specific photon of light and starts to stretch further, which may lead to breaking of the bond.
http://www.chemguide.co.uk/analysis/ir/background.html



The energy of a typical vibrational excitation of a single molecule is approximately 10^{-20}- 10^{-19} J. We would like to be able to differentiate between excitations within this energy scale, thus the needed uncertainty in energy is approximately 10^{-20}J. Going back to Heisenberg's uncertainty principle, we calculate the last part of the equation to be 1.0545 x 10^{-34}J s. $\Delta E\Delta t$ is 10^{-35} J s, thus too small and we will thus not be able to make accurate time and energy measurements! Zewail solved this problem by introducing "coherent activation". Zewail, A.H, J. Phys. Chem. A , 2000, 104 (24) 5660 – 5694.



Haskin, et al, J Chem Ed, 2001 (6) 737

Coherent activation of I_2 molecule

Coherence is generally provided by (a) the well-defined initial, equilibrium configuration of the molecules before excitation, (b) the "instantaneous" femtosecond launching and absorption of the packet of energy and (c) by the closely spaced spread of energy levels into which the molecules are activated. Consider the vibtarional energy level 0, for which the energy is exactly defined, thus $\Delta E = 0$ The wave function ($\psi(r,t)$) spreads over the allowed region of space and thus the positions of the vibrating atoms cannot be known. The position probability density, $|\psi(r,t)|^2$, is independent of time as its solution no longer contains the temporal phase part. Thus from Heisenberg's uncertainty principle, the orbitals and thus sizes of molecules in the various vibrational states, will not change with time and can be calculated.

The wave function of a single vibrational state is

$$\psi(r,t) = \psi(r)e^{\frac{-iEt}{h}}$$

Resulting in the position probability density or orbital to be independent of time:

$$|\psi(r,t)|^2 = \psi(r)e^{-\frac{iEt}{h}}\psi^*(r)e^{\frac{iEt}{h}} = |\psi(r)|^2$$

When a simple diatomic molecule such as I_2, that vibrates in a harmonic potential well, is coherently activated into a small spread of higher energy levels (n=16 to n=20 in the figure), the wave function of these combined activated states of the molecules is given by:

$$\psi(r,t) = \sum_i c_i\psi_i(r)e^{-\frac{iEt}{h}}$$

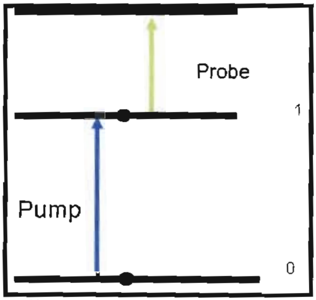
The energies of the various levels are given by the E_i values and the relative distribution between the states by c_i. The position probability denstity (ppd) in this case is given by:

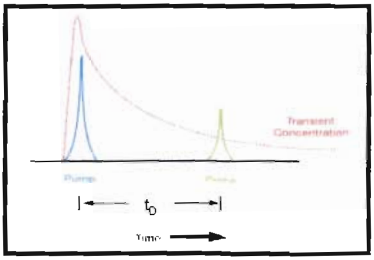
$$\psi(r,t)\psi^*(r,t) = \left[\sum_i c_i\psi_i(r)e^{-\frac{iE_it}{h}}\right]\left[\sum_j c_j\psi_j(r)e^{\frac{iE_jt}{h}}\right]$$

In this case the ppd is no longer time independent and an oscillation between the boundaries of the potential well, thus average distances of the separation of the atoms in the molecules, can be followed as a "wave packet" or energy packet. To get around Heisenberg's uncertainty principle, the introduction of the small spread in energy values of the vibrating molecules allows us to follow the average change in bond distance as the molecules vibrate coherently.

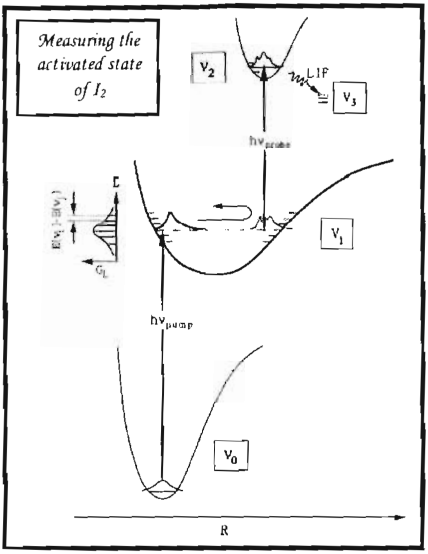
Baskin, J.S. and Zewail, A.H., J. Chem.Ed., (2001) 78 (6) 737 – 751.

To explain how the dynamics of a reaction may be followed we go on to consider the breaking-up of the I_2 molecule. The process is followed using a "pump" femto second pulse to get the molecules coherently into the activated state, the activated state is further activated by a "probe" pulse after different femto second time delay periods to obtain the number of the molecules in the first activated state .

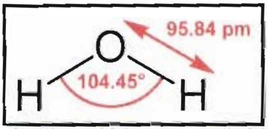




Short pump pulse $\Delta\tau \approx 70$ fs at 670 nm excites the I_2 molecules simultaneously and coherently from the vibrational ground state into several closely spaced vibrational levels in an activated state. A probe pulse promotes the molecules into a higher ion-pair state. Fluorescence from this higher state is monitored as a function of delay time Δt between pump and probe pulses.

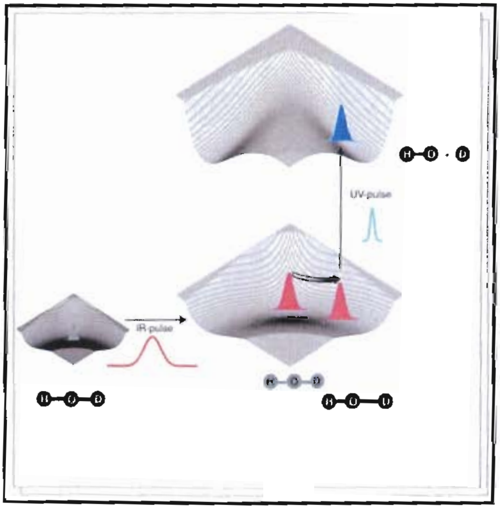

Measuring the activated state of I_2

Using femtochemistry as a tool to synthesize compounds is many a chemists' dream. The means to selectively break and activate bonds is the basis of this effort. We consider as an example the breaking of the HO-D bond in a water molecule where one of the hydrogen atoms is replaced by a deuterium atom.



http://www.globalwarmingart.com/wiki/Image:Water_Molecule_Formula_png

A femtosecond infra red pulse is used to activate only the HO-D bond of the deuterated water molecule into higher vibrational states. The activated bond is broken by a UV pulse that is aimed at the molecules within a few femtoseconds time delay after the first pulse to avoid intramolecular relaxation (IVT). During IVT, the energy of the activated bond is dissipated through the other bonds in the molecule, resulting in the whole molecule to become an activated species. IVT occurs between a few and thousands of femto-seconds after activation, depending on the energetic structure of the molecule. The ability to avoid IVT is one of the major attractions to use femto second energy pulses as a synthesis tool.



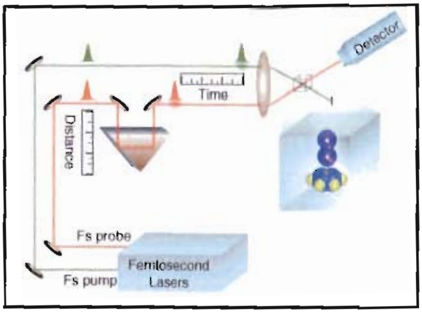
Henriksen, N.E., Chem Soc. Rev., DOI: 10.10139/b100111f

As 21st century electronics is not able to measure within femto seconds, variations in the optical path length of the laser beams are used to obtain time resolution.

Timing is accomplished by generating the pump and probe pulses from a common source and sending either the pump or probe pulse along an adjusted optical path. The path lenght difference relates to the time difference as both pulses move at the constant speed of light:

2.999792 x 10^8 m/s.

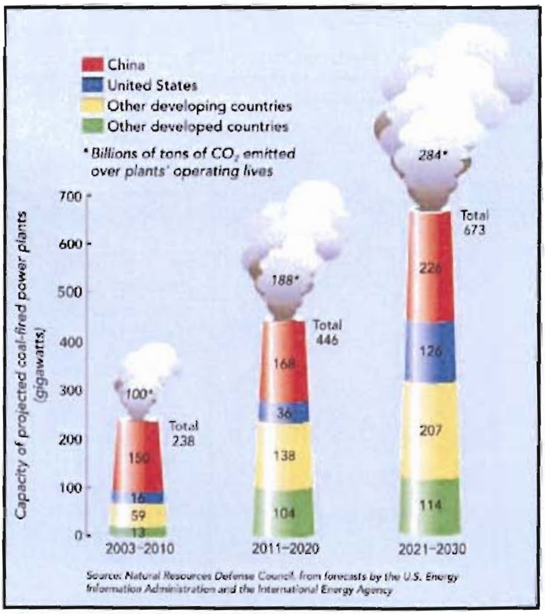
Baskin, J.S. and Zewail, A.H., J. Chem.Ed., (2001) 78 (6) 737 – 751.



This playroom of chemistry is still in its baby shoes, but the future of chemistry and related fields such as pharmacology will surely be influenced greatly by further developments and research..

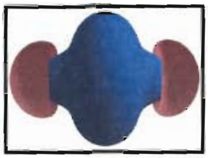
4. Closing Remarks

Choosing to briefly describe two playrooms as diverse as coal chemistry and femtochemistry might seem to be strange, but I have a specific aim in mind. As explained before, the world economy largely depends on coal as a source of energy. The energy producing processes produce large amounts of carbon dioxide, CO_2. All the world's uses of coal account for approximately 40% of the CO_2 emitted into the atmosphere. The included figure shows the projected new coal-fired generating capacity up to 2030. Clearly no decrease in emitted CO_2 is envisioned! Combine this with the astonishing fact that up to 34% of the carbon initially in coal is lost as CO_2! My proposal is that we change our question from how we can get rid of the CO_2 to how we can harvest the carbon from it. With newly developed scientific technologies such as femtochemistry we might be able to contribute in breaking the bonds and then capture the carbon in other beneficial compounds. http:\\www.naturalhistorymag.com/0506/0506_feature.html



Source: Natural Resources Defense Council, from forecasts by the U.S. Energy Information Administration and the International Energy Agency

Very rarely in science do we just stumble upon solutions to problems, we need to ask the questions first. Doing some lateral thinking, especially in the case of the problem of global warming, may lead to suprising developments, such as that we may start to consider the greenhouse gases as valuable resources!



CO_2 *molecule*

To conclude, chemists' playrooms are both immensely small, but within that space incredibly big. A part of the well-known poem by William Blake in his Auguries of Innocence (1780) descibes it beautifully:

> *"To see a World in a Grain of Sand*
> *And a Heaven in a Wild Flower,*
> *Hold infinity in the palm of your hand*
> *And Eternity in an hour."*

Butter, Peter, "Everyman's Poetry: William Blake", J.M. Dent, 1996.

I hope I have made you aware of the amazing science that we are involved in and that in my fellow chemists' I have touched the hearts of real scholars, who are always intrigued by understanding our reality. It is a privilege to spend my days with my chemical playmates!