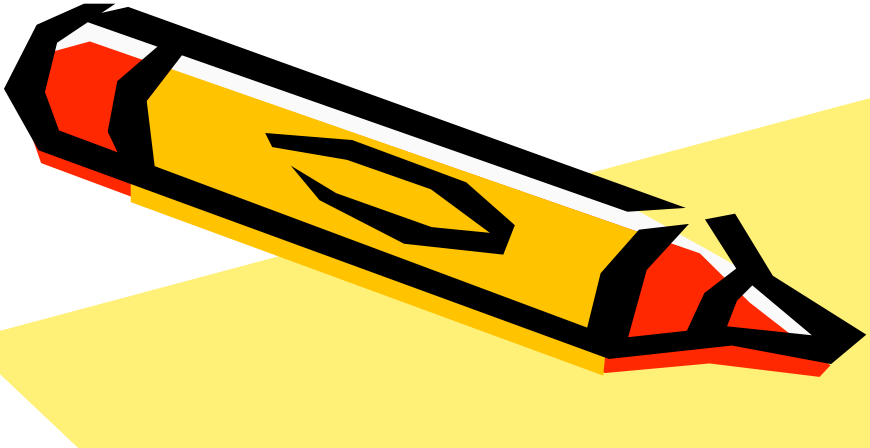

Structure, Function and Measurement

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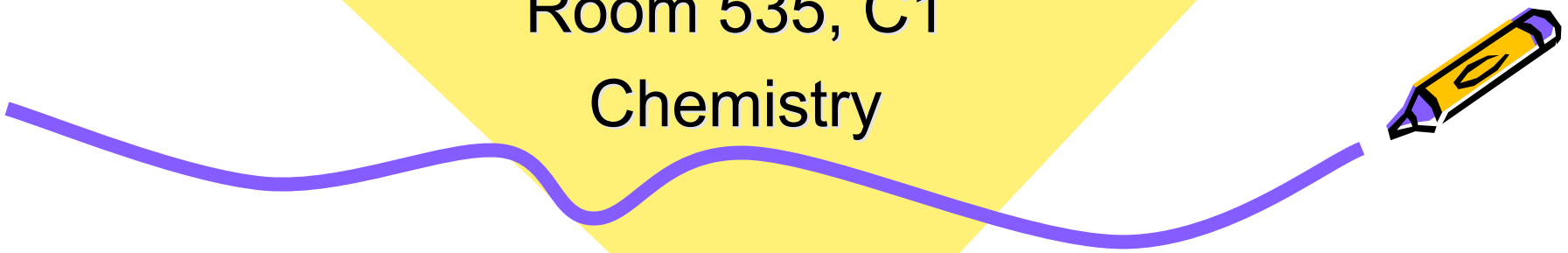
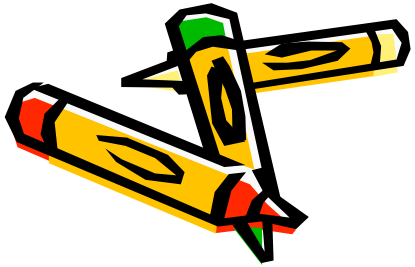
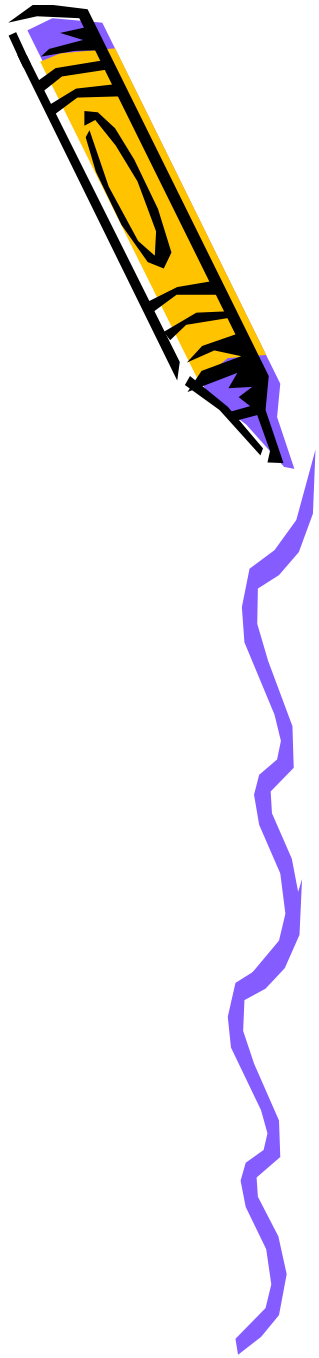


Course synopsis

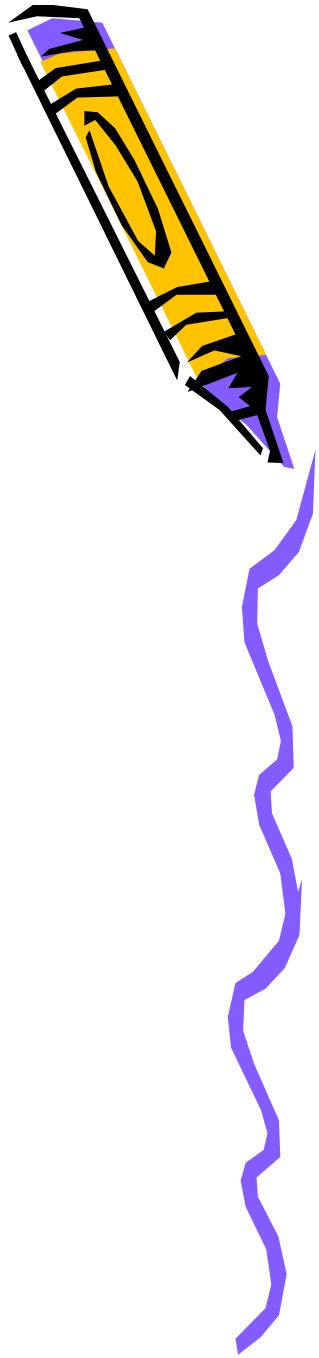
- Determination of molecular structure
  - X-ray and Neutron Diffraction
  - Scanning Tunneling Microscopy
  - Atomic Force Microscopy
  - Spatial and Temporal information

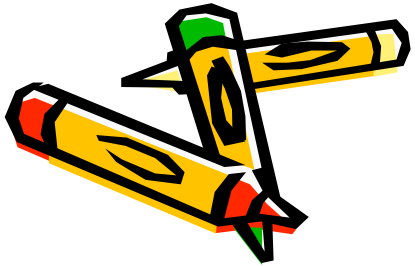




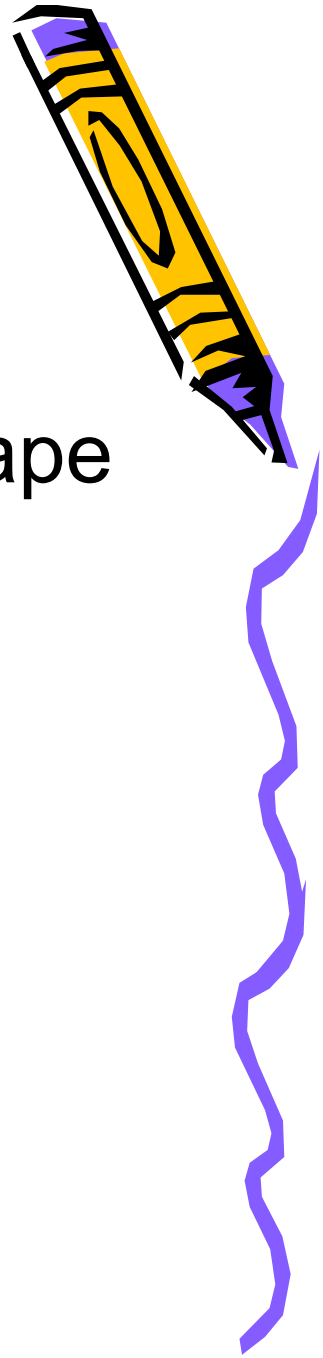
Course synopsis

- Reactivity and Dynamics
  - Laser Spectroscopy
  - Catalysis
    - Atmospheric
    - Enzymatic
  - Molecules in Motion

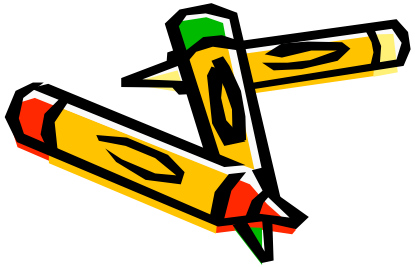




X-Ray and Neutron diffraction

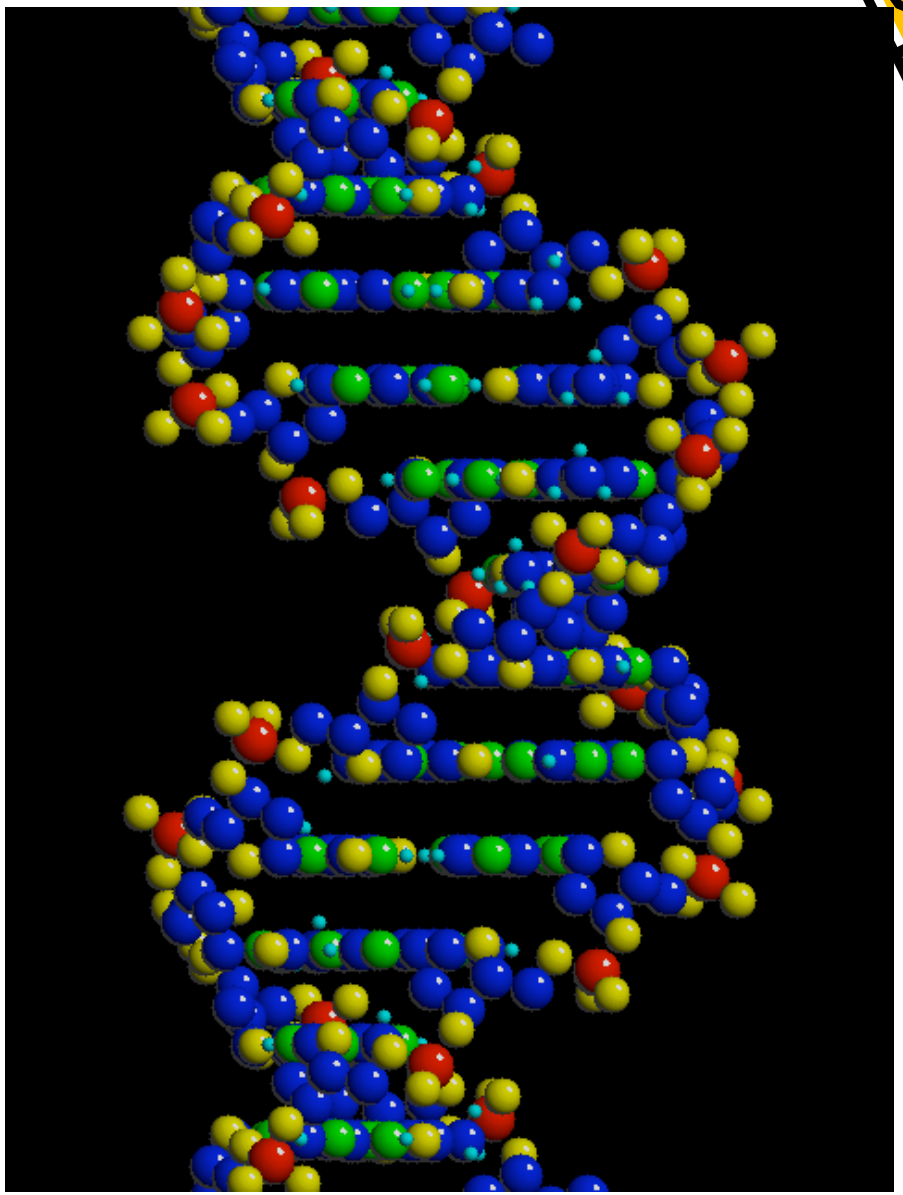


- How do we know the 3 Dimensional shape of molecules?
- Why do we care?
- How does it work?
- What are the limitations?



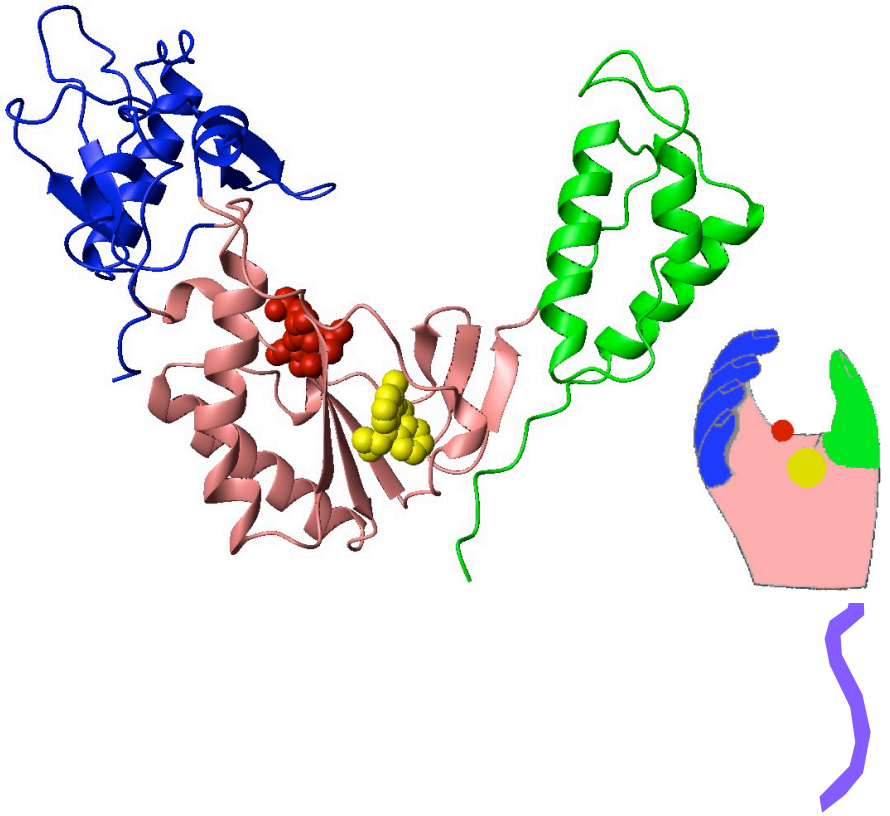
1953 - DNA

- Probably most famous publicly aware use of X-ray crystallography
- Started the explosion in molecular biology

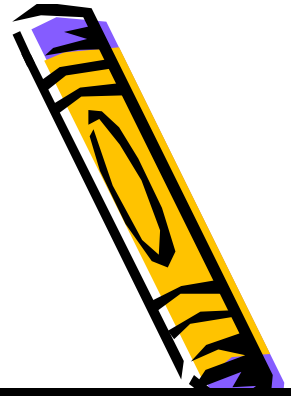


HIV and Drug design

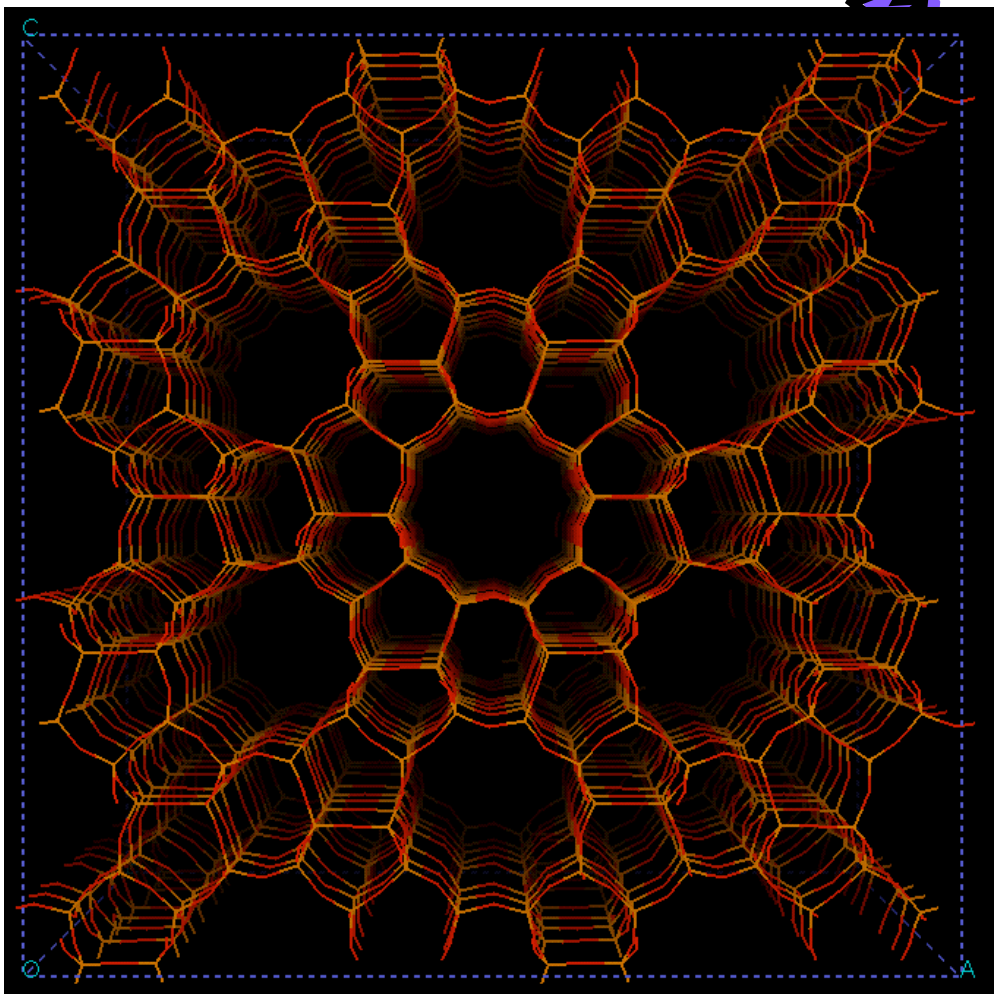
- **A Handy Enzyme** This ribbon representation of the RT active domain illustrates its hand-like structure, showing fingers (blue palm (pink) and thumb (green). The active site (red atoms), where DNA is elongated, is in the palm region. Also shown is an RT-inhibitor drug (yellow) in the pocket where it binds.

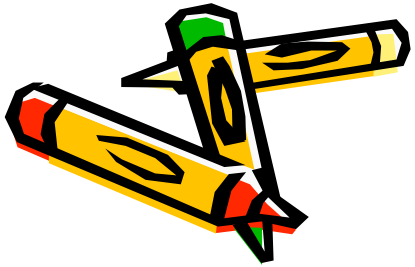


Solids -Zeolites



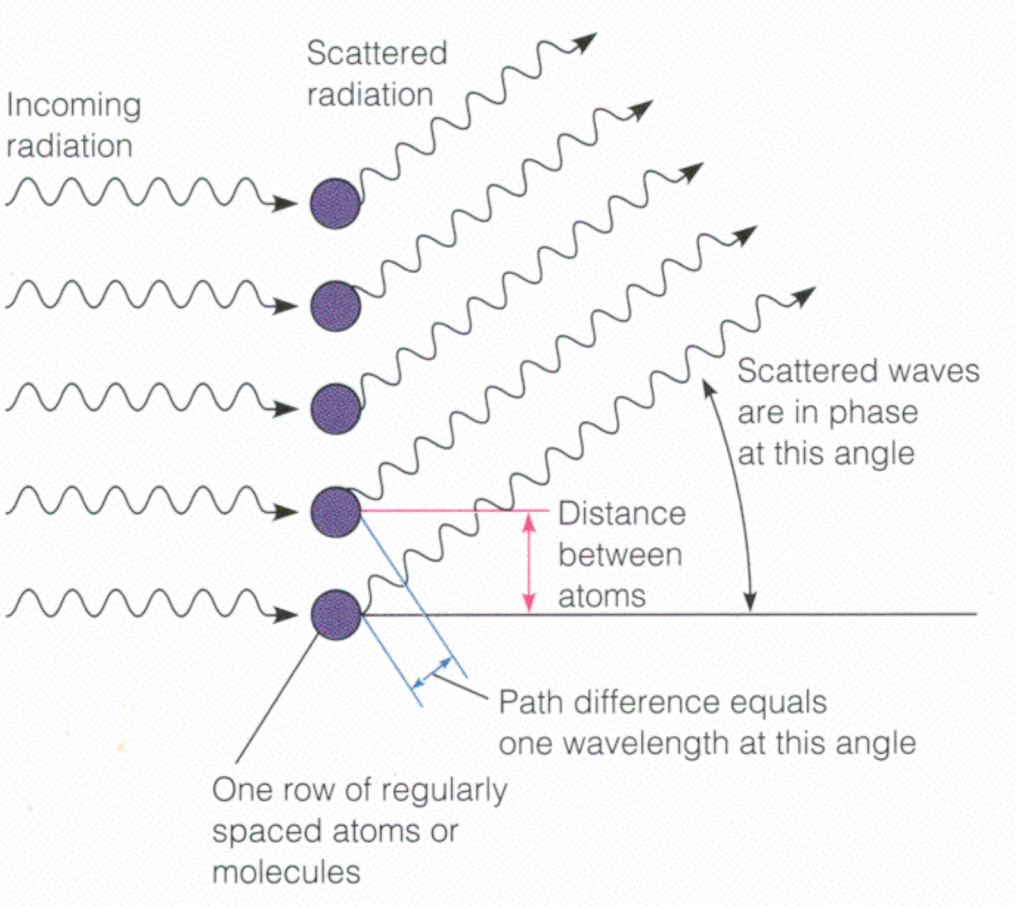
- Not restricted to just biological applications
- Zeolites are important solids used in petrochemical industry
- Knowledge of 3-D shape and dimensions important in “tuning” properties





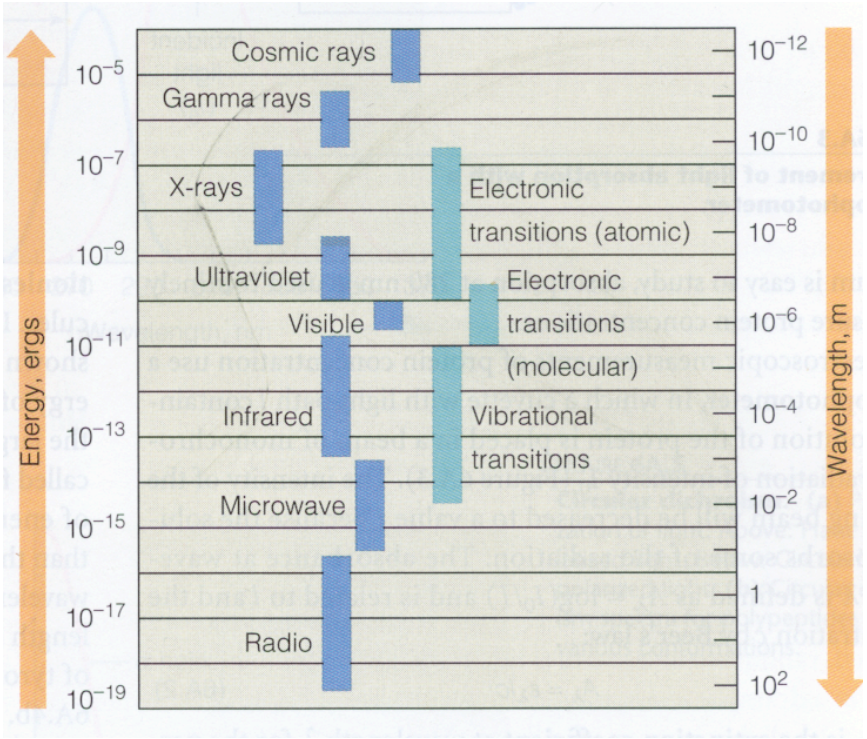
Diffraction

- Radiation passes through a regular, repeating structure, diffraction is observed.
- For diffraction pattern to be sharp, essential that λ of the radiation is shorter than the regular spacing between the elements of the structure



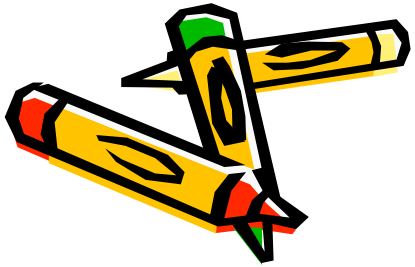
Why X-ray diffraction?

- X-rays are used in studying molecules, for X-rays have λ of only a few tenths of a nanometre.



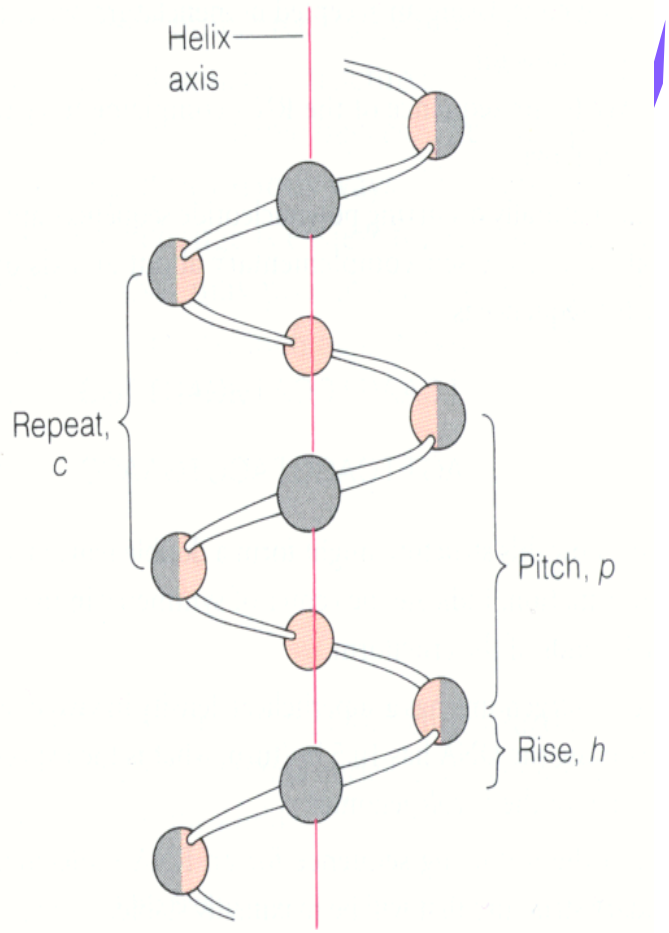
Simple rules

- Short spacings in periodic structure correspond to large spacings in the diffraction pattern
- By determining the relative intensities of different spots we can tell how matter is distributed within each repeat of the structure.



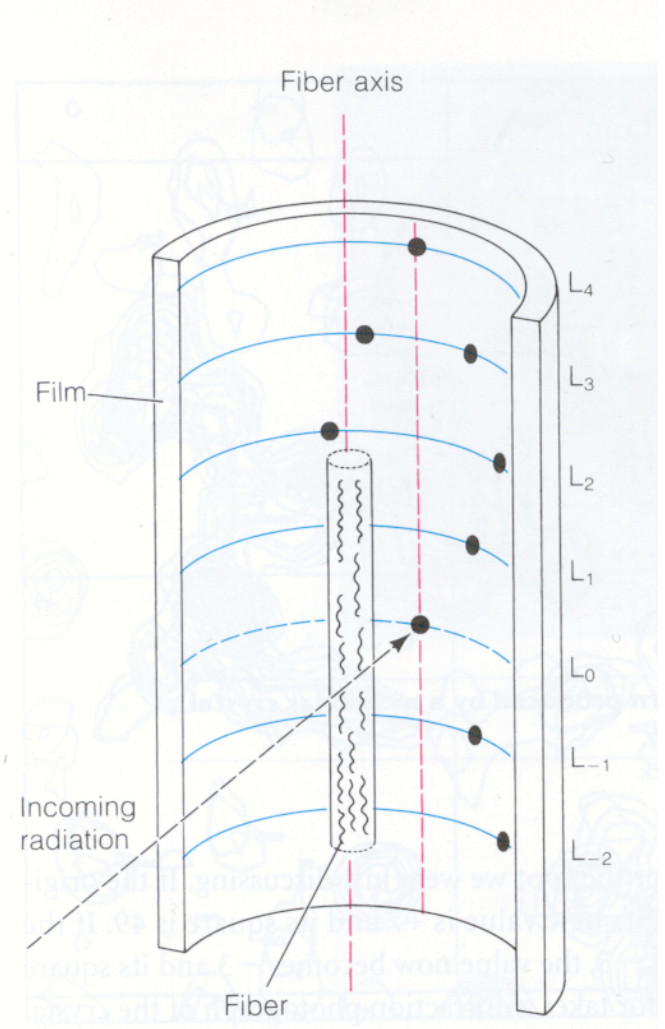
Fibre Diffraction

- Repeat (c) of helix is the distance parallel to axis in which structure exactly repeats itself. Integral number (m) of residues, m=4
- Pitch (p) of helix is distance parallel to helix axis in which helix makes one turn If an integral number of residues per turn, pitch and repeat are equal
- Rise (h) of helix is distance parallel to axis from the level of one residue to the next, so h= c/m.



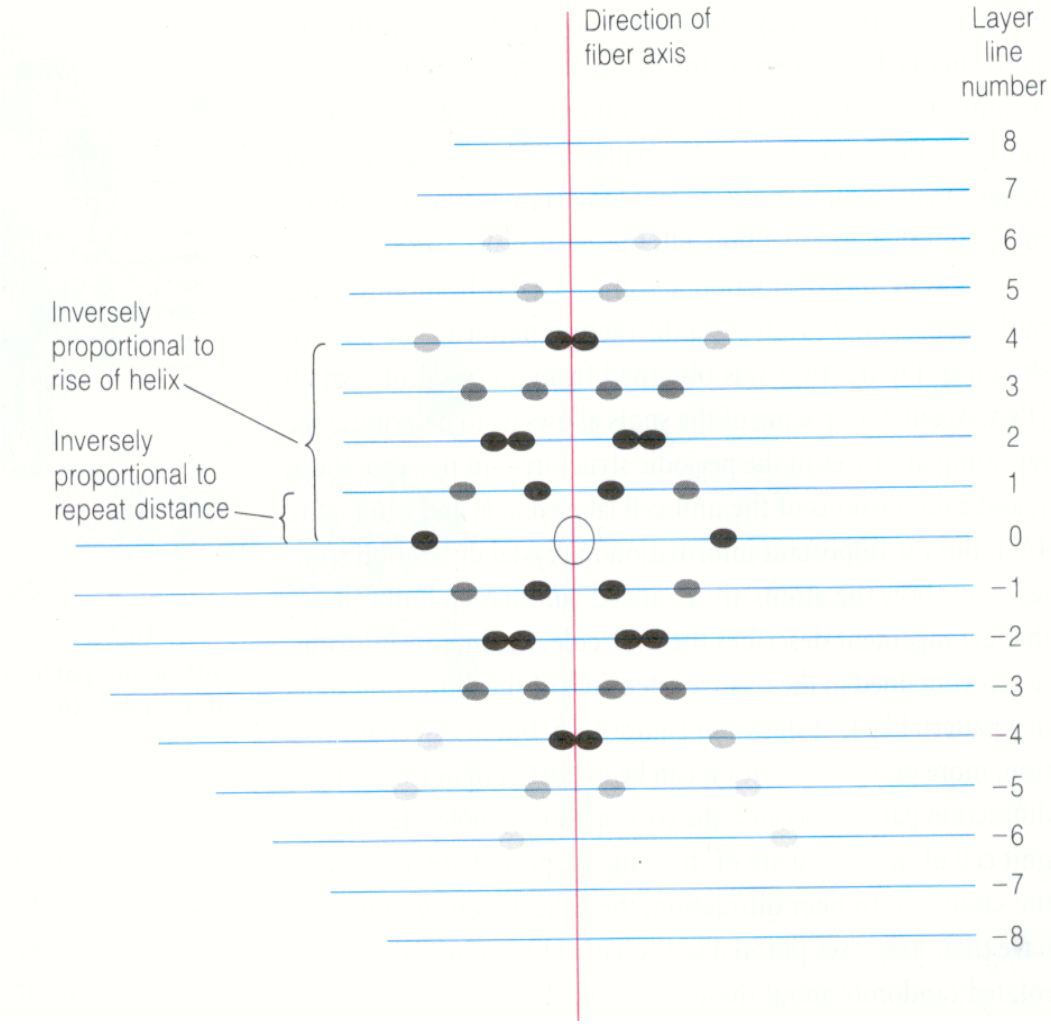
Fibre diffraction

- To investigate a polymer with helical structure a fibre is pulled from a concentrated solution of the polymer. Stretching fibre further produces approximate alignment of the long helical molecules with the fibre axis. Fibre placed in X-ray beam and a photographic film is positioned behind it



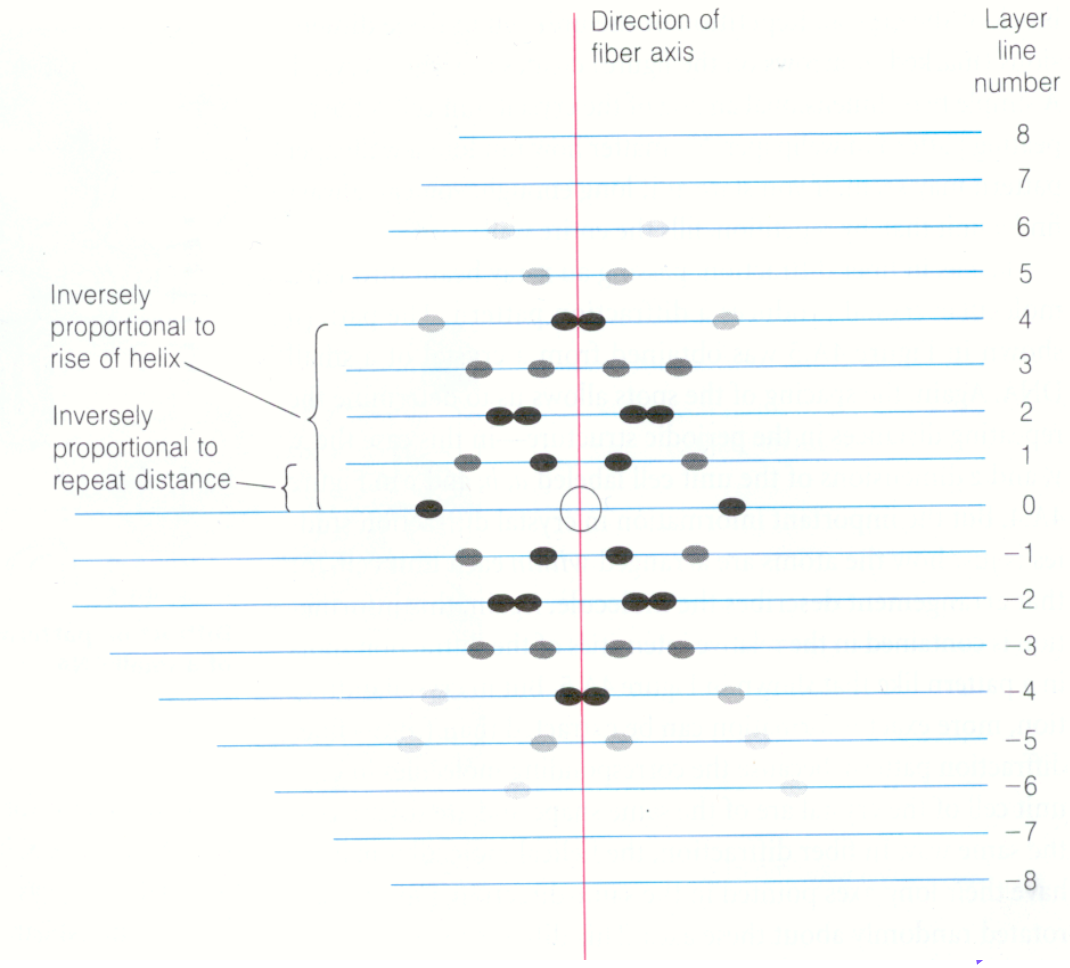
Fibre diffraction

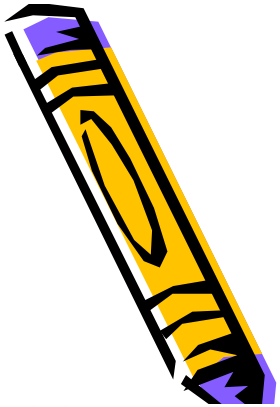
- A helix always gives rise to this kind of cross-shaped pattern. Spots lie on lines perpendicular to fibre axis, **Layer lines**. Spacing between these lines is inversely proportional to the repeat of the helix, c, which in this case equals the pitch.



Fibre diffraction

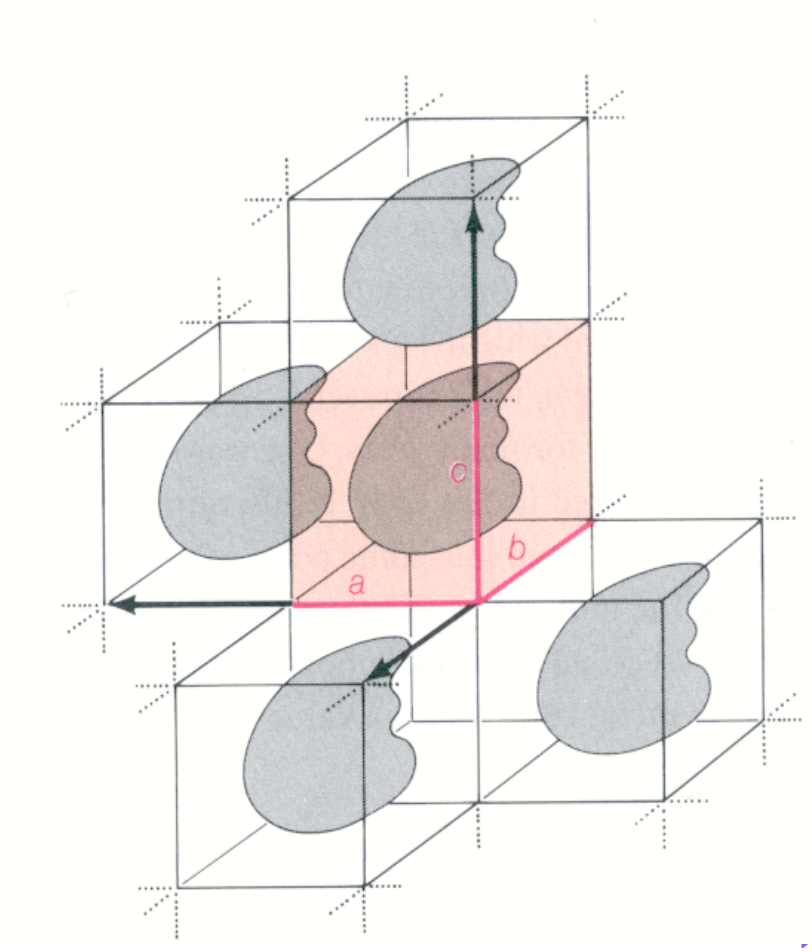
- Cross pattern repeats itself on every fourth layer line. Repetition pattern tells us that there are exactly 4 residues per turn in the helix. Rise in helix is c/4. This evidence told Watson and Crick that B-DNA was a helix with 10 residues per turn

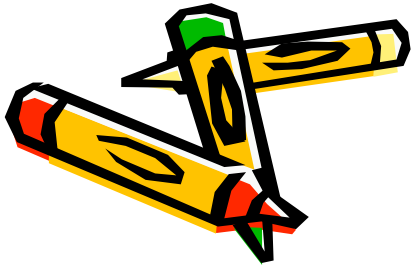




X-ray crystal diffraction

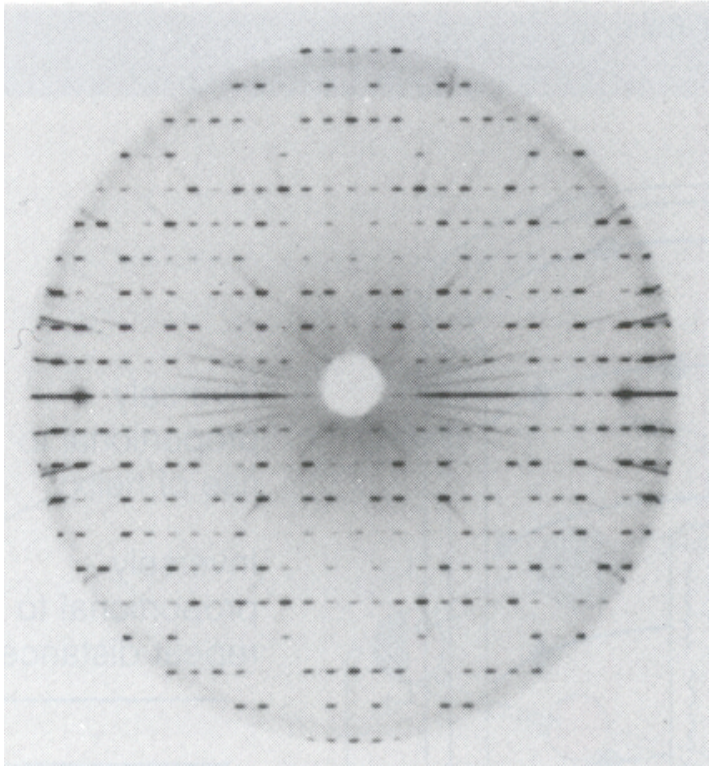
- Repeating unit is now the **unit cell**, which may contain one, two, or more molecules. Unit cell is basic building block of crystal. Repetition of unit cell in 3-D creates whole crystal
- Just as in fibre diffraction, passing an x-ray beam through a molecular crystal produces a diffraction pattern





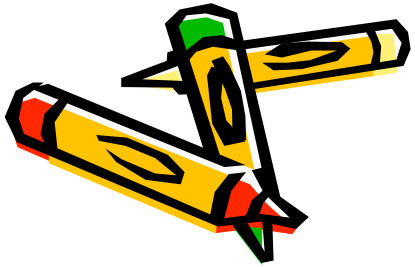
X-ray crystal diffraction

- Pattern shown obtained from a crystal of a small DNA. Spacing of spots allows us to determine repeating distances in periodic structure; important information in crystal diffraction studies is just how the atoms are arranged within each unit cell, for that arrangement describes the molecule. This information is contained in the relative intensities of the diffraction spots in the pattern.

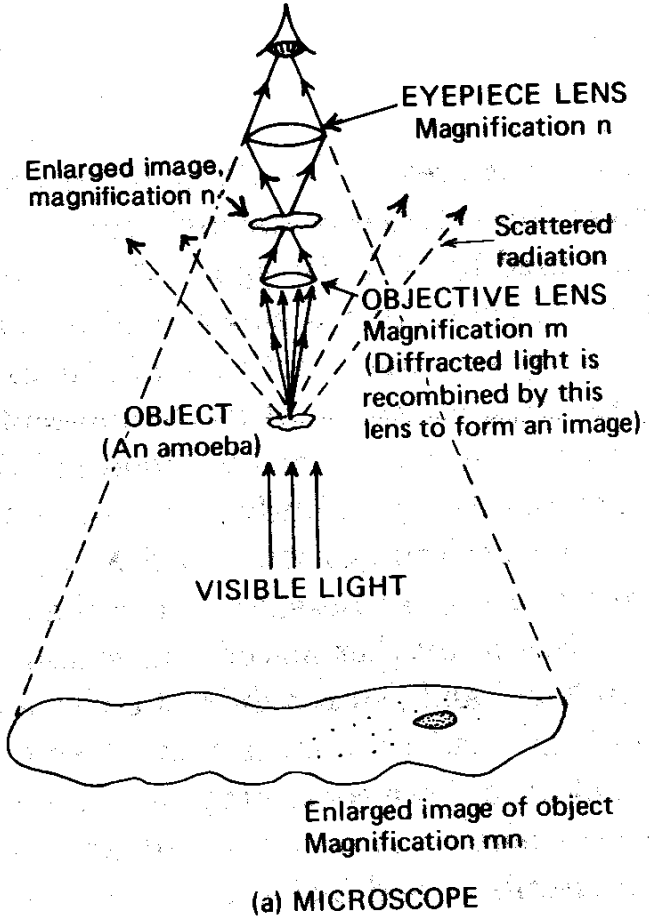


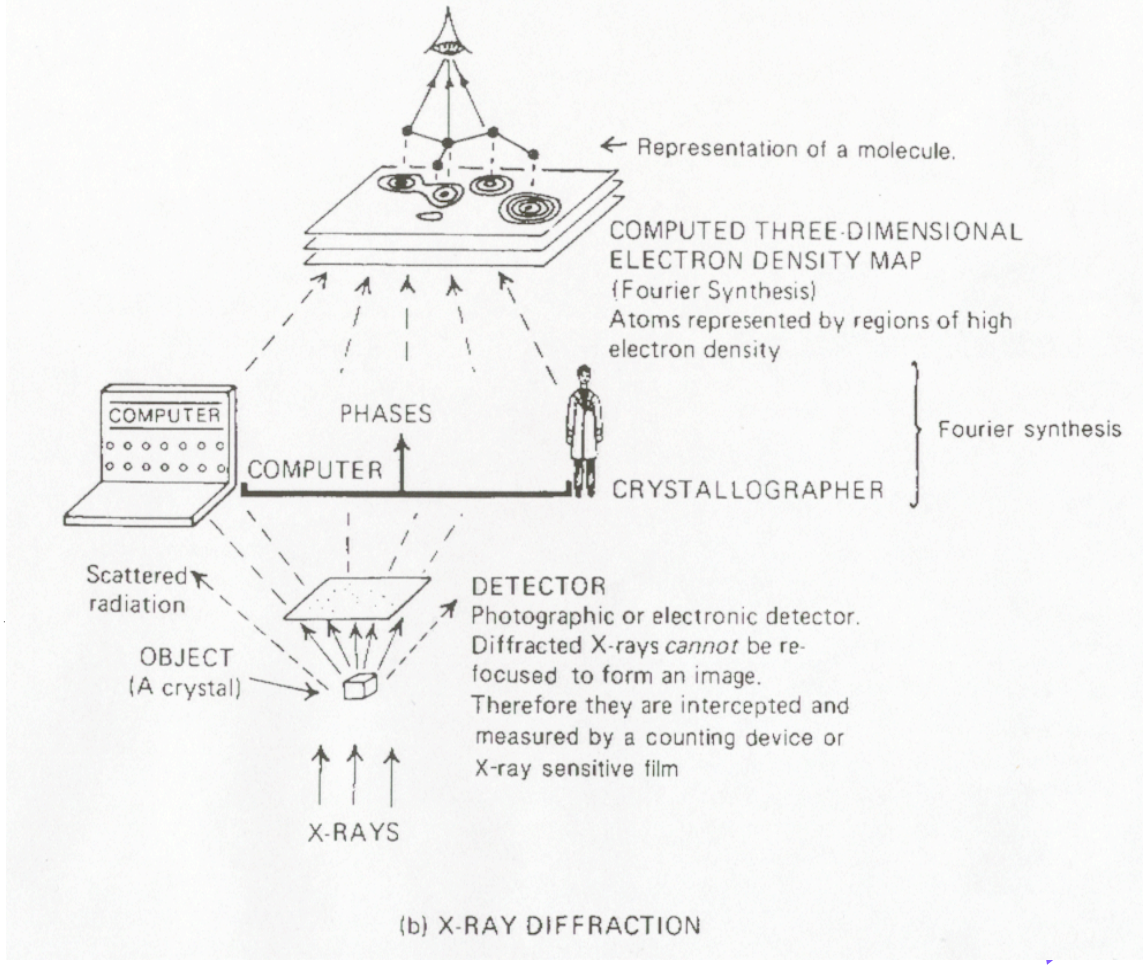
X-ray crystal diffraction

- In X-ray crystal diffraction more exact information can be extracted than from a fibre diffraction pattern, because the corresponding molecules in each unit cell of the crystal are of the same shape and are orientated in the same way. In fibre diffraction, helical molecules may all have their long axes pointed in the same direction, but they are rotated randomly about these axes, this leads to a very less sharp diffraction pattern.



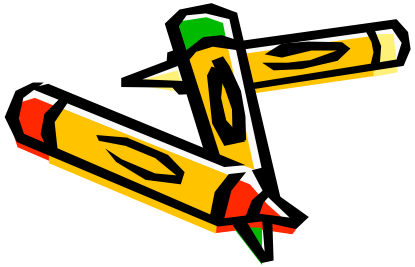
X-ray crystal diffraction
The focusing problem



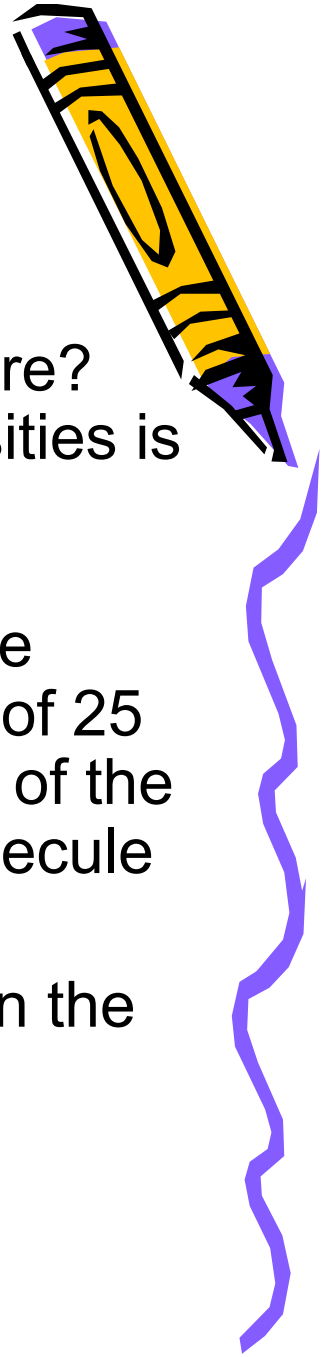


X-ray crystal diffraction
How do we get structures?

- Since we can not focus X-rays, the result of an experiment is a diffraction pattern. We also need to measure the intensities of a large number of the spots to aid in the generation of a structure. For small molecules we can make an educated guess to the structure and calculate the expected intensities and compare them with the observed intensities. The structure is refined until the relative intensities of all spots are correctly predicted. However, this is not a sensible option for large molecules, > 100 atoms



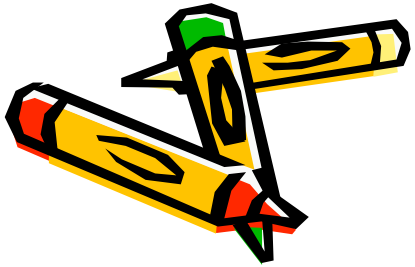
X-ray crystal diffraction
How do we get structures?



- Why not proceed directly from spot intensities to structure? Difficulty is some of information contained in spot intensities is hidden. A gross over simplification is that the **structure factors** that the experimentalist needs to determine the structure are the square roots of the intensities; structure factors are complex numbers in reality. For an intensity of 25 the structure factor can be -5 or +5. This is the essence of the **phase problem**, which prevented progress in large molecule crystallography for many years.
- Introduce a heavy metal atom, e.g. Pt, into some point in the molecule in such a way that molecule and crystal are otherwise unchanged. **Isomorphous Replacement**

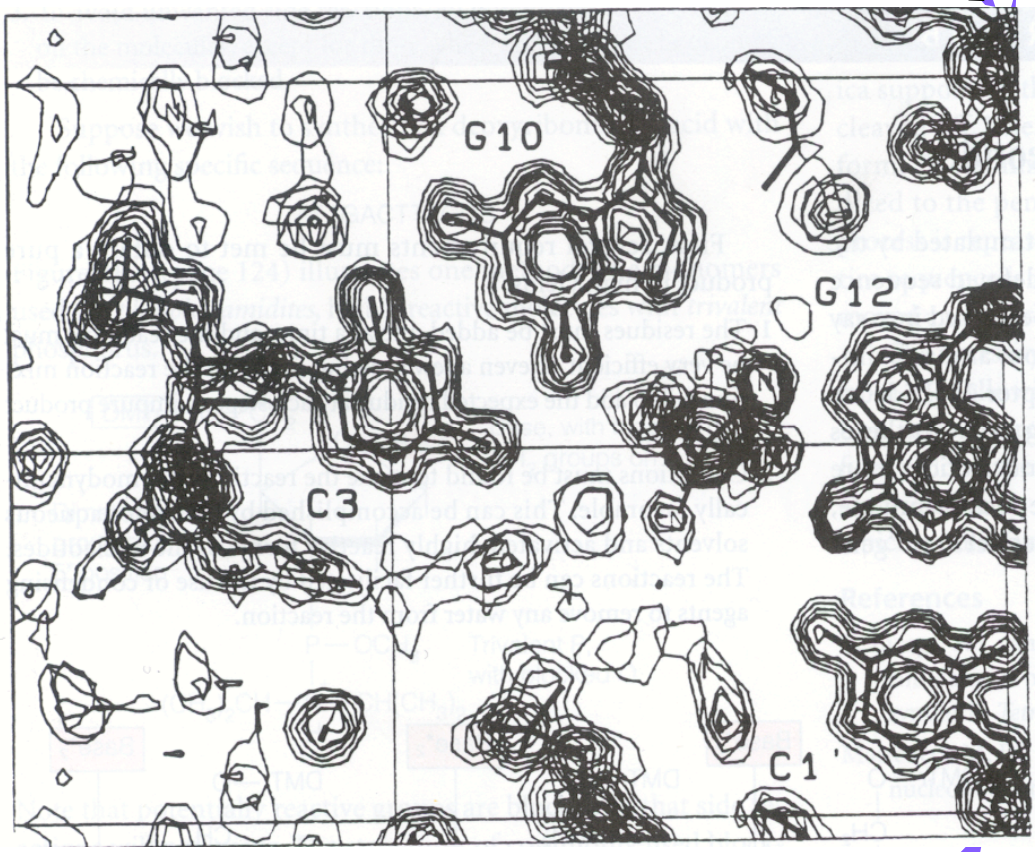
X-ray crystal diffraction Isomorphous Replacement

- Imagine the heavy metal contributes a value of +2 to the structure factor. If the original value was +5, its new value is +7 and its square 49. If original value -5 then new value is -3, and the square +9. Experimentalist takes diffraction pattern of crystal with heavy atom inserted. If new crystal has an intensity of 9 for this spot, the original structure factor must have been -5. Usually, multiple isomorphous replacements are necessary to determine the phases of structure factors.

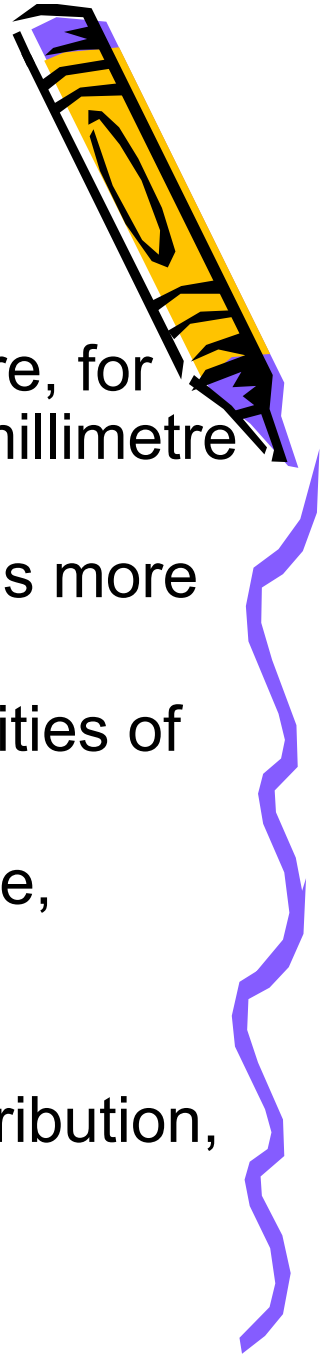


X-ray crystal diffraction
What you really get

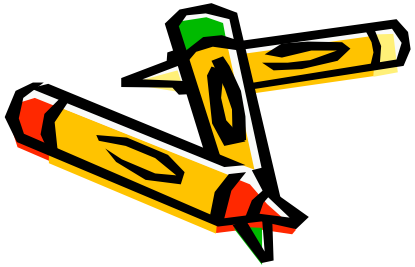
- Given structure factors for all spots, experimentalist can calculate positions of all atoms in unit cell. **Electron density** distribution for regions of high electron density are were atoms are.
- We are looking at 2-D “slice” through 3-D electron density distribution



X-ray crystal diffraction Cookbook

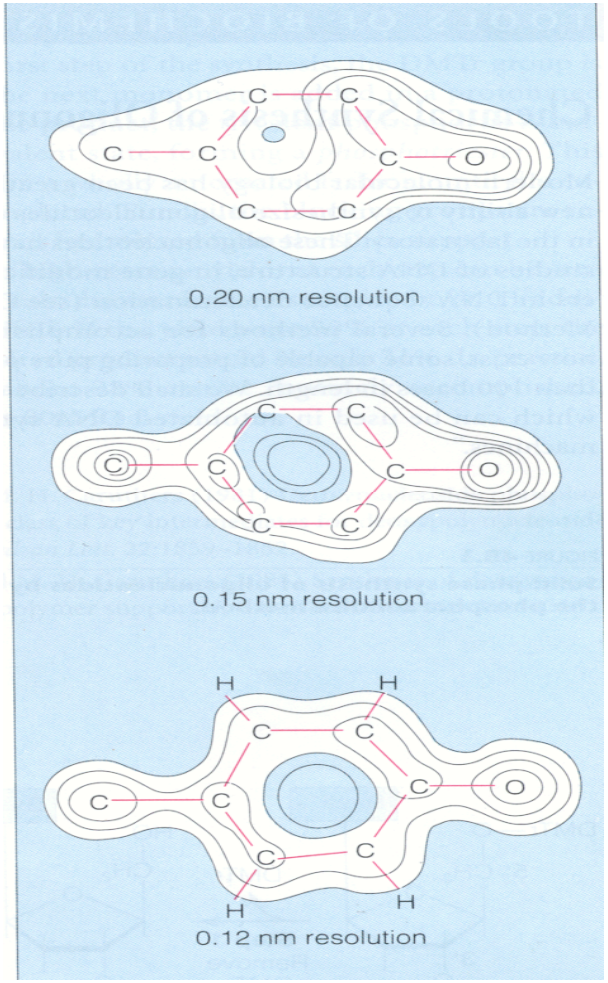


- Obtain satisfactory crystals. Often hardest part of procedure, for crystals must be of good quality and at least a 10ths of a millimetre in minimum dimension. Crystals too small don't give sharp diffraction patterns. Getting macromolecules to crystallise is more magic than science.
- Record diffraction pattern from crystal and measure intensities of many of the spots
- Find a way to make Isomorphous replacements in molecule, usually one or two required
- Repeat steps 1 and 2 for each isomorphous derivative
- Calculate structure factors and hence electron density distribution, requires a reasonably powerful computer



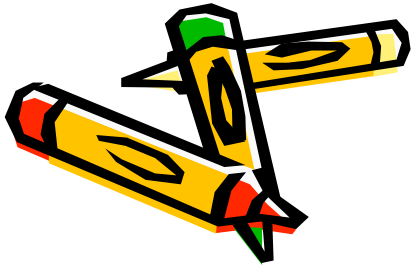
X-ray crystal diffraction Resolution

- **Unit Alert**: Unfortunately it is standard practice in the crystallography world to use a very non-SI unit to measure distance and resolution. The unit in question is the Angstrom, Å, which is 10^{-10} M compared to the Nanometre 10^{-9} M. So you will frequently see/hear people talking about resolution of say 1.2 Å, this level of resolution is not sufficient to uniquely identify Hydrogen atoms in a structure.



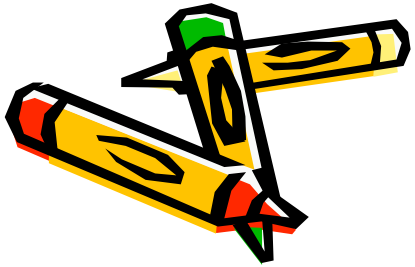
X-ray crystal diffraction Issues and future

- Obvious issue is that you must be able to crystallise your molecule
- Another less obvious is that your crystal must diffract
- Degradation of crystal due to exposure to x-rays, if you have very little of your material this can be a big issue. So need crystals that don't degrade to quickly with exposure to X-rays
- Traditional X-ray diffraction techniques give static pictures and are not useful in studies of dynamics and reactivity.



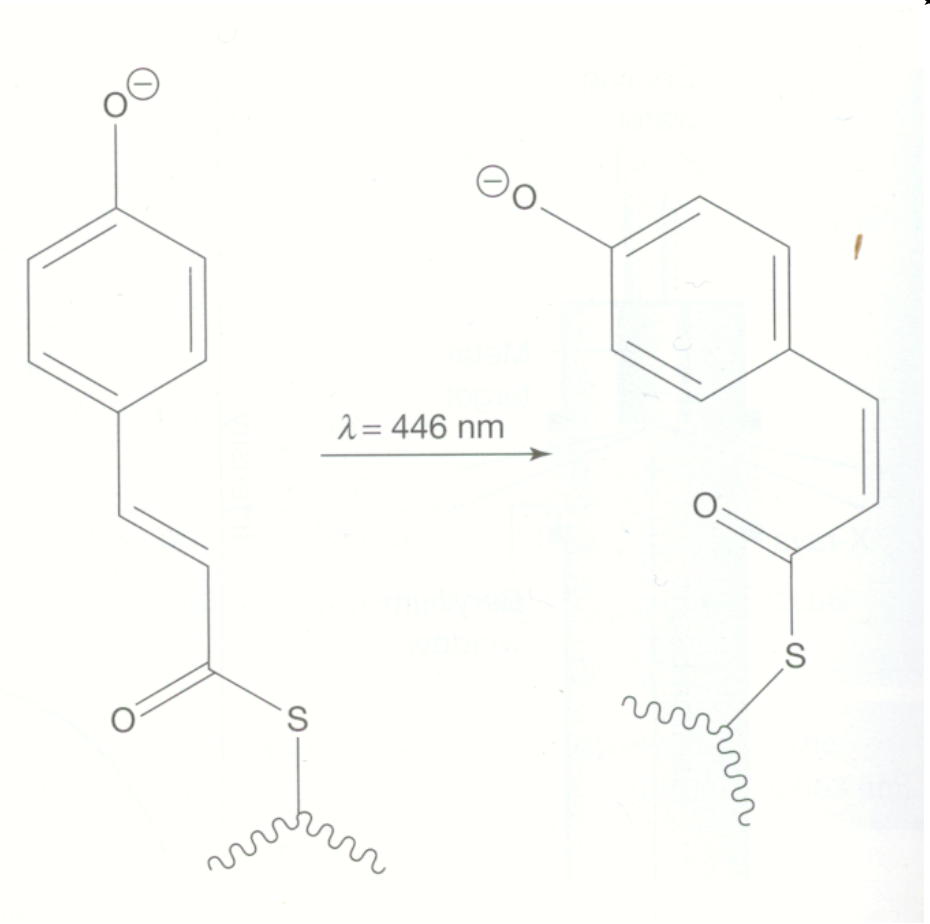
X-ray crystal diffraction
Future

- Special time-resolved X-ray diffraction techniques have become available in recent years and it is now possible to make exquisitely detailed measurements of atomic motions during chemical and biochemical reactions.
- Time resolved X-ray diffraction techniques make use of synchrotron sources, polychromatic pulses of X-ray radiation with pulse widths of 100 to 200ps
- Good diffraction data cannot be obtained from a a single X-ray pulse and several pulses have to be averaged together; this dictates the time resolution of the experiment = tens of microseconds

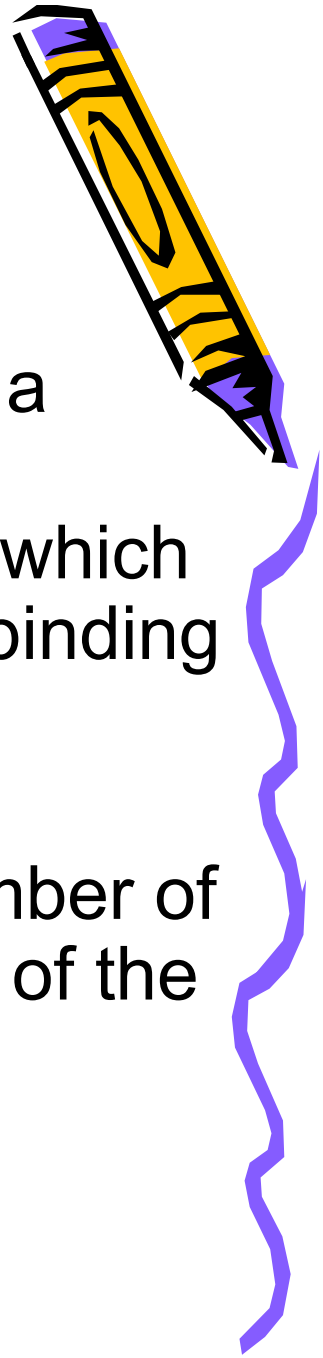


X-ray crystal diffraction
Future

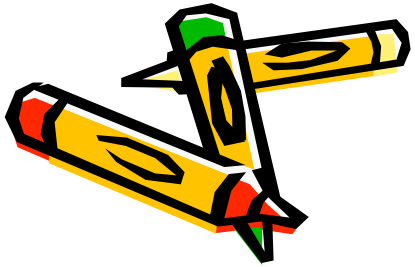
- Recent example of power of time-resolved x-ray crystallography is the elucidation of structural changes that accompany the activation by light of the photoactive yellow protein of the bacterium *Ectothiorhodospira halophilia*.



X-ray crystal diffraction
Future



- Within 1ns after absorption of a photon λ=446nm, a protein bound phenolate ion undergoes trans-cis isomerisation. A series of rearrangements follows which includes the ejection of the chromophore from its binding site deep in the protein
- Time-resolved X-ray diffraction studies in the nanosecond to millisecond ranges identified a number of structural changes that follow electronic excitation of the chromophore with a laser pulse.

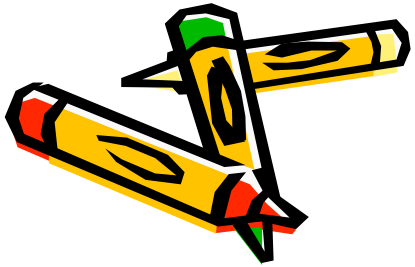


Neutron diffraction

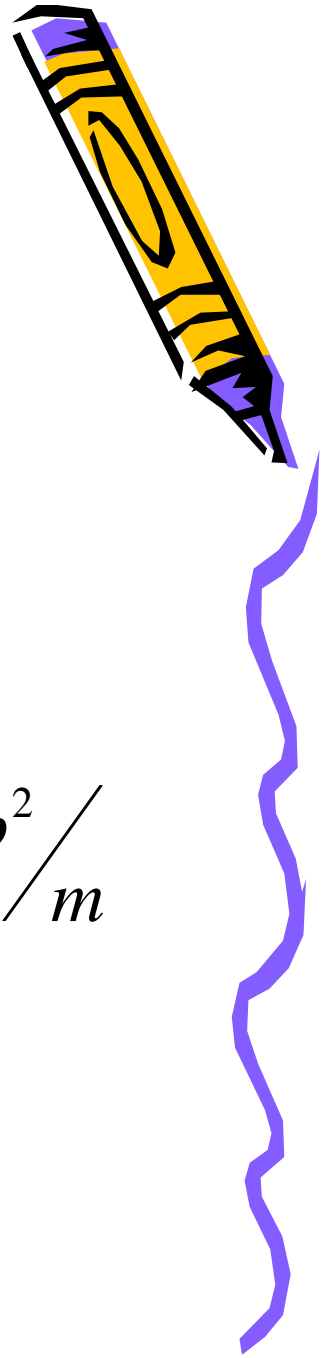
- Neutrons generated in a nuclear reactor and then slowed to thermal velocities have λ's similar to those of x-rays and so can be used for diffraction studies.
- Picture is of the SNS facility at Oak Ridge National Lab, $1.4 billion facility to come online in 2006

Neutron Diffraction

- Neutrons generated in a reactor and slowed to thermal velocities by repeated collisions with a moderator, graphite, until it has a velocity of 4 Km S^{-1} has a λ of about 100pm
- Range of λ's occurs in a neutron beam, but monochromatic beam can be selected by diffraction from a crystal, e.g. single crystal of germanium



Calculating typical λ of thermal neutrons



- Calculate typical λ of neutrons that have temperature of 373K
- de Broglie states $\lambda = h/p$ Also know that translational kinetic energy at temperature T

  $E_k = \frac{1}{2}kT$ The kinetic energy is also equal to p^2/m
- Hence $p = (mkT)^{1/2}$

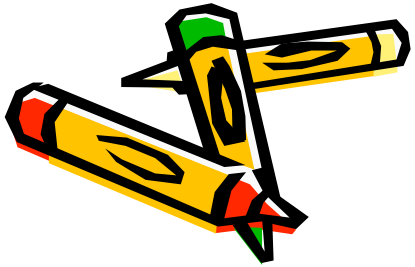
$$\lambda = \frac{h}{(mkT)^{\frac{1}{2}}}$$

At 373K λ = 226pm

Neutron diffraction

- Neutron diffraction differs from X-ray diffraction in 3 main respects.

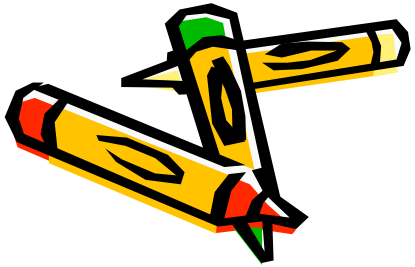
  1) Neutrons pass through extra-nuclear electrons of atoms and interact with then nuclei. Intensity with which neutrons scattered is independent of the number of electrons and neighbouring elements in the periodic table may scatter neutrons with markedly different intensities. Good for distinguishing between say Ni and Co in the same compound.



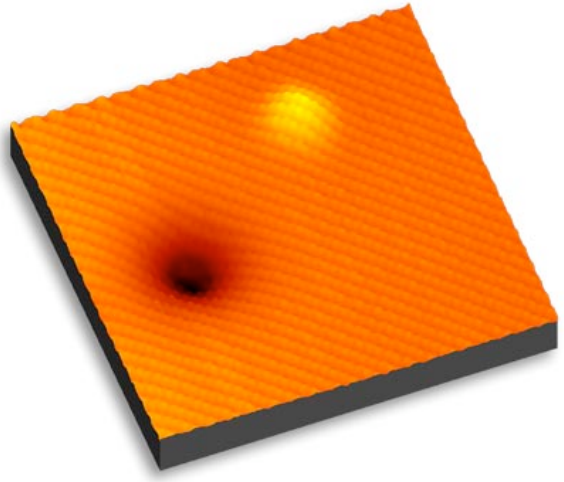
Neutron diffraction

2) Neutrons possess a magnetic moment due to their spin. This magnetic moment can couple to the magnetic fields of atoms or ions in a crystal, ions must have unpaired electrons, and modify diffraction pattern. Neutron diffraction well suited to investigation of magnetically ordered lattices.

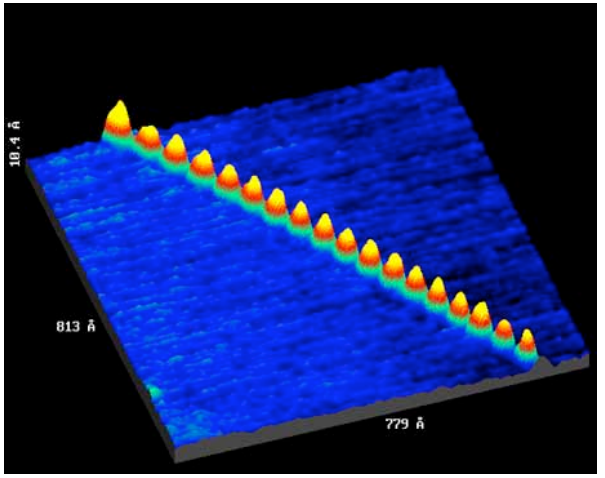
3) Resolution is of the order of <0.1 nm so we can see those all important hydrogen atoms



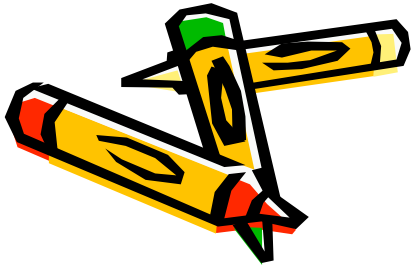
Scanning Tunneling Microscope (STM)



- Ultra High Vacuum (UHV) cleaved GaAs (110) with subsurface Si donor (bright spot) and Ga vacancy (dark spot). 17.3 x 17.7 nm. UHV STM scan.

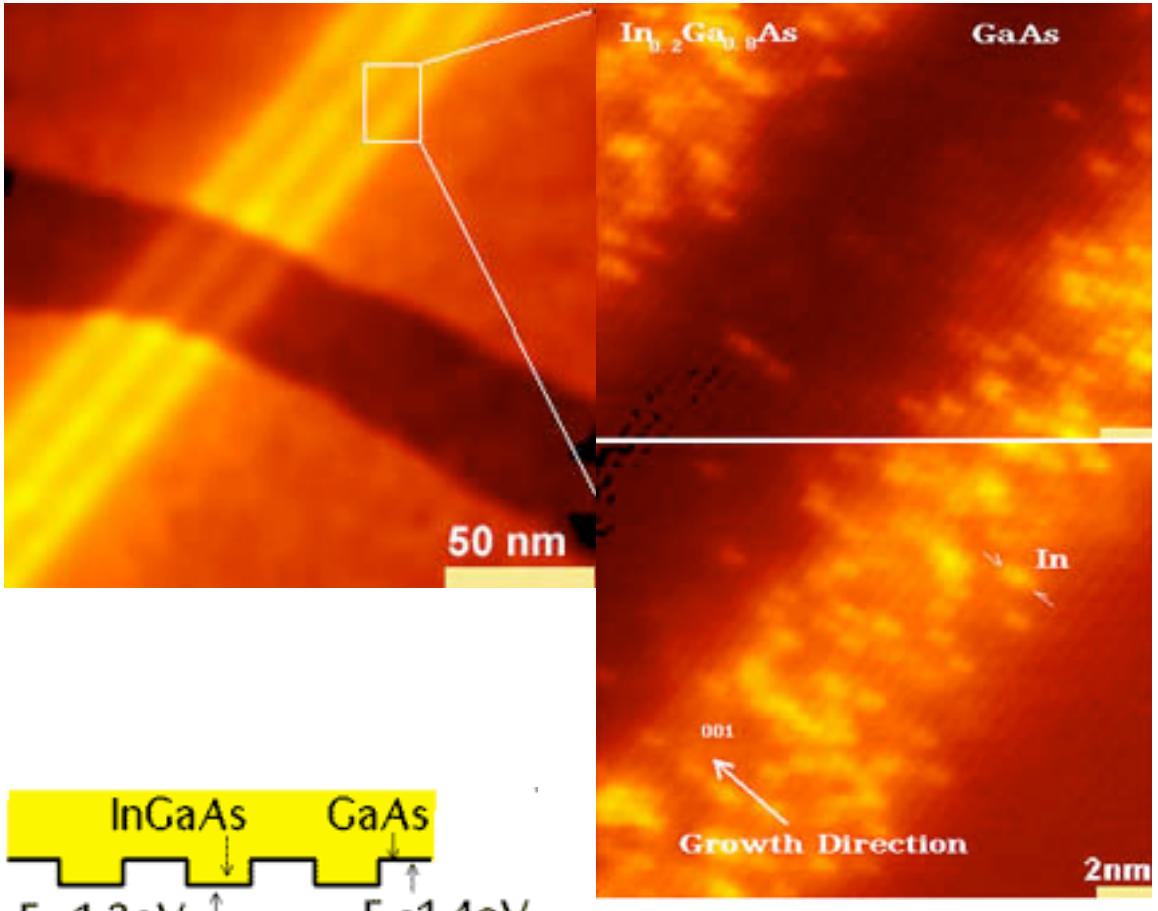


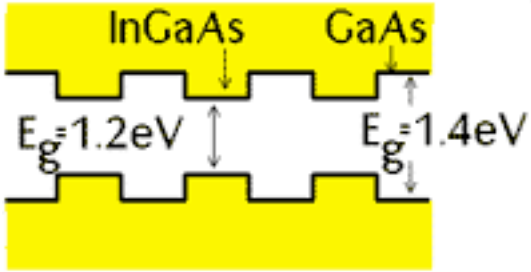
UHV STM image of a polypropylene molecule on graphite acquired at 22 pA



Scanning Tunneling Microscope (STM)

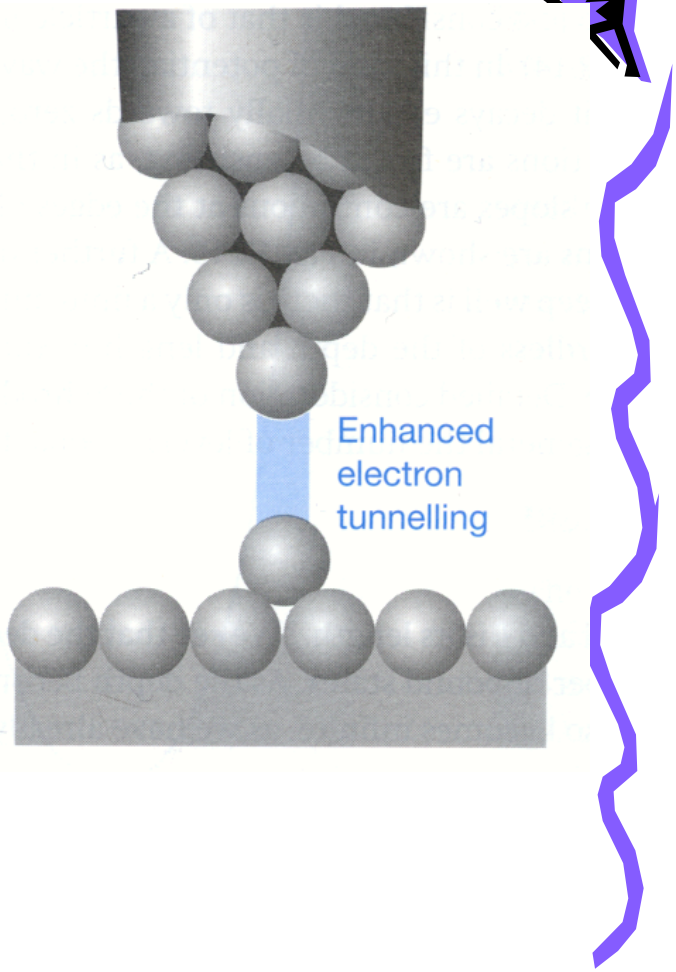
In0.2Ga0.8As / GaAs multi-quantum well structure. InGaAs layers appear brighter than the GaAs layers (right). Within the InGaAs layer the In atoms appear as bright spots (lower right). Also, visible bright spots in the GaAs layer indicate that some Indium migrated into the GaAs layer during growth. Note that the interface between the GaAs and InGaAs layer appears rough on the atomic scale. Closer look reveals that the GaAs on InGaAs interface is rougher than the GaAs on InGaAs interface (growth direction <001> from botton right to to left as indicated).

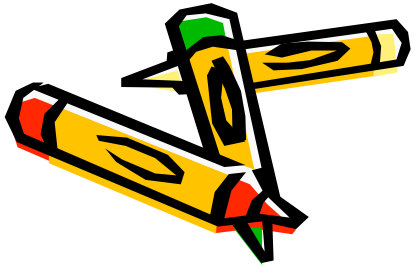




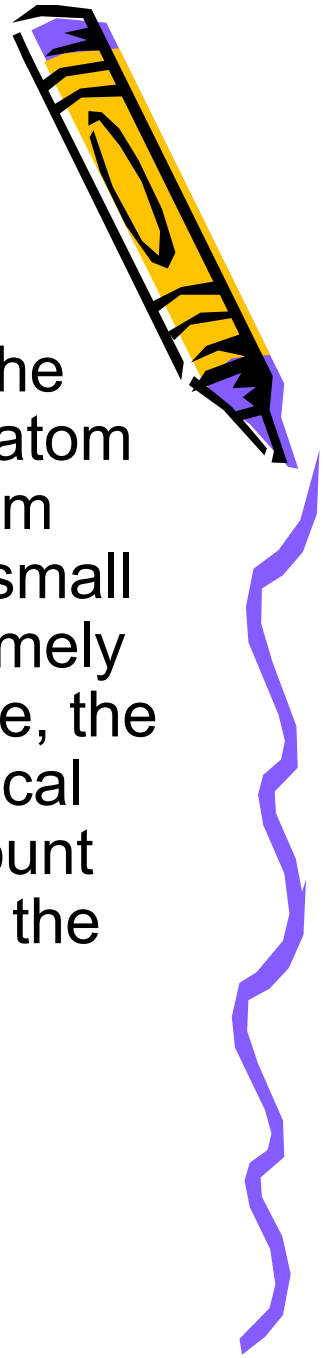
Scanning Tunneling Microscope (STM)

- The basic principle of scanning tunneling microscopy (STM) is based on the tunneling current between a metallic tip, which is sharpened to a single atom point and a conducting material. A small bias voltage (mV to 3 V) is applied between the tip and the sample. If the distance between the tip and the sample is large no current flow. However, when the tip is brought very close (~1 nm) without physical contact, a current (pA to nA) flows across the gap between the tip and the sample.

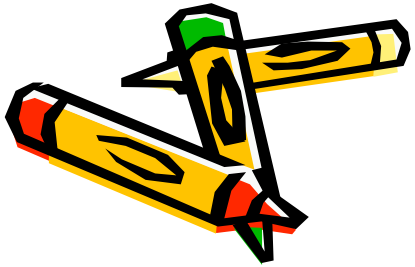




STM

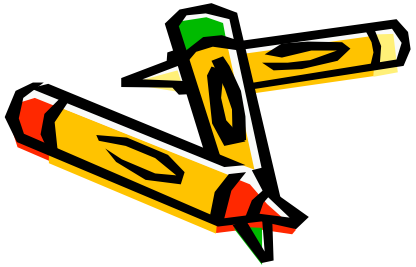


- Such current is known as the tunneling current which is the result of the overlapping wave functions between the tip atom and surface atom, electrons can tunnel across the vacuum barrier separating the tip and sample in the presence of small bias voltage. The magnitude of tunneling current is extremely sensitivity to the gap distance between the tip and sample, the local density of electronic states of the sample and the local barrier height. The density of electronic states is the amount of electrons that exist at specific energy. As we measure the current with the tip moving across the surface, atomic information of the surface can be mapped out.



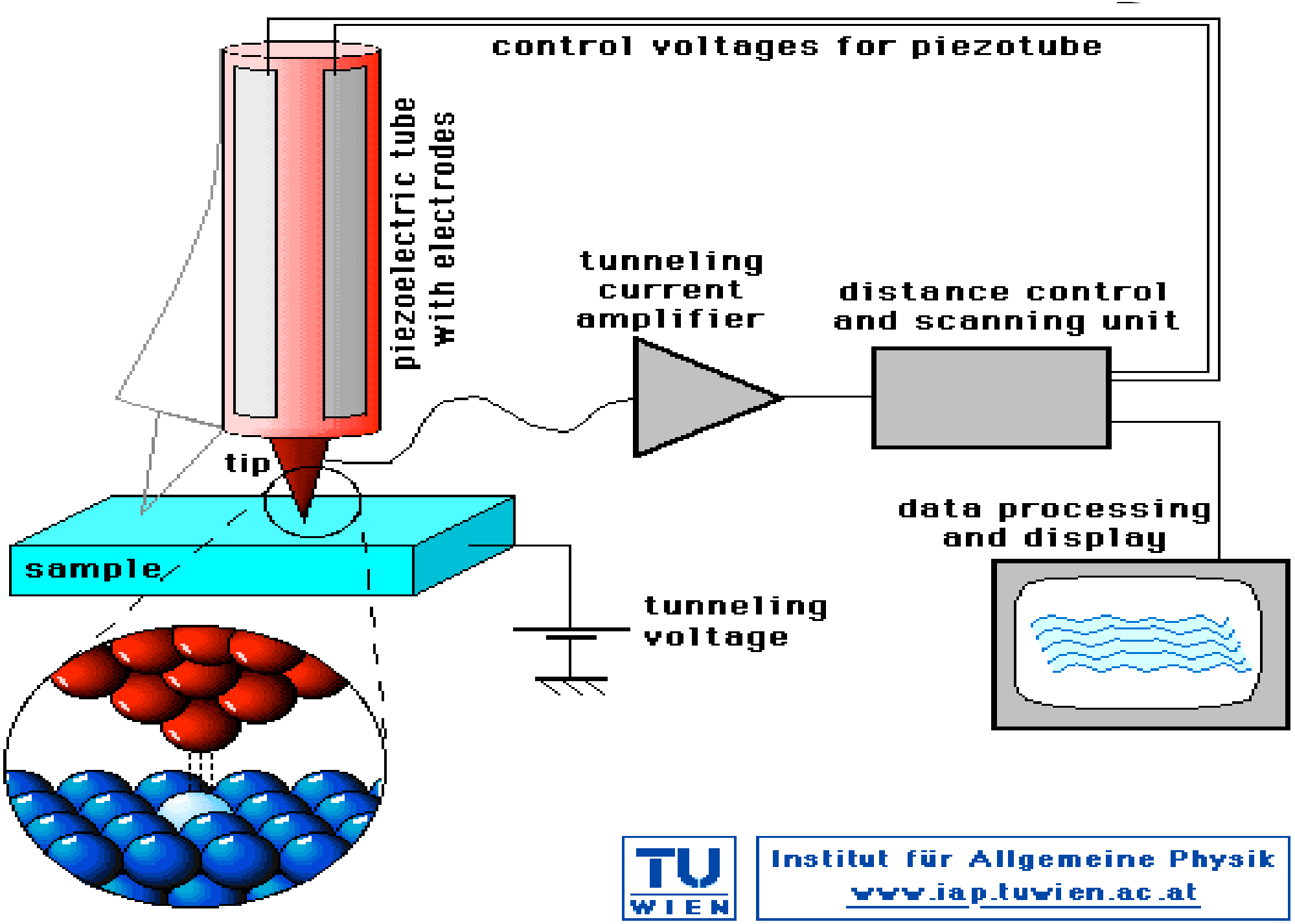
STM

- There are two modes of operation
  - In the constant current mode of operation, the tip moves up and down corresponding to the form of the surface, and the topography of the surface, including any adsorbates, can be mapped on an atomic scale. The vertical position of the tip is achieved by fixing it to a piezoelectric cylinder, which contracts or expands according to the potential difference it experiences.



STM

- In constant z-mode, vertical position of the tip is held constant and the current is monitored. Because tunneling probability is very sensitive to the size of the gap, the microscope can detect tiny, atom-scale variations in the height.



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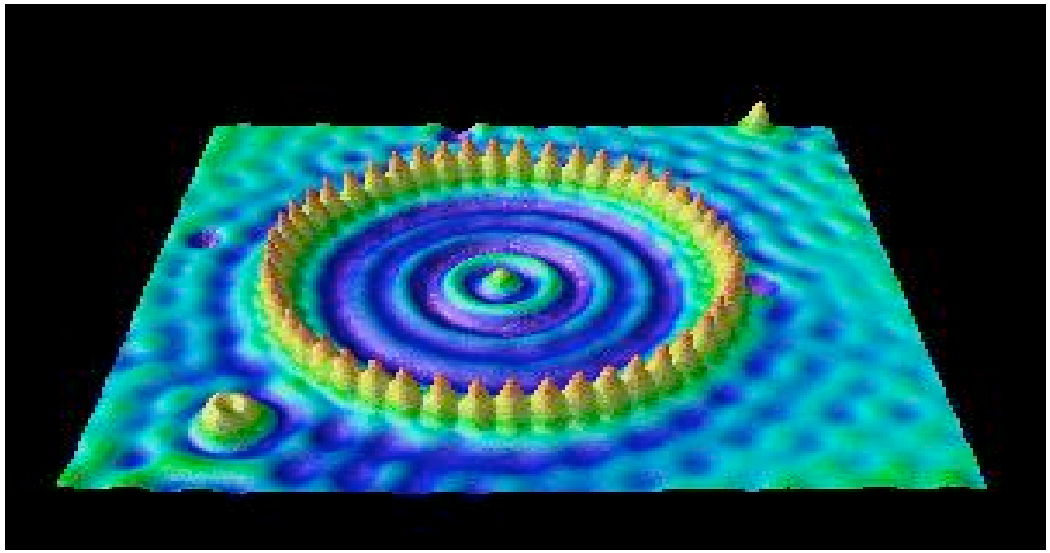
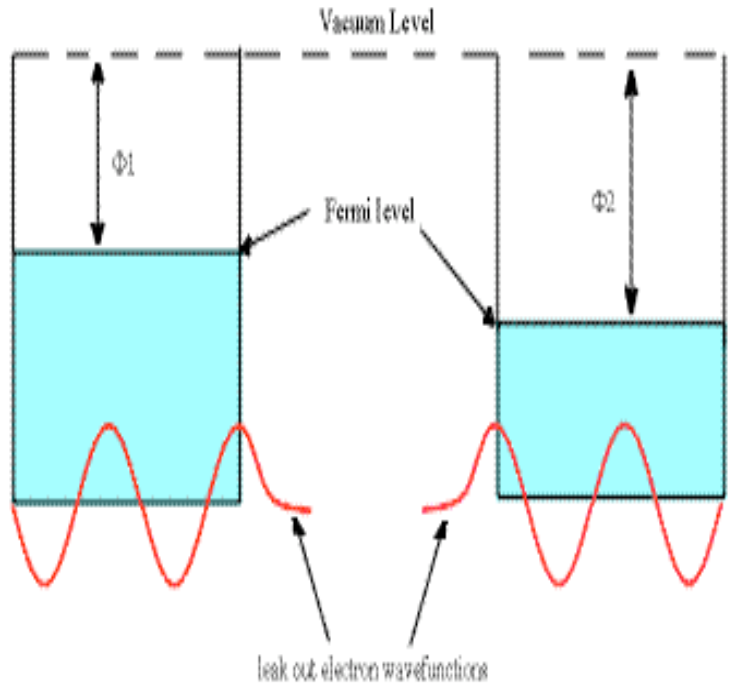
STM

- Here is an STM image showing iron atoms adsorbed on a copper (111) surface forming a "quantum corral" at a very low temperature (4K). Actually, the image shows the contour of the local density of electron states. The corral is about 14.3 nm in diameter.



STM
Tunneling current

Tunneling current originates from the wavelike properties of particles (electrons. in this case) in quantum mechanics. When an electron is incident upon a vacuum barrier with potential energy larger than the kinetic energy of the electron, there is still a non-zero probability that it may traverse the forbidden region and reappear on the other side of the barrier. It is shown by the leak out electron wave function in the picture.

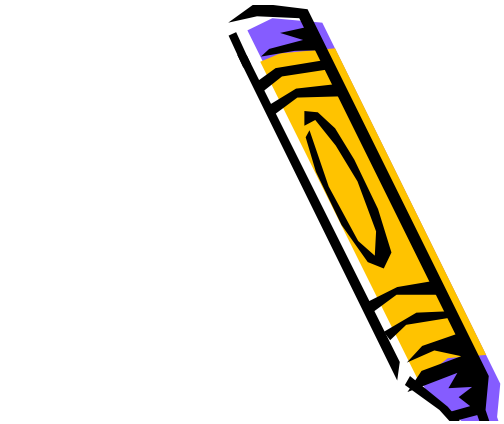


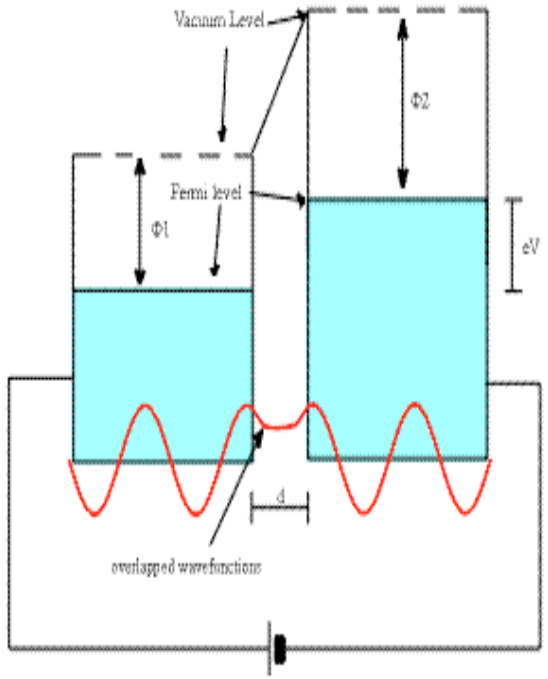
STM
Tunneling current

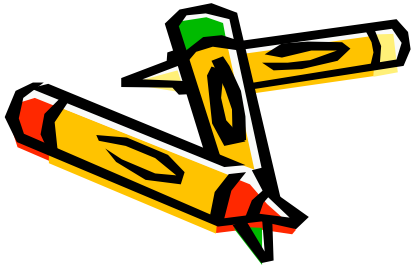
If two conductors are so close that their leak out electron wave functions overlap. The electron wave functions at the Femi level have a characteristic exponential inverse decay length κ given by

$$k = \left(\frac{2m_e(V - E)}{\hbar^2} \right)^{\frac{1}{2}}$$

m is mass of electron, (V-E) is the local tunneling barrier height or the average work function of the tip and sample. When a small voltage, V is applied between the tip and the sample, the overlapped electron wavefunction permits quantum mechanical tunneling and a current, I will flow across the vacuum gap.





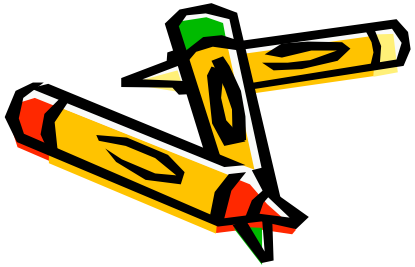


STM
Tunneling current

- At low voltage and temperature

$$I \propto \exp(-2kd)$$

d is the distance between tip and sample. If the distance increased by 0.1 nm, the current flow decreased by an order of magnitude, so the sensitivity to vertical distance is terribly high. As the tip scans across the surface, it gives atomic resolution image you now see.



STM
Tunneling current

- To get an idea of distance dependence of the tunneling current in STM take V-E = 2.0 e.V. Calculate current drop for moving tip from 0.5nm to 0.6 nm from surface

$$I \propto \exp(-2kd)$$

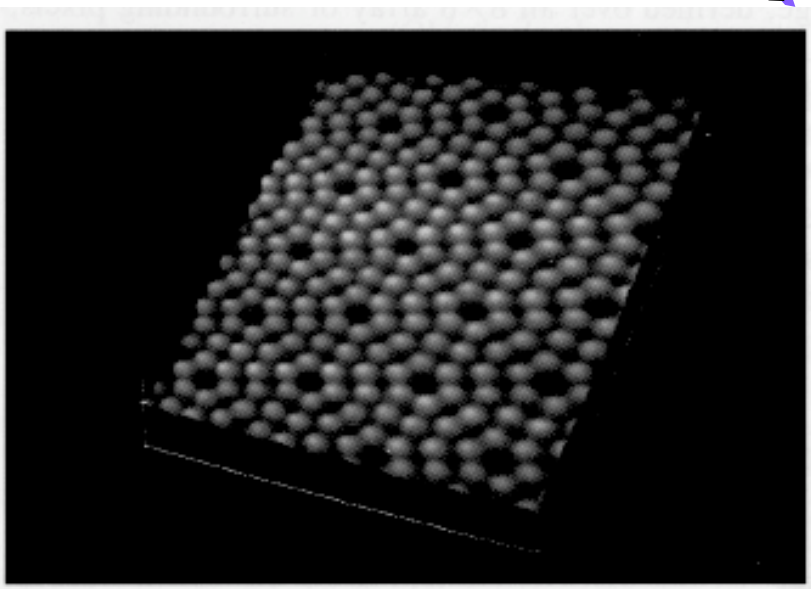
$$k = \left(2*9.109*10^{-31}*(2*1.6021*10^{-19})/(6.626176*10^{-34}/2*\pi)^2\right)^{\frac{1}{2}}$$

$$I(0.5nm) \propto \exp(-2*k*0.5*10^{-9}), I(0.6nm) \propto \exp(-2*k*0.6*10^{-9})$$

$$I(0.6nm)/I(0.5nm) = 0.235$$

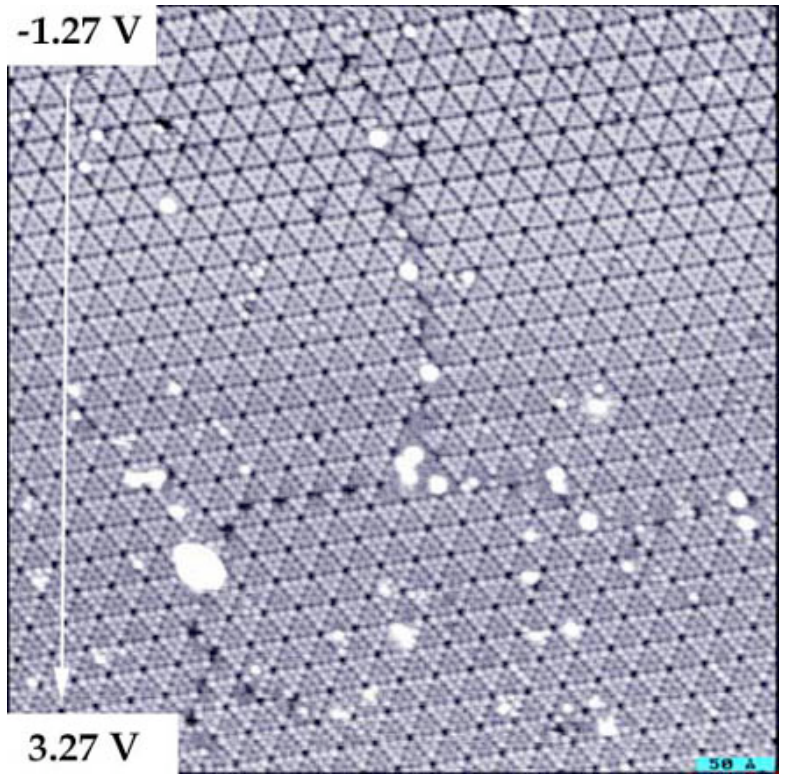
STM
Tunneling current

- This is the STM image of Si(111)-7x7 surface, the white spots represents the position of the atoms.
- **Remember !** STM does NOT probe the nuclear position directly, but rather it is a probe of the electron density, so STM images do not always show the position of the atoms, and it depends on the nature of the surface and the magnitude and sign of the tunneling current.

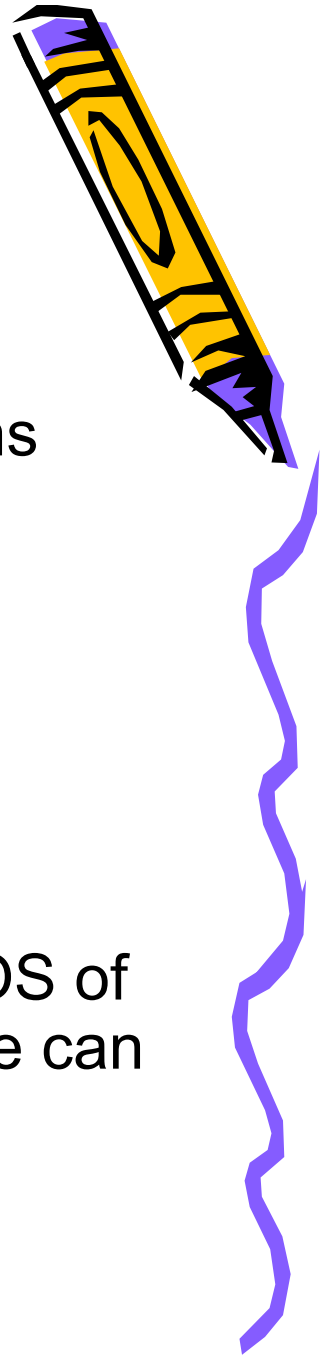


STM
Tunneling current

- UHV300 STM image of Si(111) 7 x 7. The Image was acquired in Image Spectroscopy mode, where the tip bias was ramped from -1.27 V to -3.27V



Local Density Of States (LDOS)

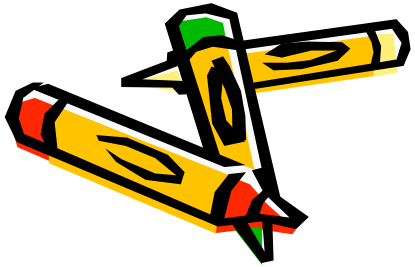


- Density of States (DOS) represents the amount of electrons that exist at specific values of energy. The tunneling conductance, σ (or I/V) is proportional to the LDOS

$$\sigma \propto \rho(r_0, E)$$

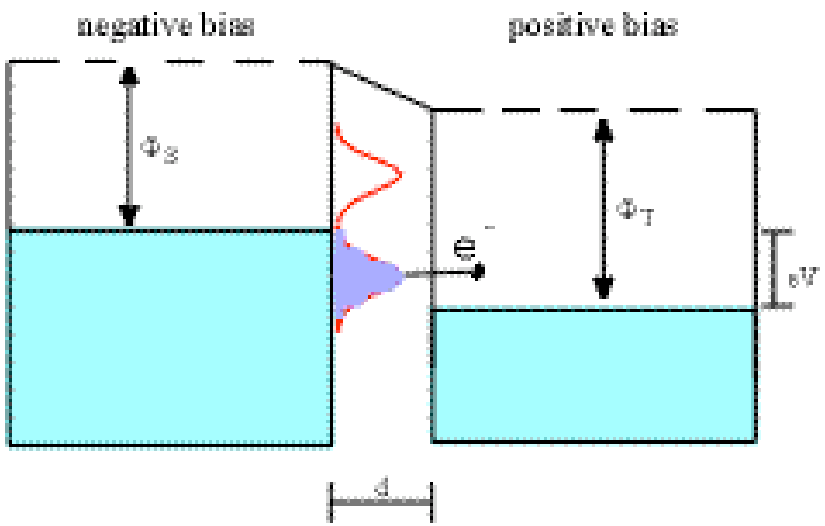
where $\rho(r_0,E)$ is the local density of states of the sample.

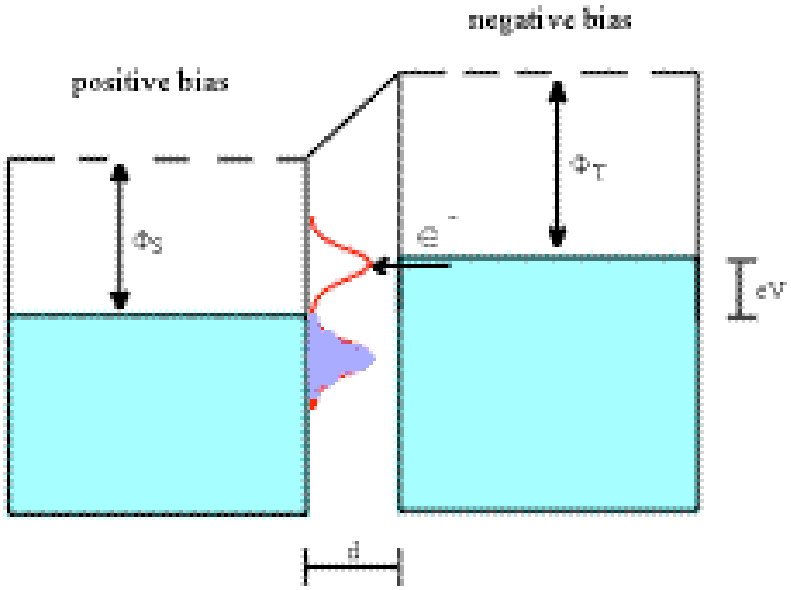
- Keeping the gap distance constant, measure the current change with respect to the bias voltage can probe the LDOS of the sample. Moreover, changing the polarity of bias voltage can get information on local occupied and unoccupied states.



Local Density Of States

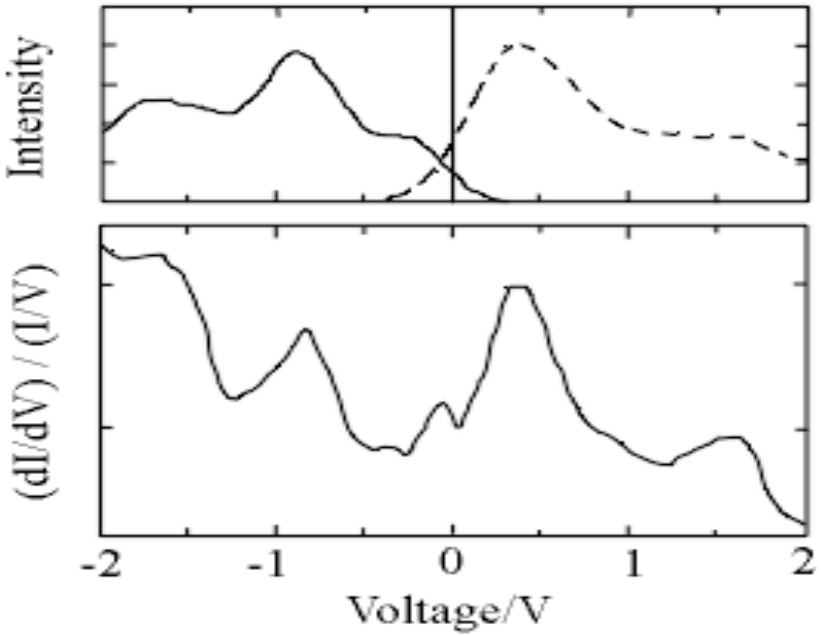
- When the tip is negatively biased, electrons tunnel from the occupied states of the tip to the unoccupied states of the sample. If the tip is positively biased, electrons tunnel from the occupied states of sample to the unoccupied states of the tip.



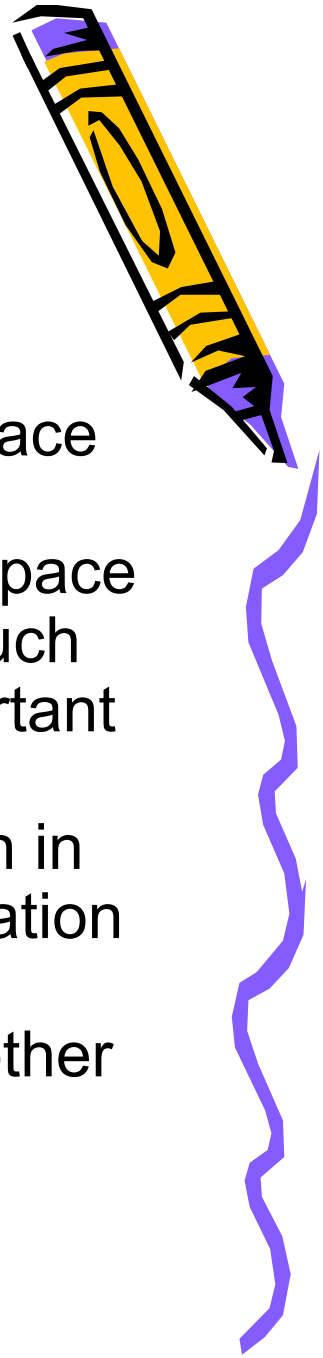


Local Density Of States

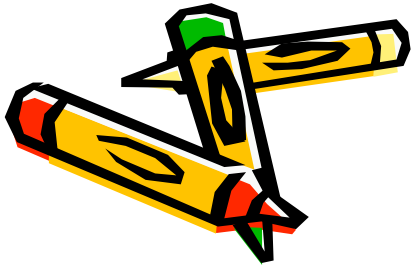
- Here are the spectra for Si(111)-7 x 7 surface. The bottom spectrum is the area averaged tunneling conductance measured by STM, and the top spectrum is the surface states spectrum measures photoemision and inverse photoemision. Both spectra show similar features.



STM: Some Applications
Surface science

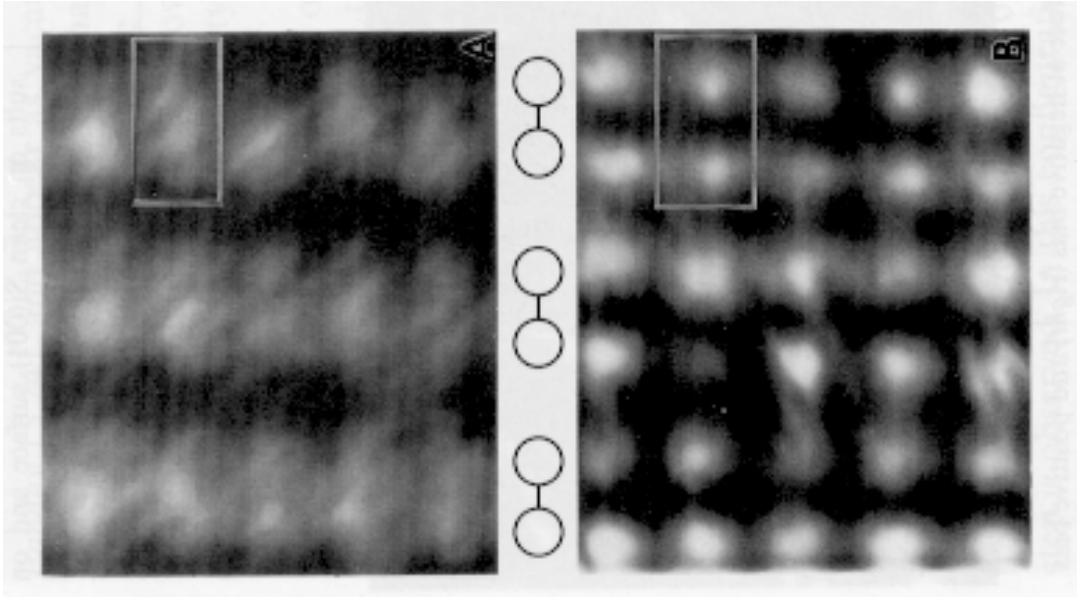


- The invention of STM has had a great impact on surface science. Uses of STM to study metals and semiconductors surface can provide non-trivial real space information, especially in studying semiconductors such as Si(100) surface, which is the technologically important Si substrate material for microelectronics device fabrication. The STM image of Si(100) surface shown in the next slide gives direct confirmation of dimer formation during surface reconstruction, although it has been previously suggested by theoretical calculation and other experimental observations.



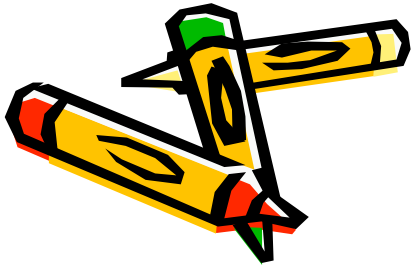
Surface science

- Here are the bias-dependent STM images, the left image, with positive bias to the tip, the right one, with negative bias to the tip. The images directly reflect the spatial distribution of the occupied π -bonding state is between the dimer atoms, while the unoccupied π^* –antibonding states are localized away from the dimer.

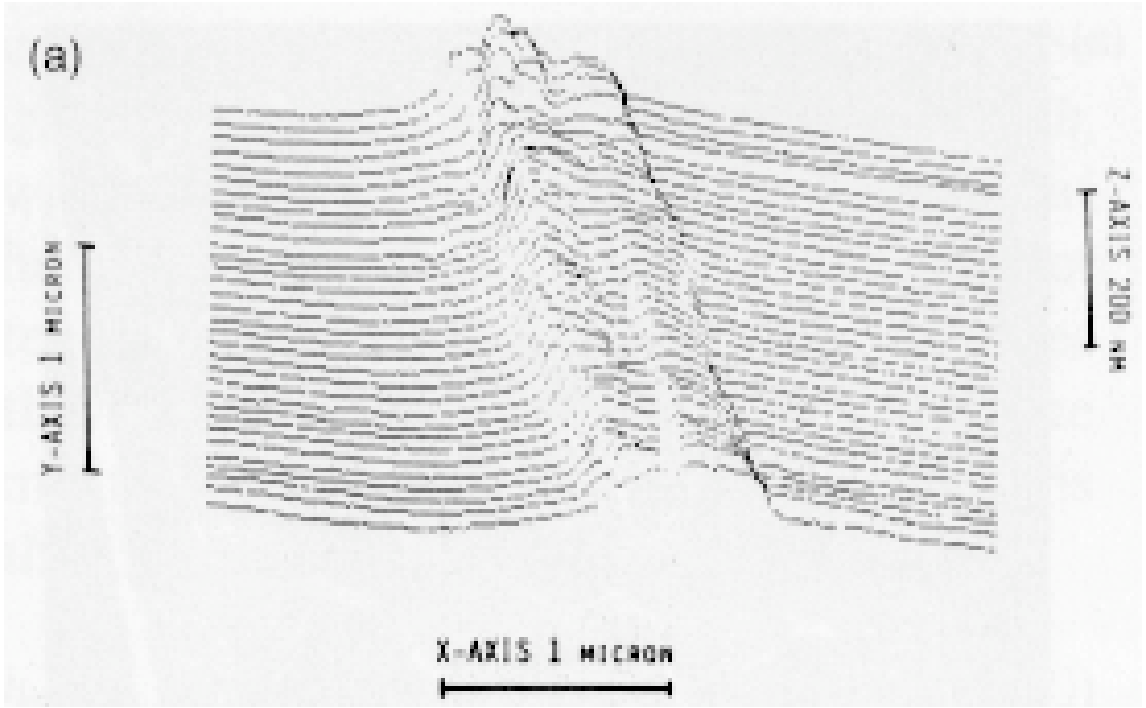


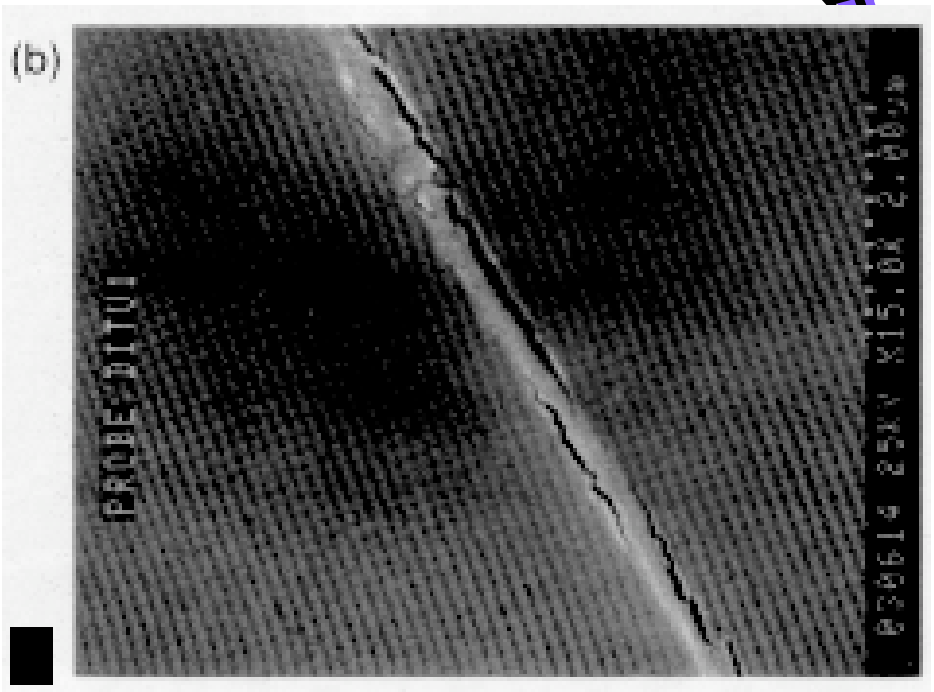
Metrological Applications

- The micro-topography and nano-topography of a surface is crucial in many applications, such as for high precision optical components and disk drive surface roughness of machined or ground surfaces in area where such a finish is crucial. The STM image on the next slide is of an individual turn mark on a diamond-turned Al substrate to be used for subsequent magnetic film deposition for a high capacity hard disc drive. The image obtained by scanning electron microscope (SEM) is shown to the right for comparison. The high spatial resolution of STM provides an important complement to the SEM



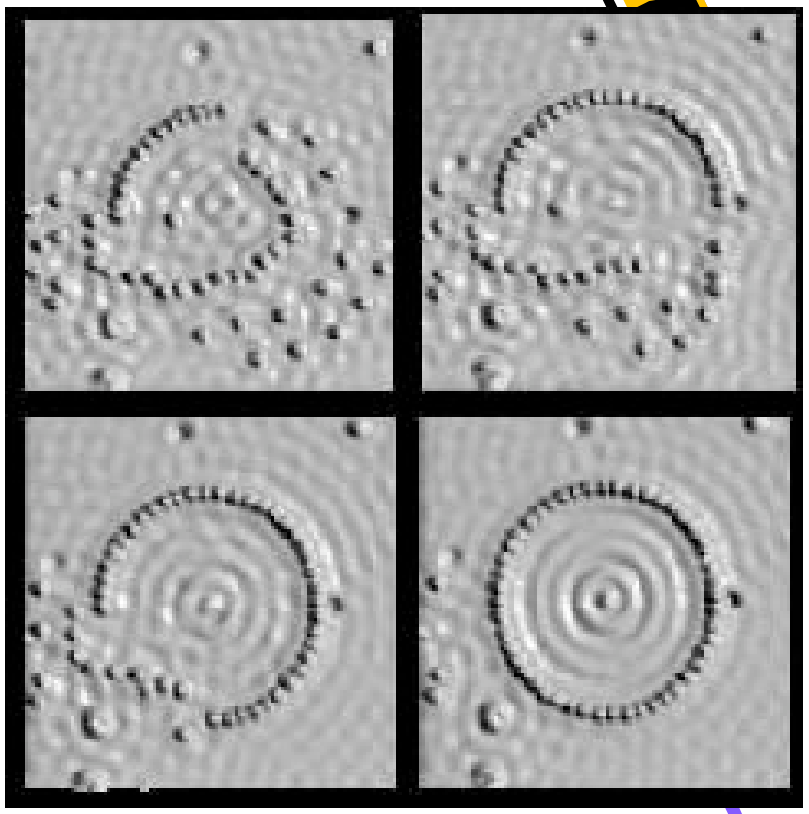
Metrological Applications





Manipulation of Atoms

One innovative applications of STM recently found is manipulation of atoms. Here is an example, Iron atoms are placed on Cu(111) surface at very low temperature (4K), Iron atoms are first physisorbed on the Cu surface, then the tip is placed directly over a physisorbed atom and lowered to increase the attractive force by increasing the tunneling current, the atom was dragged by the tip and moves across the surface to a desired position. Then, the tip was withdrawn by lowering the tunneling current.



Atomic Force Microscopy

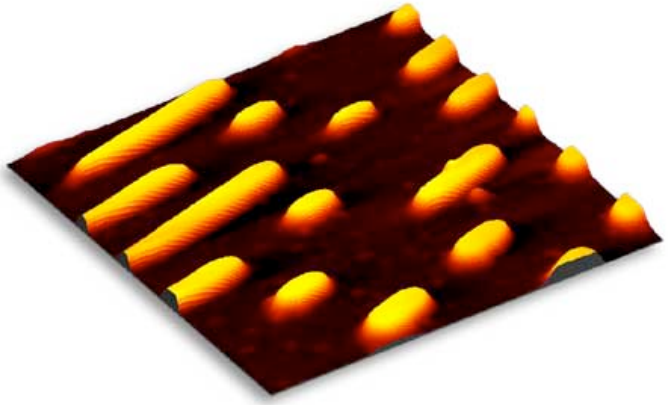
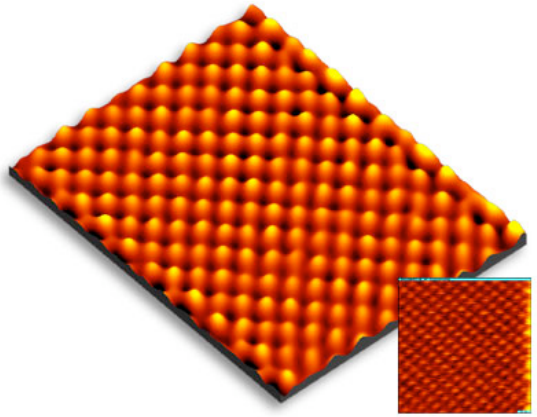
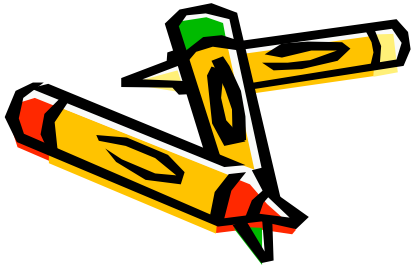
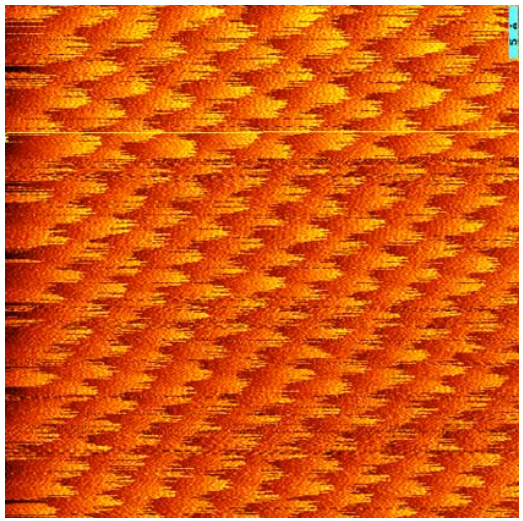


Image of CD-ROM stamper, the device used to "stamp" standard production CD-ROMs



AFM image of NaCl on mica, resolving the crystalline atomic structure of the (100) surface. Unfiltered data is displayed at the bottom right. 5 nm x 4.8 nm scan



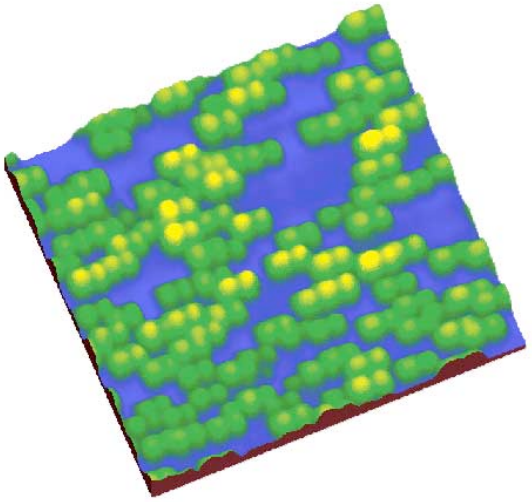


AFM friction data. Atomic lattice resolution on muscovite mica. Unprocessed raw data is displayed. Image was taken in air with a silicon nitride cantilever, force constant = 0.12 N/m, 1.67 scanning frequency.

ALL of these images were produced under Ultra High Vacuum (UHV) conditions

Atomic Force Microscopy

Automated AFM nanografting with mercapto-hexadecanoic acid in a mixed hexanethiol/ octadecanethiol SAM



AFM image of latex particles on Au

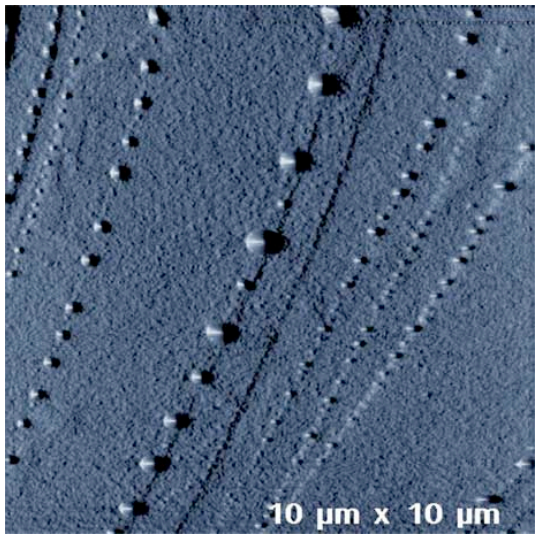
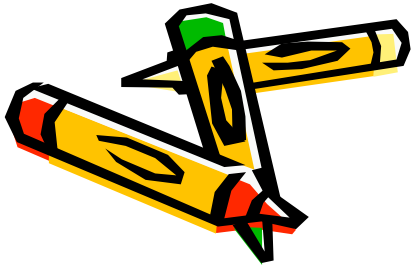


Image of aqueous KOH on highly oriented pyrolytic graphite (HOPG). The droplets are predominantly trapped at the atomic steps present on the surface and the terraces are almost devoid of liquid. The image was acquired at room temperature with a relative humidity of 35%-40%AFM friction data.

ALL of these images were produced with fluid AFM

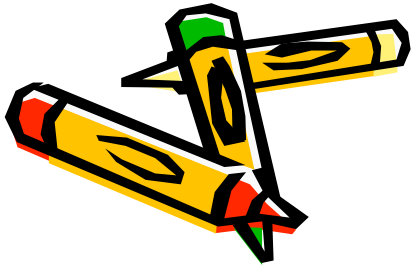
Atomic Force Microscope

The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The materials being investigated include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM one cannot only image the surface in atomic resolution but also measure the force at nano-newton scale



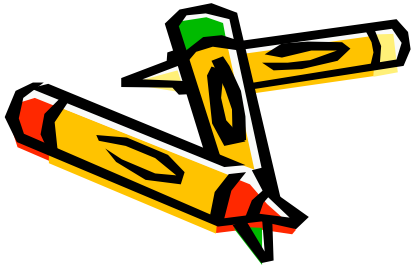
AFM

The first AFM was made by meticulously gluing a tiny shard of diamond onto one end of a tiny strip of gold foil. In the fall of 1985 Gerd Binnig and Christoph Gerber used the cantilever to examine insulating surfaces. A small hook at the end of the cantilever was pressed against the surface while the sample was scanned beneath the tip. The force between tip and sample was measured by tracking the deflection of the cantilever. This was done by monitoring the tunneling current to a second tip positioned above the cantilever. They could delineate lateral features as small as 30 nm. The force microscope emerged in this way. In fact, without the breakthrough in tip manufacture, the AFM probably would have remained a curiosity in many research groups.

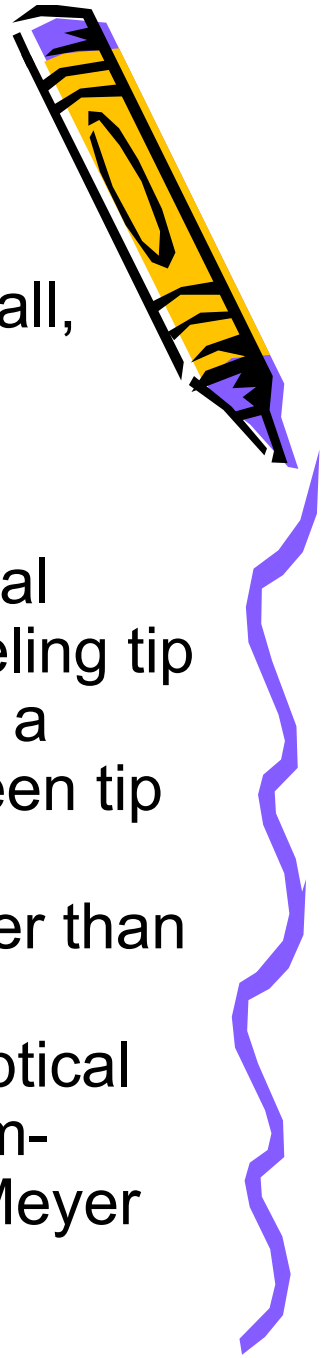


AFM

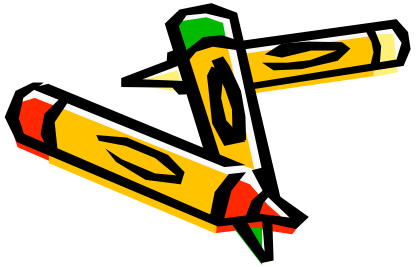
It was Albrecht, a fresh graduate student, who fabricated the first silicon micro-cantilever and measured the atomic structure of boron nitride. Today the tip-cantilever assembly typically is micro-fabricated from Si or Si3N4. The era of AFM came finally when the Zurich group released the image of a silicon (111) 7X7 pattern. The world of surface science knew that a new tool for surface microscope was at hand. After several years the micro-cantilevers have been perfected, and the instrument has been embraced by scientists and technologist.



AFM

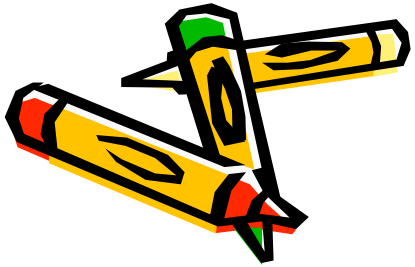


The force between the tip and the sample surface is very small, usually less than 10^{-9} N. How to monitor such small forces is another story. The detection system does not measure force directly. It senses the deflection of the micro-cantilever. The detecting systems for monitoring the deflection fall into several categories. The first device introduced by Binnig was a tunneling tip placed above the metallized surface of the cantilever. This is a sensitive system where a change in spacing of 0.1 nm between tip and cantilever changes the tunneling current by an order of magnitude. It is straightforward to measure deflections smaller than 0.001 nm. Subsequent systems were based on the optical techniques. The interferometer is the most sensitive of the optical methods, but it is somewhat more complicated than the beam-bounce method which was introduced by Meyer and Amer.

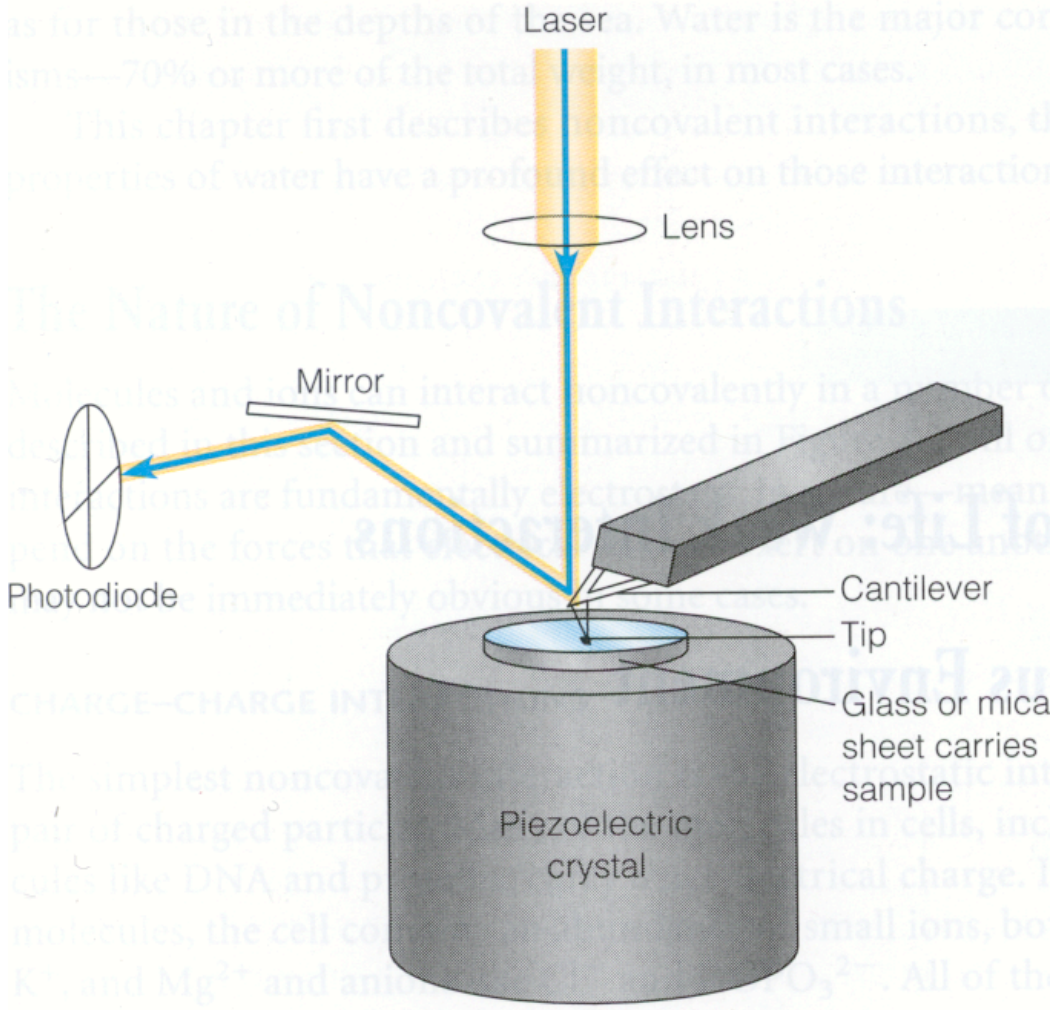


AFM

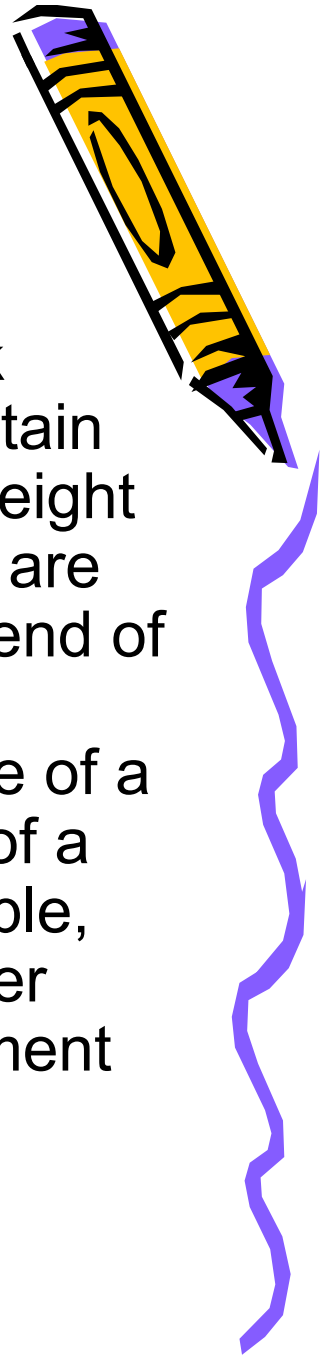
- The beam-bounce method is now widely used as a result of the work by Alexander and colleagues. In this system an optical beam is reflected from the mirrored surface on the back side of the cantilever onto a position-sensitive photodetector. In this arrangement a small deflection of the cantilever will tilt the reflected beam and change the position of beam on the photodetector. A third optical system introduced by Sarid uses the cantilever as one of the mirrors in the cavity of a diode laser. Motion of the cantilever has a strong effect on the laser output, and this is exploited as a motion detector



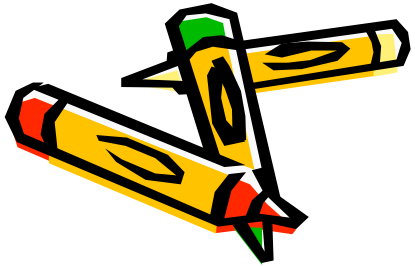
AFM: Operation



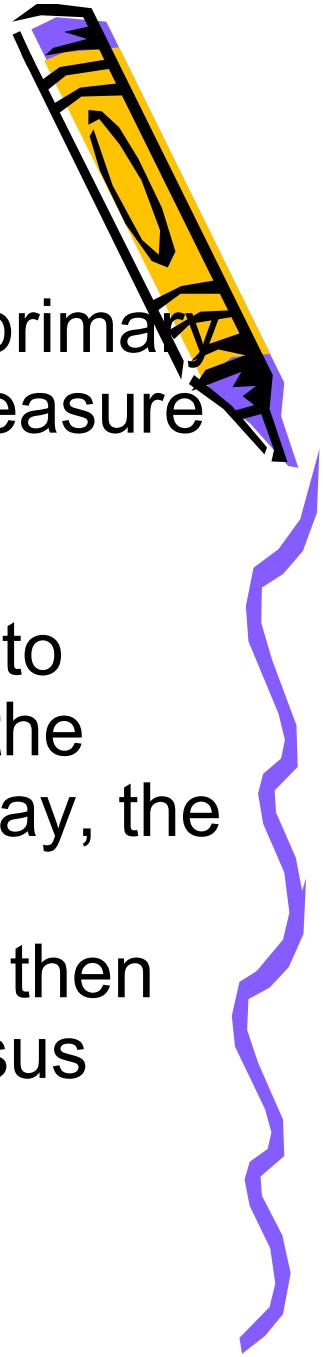
AFM: Operation



The principles of how the AFM works are very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si3N4 or Si, and extend down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode.

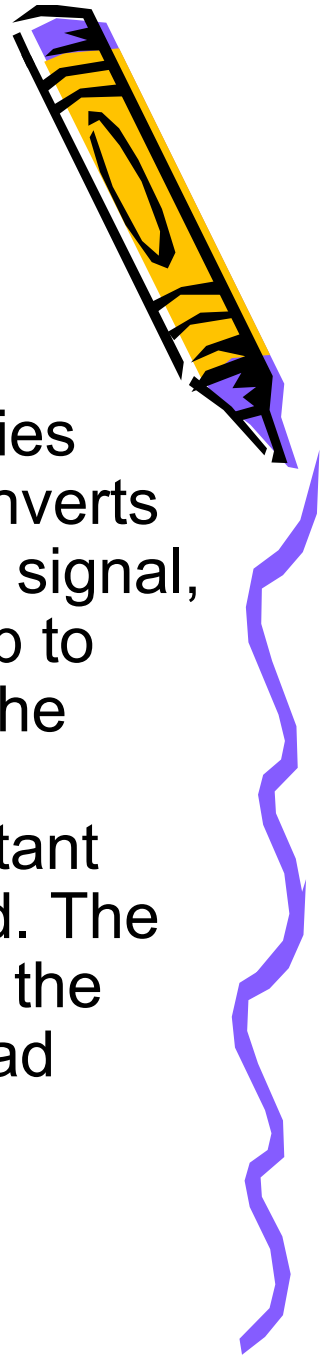


AFM: Operation

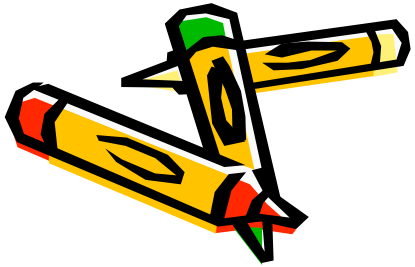


Some AFM's can accept full 200 mm wafers. The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01nm vertical resolution on all types of samples. Depending on the AFM design, scanners are used to translate either the sample under the cantilever or the cantilever over the sample. By scanning in either way, the local height of the sample is measured. Three dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position

AFM: Operation

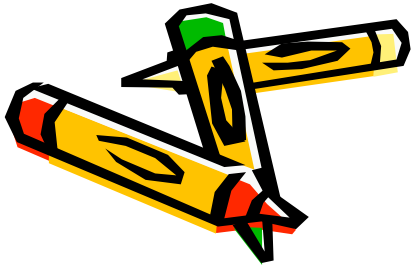


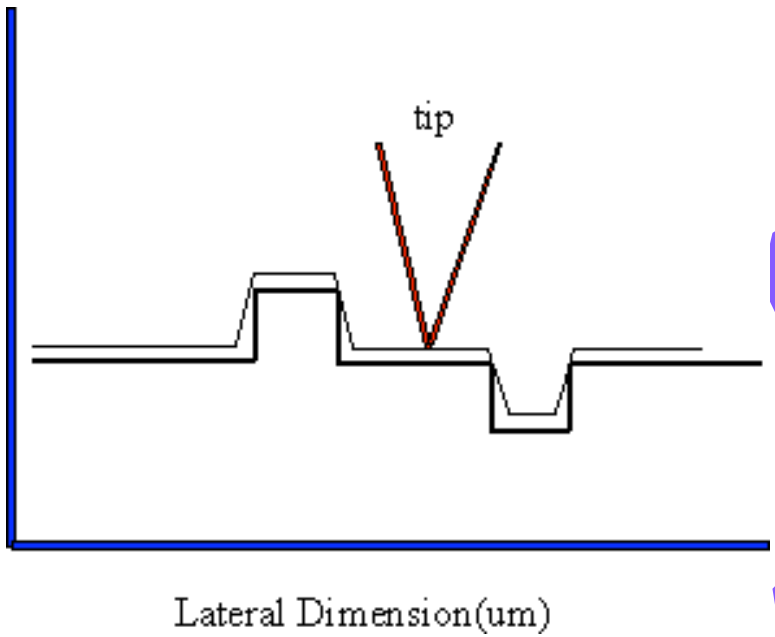
The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts this to a voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezo-electronic transducer monitors real time height deviation. In the constant height mode the deflection force on the sample is recorded. The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope.



AFM: Resolution

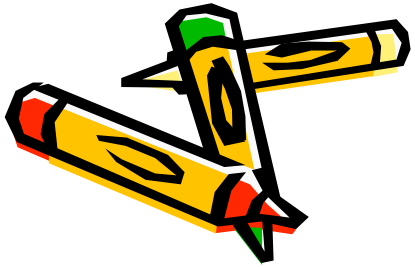
- The concept of resolution in AFM is different from radiation based microscopies because AFM imaging is a three dimensional imaging technique. The ability to distinguish two separate points on an image is the standard by which lateral resolution is usually defined. There is clearly an important distinction between images resolved by wave optics and scanning probe techniques. The former is limited by diffraction, and later primarily by apical probe geometry and sample geometry. Usually the width of a DNA molecule is loosely used as a measure of resolution, because it has a known diameter of 2.0 nm in the B form. Some of the best values for AFM imaging are 3.0 nm quoted for DNA in propanol. Unfortunately, this definition of resolution can be misleading because the sample height clearly effects this value.





AFM versus STM

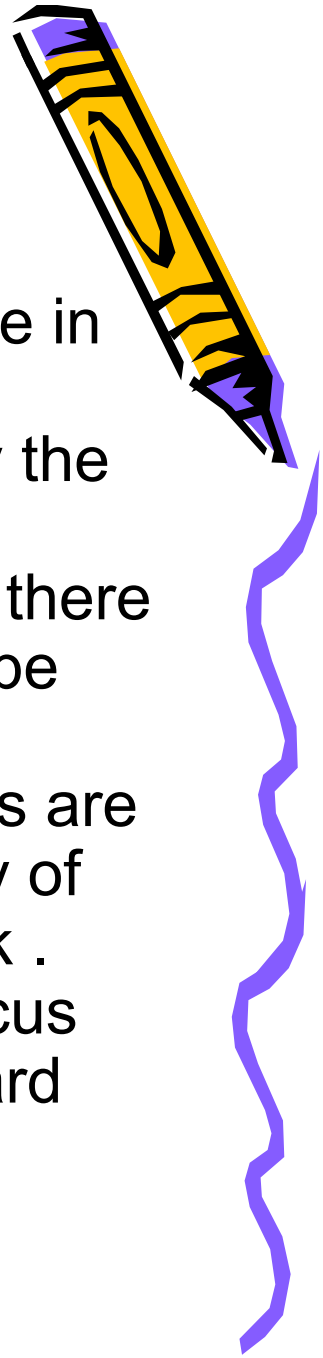
- It's interesting to compare AFM and its precursor -- Scanning Tunneling Microscope. In some cases, the resolution of STM is better than AFM because of the exponential dependence of the tunneling current on distance. The force-distance dependence in AFM is much more complex when characteristics such as tip shape and contact force are considered. STM is generally applicable only to conducting samples while AFM is applied to both conductors and insulators. In terms of versatility, needless to say, the AFM wins. Furthermore, the AFM offers the advantage that the writing voltage and tip-to-substrate spacing can be controlled independently, whereas with STM the two parameters are integrally linked.



AFM Modes: Contact

The contact mode where the tip scans the sample in close contact with the surface is the common mode used in the force microscope. The force on the tip is repulsive with a mean value of 10^{-9} N. This force is set by pushing the cantilever against the sample surface with a piezoelectric positioning element. In contact mode AFM the deflection of the cantilever is sensed and compared in a DC feedback amplifier to some desired value of deflection. If the measured deflection is different from the desired value the feedback amplifier applies a voltage to the piezo to raise or lower the sample relative to the cantilever to restore the desired value of deflection. The voltage that the feedback amplifier applies to the piezo is a measure of the height of features on the sample surface. It is displayed as a function of the lateral position of the sample.

AFM: Contact mode

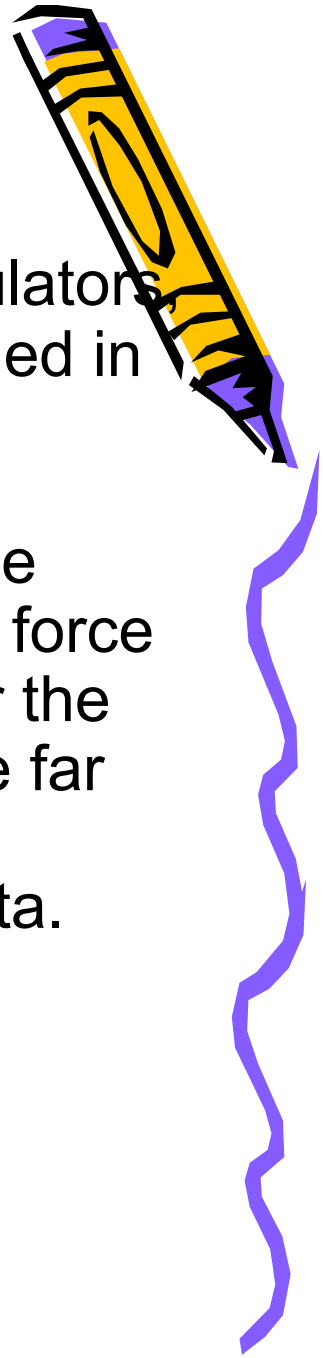


A few instruments operate in UHV but the majority operate in ambient atmosphere, or in liquids. Problems with contact mode are caused by excessive tracking forces applied by the probe to the sample. The effects can be reduced by minimizing tracking force of the probe on the sample, but there are practical limits to the magnitude of the force that can be controlled by the user during operation in ambient environments. Under ambient conditions, sample surfaces are covered by a layer of adsorbed gases consisting primarily of water vapor and nitrogen which is 10-30 monolayers thick . When the probe touches this contaminant layer, a meniscus forms and the cantilever is pulled by surface tension toward the sample surface.

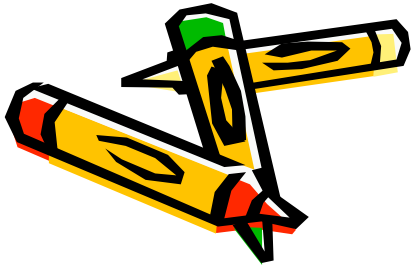
AFM: Contact mode

The magnitude of the force depends on the details of the probe geometry, but is typically on the order of 100 nanoNewtons. This meniscus force and other attractive forces may be neutralized by operating with the probe and part or all of the sample totally immersed in liquid. There are many advantages to operate AFM with the sample and cantilever immersed in a fluid. These advantages include the elimination of capillary forces, the reduction of Van der Waals' forces and the ability to study technologically or biologically important processes at liquid solid interfaces. However there are also some disadvantages involved in working in liquids. These range from nuisances such as leaks to more fundamental problems such as sample damage on hydrated and vulnerable biological samples.

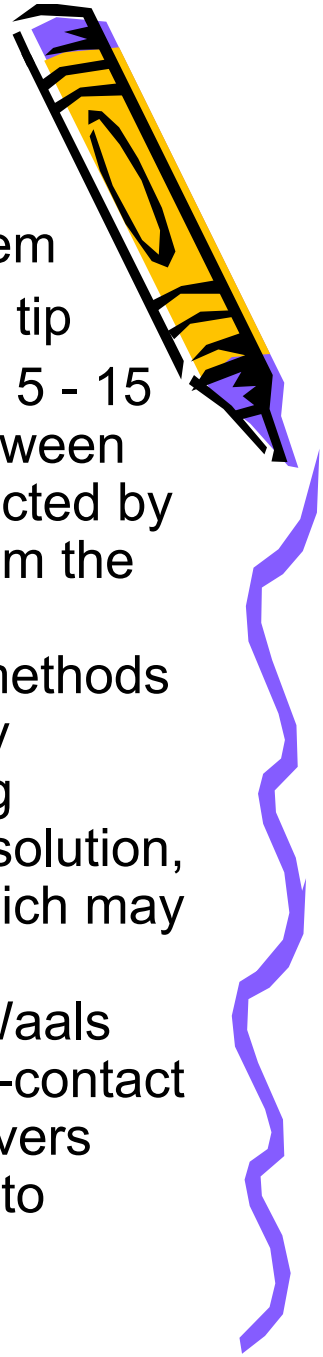
AFM:Contact mode



A large class of samples, including semiconductors and insulators, can trap electrostatic charge (partially dissipated and screened in liquid). This charge can contribute to additional, substantial, attractive forces between the probe and sample. All of these forces combine to define a minimum normal force that can be controllably applied by the probe to the sample. This normal force creates a substantial frictional force as the probe scans over the sample. In practice, it appears that these frictional forces are far more destructive than the normal force and can damage the sample, dull the cantilever probe and distort the resulting data. Also many samples such as semiconductor wafers can not practically be immersed in liquid. An attempt to avoid these problem is the Non-contact Mode



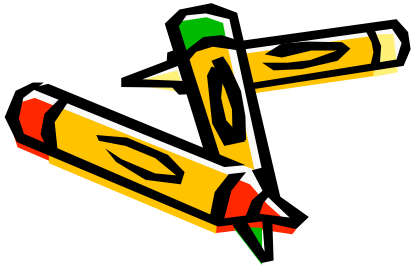
AFM: Non Contact mode



A new era in imaging was opened when microscopists introduced a system for implementing the non-contact mode which is used in situations where tip contact might alter the sample in subtle ways. In this mode the tip hovers 5 - 15 nm above the sample surface. Attractive van der Waals forces acting between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. Unfortunately the attractive forces from the sample are substantially weaker than the forces used by contact mode. Therefore the tip must be given a small oscillation so that AC detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample. For highest resolution, it is necessary to measure force gradients from Van der Waals forces which may extend only a nanometre from the sample surface. In general, the fluid contaminant layer is substantially thicker than the range of the Van der Waals force gradient and therefore, attempts to image the true surface with non-contact AFM fail as the oscillating probe becomes trapped in the fluid layer or hovers beyond the effective range of the forces it attempts to measure.

AFM: Tapping mode

Tapping mode is a potent technique allows high resolution topographic imaging of sample surfaces that are easily damaged, loosely hold to their substrate, or difficult to image by other AFM techniques. Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces, and other difficulties that an plague conventional AFM scanning methods by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilever's resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a high amplitude(typically greater than 20nm) when the tip is not in contact with the surface.



AFM: Tapping mode

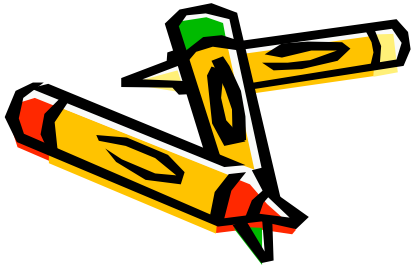
The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000 to 500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features. Tapping mode operation in fluid has the same advantages as in the air or vacuum. However imaging in a fluid medium tends to damp the cantilever's normal resonant frequency. In this case, the entire fluid cell can be oscillated to drive the cantilever into oscillation. This is different from the tapping or non-contact operation in air or vacuum where the cantilever itself is oscillating. When an appropriate frequency is selected (usually in the range of 5,000 to 40,000 cycles per second), the amplitude of the cantilever will decrease when the tip begins to tap the sample, similar to TappingMode operation in air. Alternatively, the very soft cantilevers can be used to get the good results in fluid. The spring constant is typically 0.1 N/m compared to the tapping mode in air where the cantilever may be in the range of 1-100 N/m.

AFM: Mode Summary

In contact mode AFM electrostatic and/or surface tension forces from the adsorbed gas layer pull the scanning tip toward the surface. It can damage samples and distort image data. Therefore, contact mode imaging is heavily influenced by frictional and adhesive forces compared to non-contact or tapping mode.

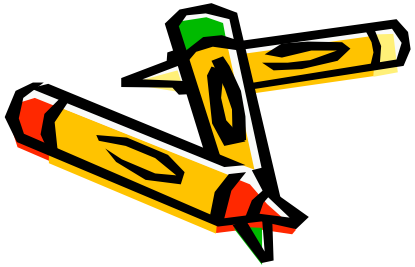
Non-contact imaging generally provides low resolution and can also be hampered by the contaminant layer which can interfere with oscillation.

Tapping mode AFM was developed as a method to achieve high resolution without inducing destructive frictional forces both in air and fluid. With the Tapping mode technique, the very soft and fragile samples can be imaged successfully.

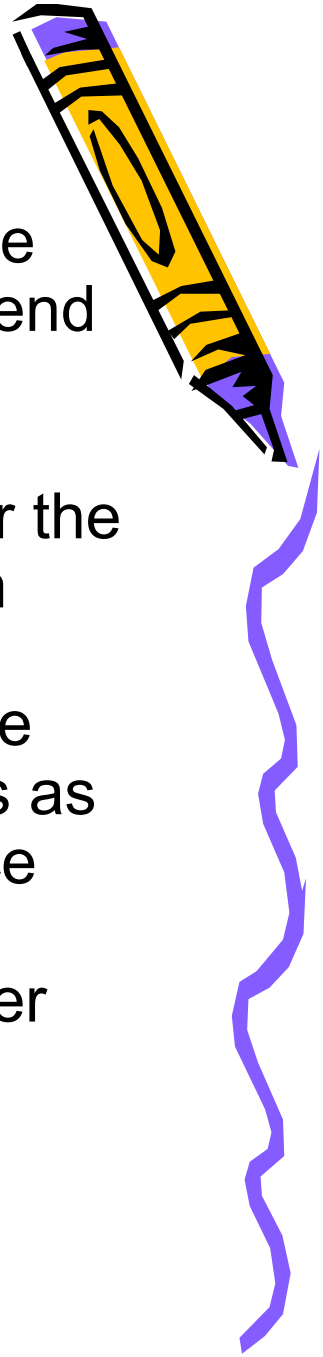


Force Curve Measurements

AFM can record the amount of force felt by the cantilever as the probe tip is brought close to and even indented into a sample surface and then pulled away. This technique can be used to measure the long range attractive or repulsive forces between the probe tip and the sample surface, elucidating local chemical and mechanical properties like adhesion and elasticity, and even thickness of adsorbed molecular layers or bond rupture lengths.

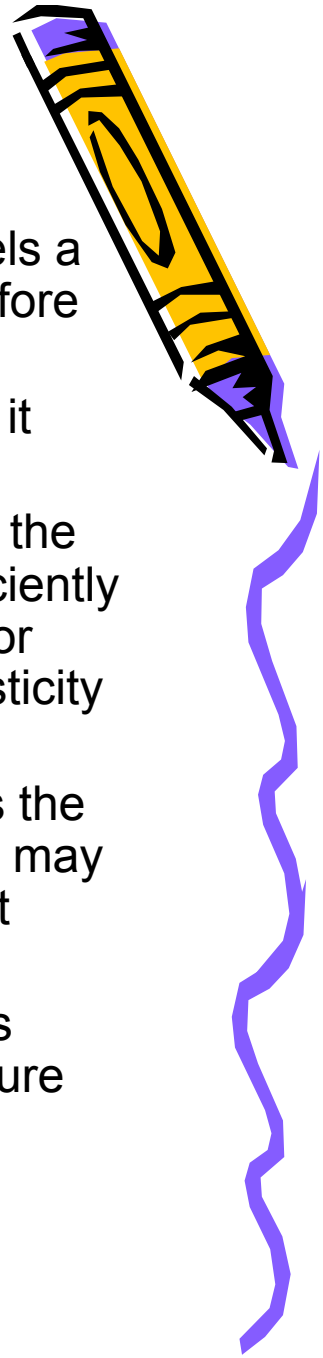


Force Curve Measurements



Force curves(force-versus-distance curve) typically show the deflection of the free end of the AFM cantilever as the fixed end of the cantilever is brought vertically towards and then away from the sample surface. Experimentally, this is done by applying a triangle-wave voltage pattern to the electrodes for the z-axis scanner. This causes the scanner to expand and then contract in the vertical direction, generating relative motion between the cantilever and sample. The deflection of the free end of the cantilever is measured and plotted at many points as the z-axis scanner extends the cantilever towards the surface and then retracts it again. By controlling the amplitude and frequency of the triangle-wave voltage pattern, the researcher can vary the distance and speed that the AFM cantilever tip travels during the force measurement.

Anatomy of a Force Curve



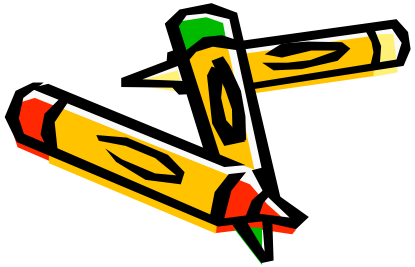
A:The cantilever starts not touching the surface. In this region, if the cantilever feels a long-range attractive (or repulsive) force it will deflect downwards (or upwards) before making contact with the surface.

B: As the probe tip is brought very close to the surface, it may jump into contact if it feels sufficient attractive force from the sample.

C: Once the tip is in contact with the surface, cantilever deflection will increase as the fixed end of the cantilever is brought closer to the sample. If the cantilever is sufficiently stiff, the probe tip may indent into the surface at this point. In this case, the slope or shape of the contact part of the force curve can provide information about the elasticity of the sample surface.

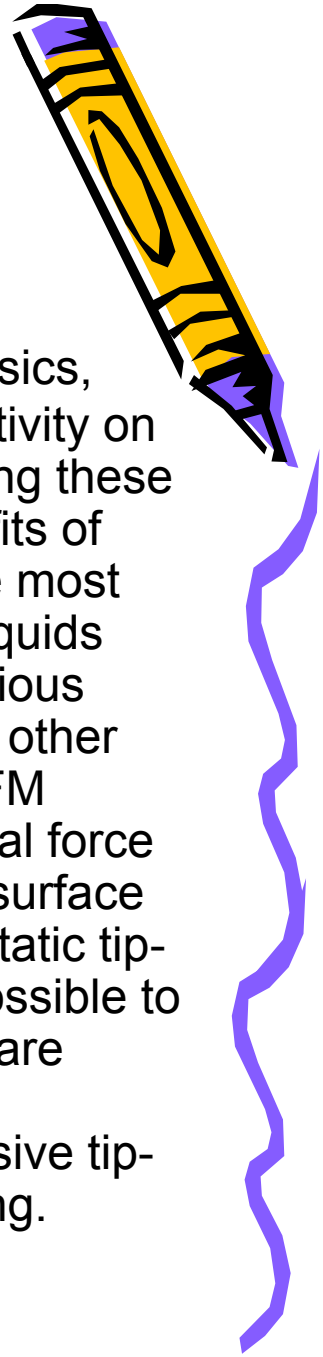
D:After loading the cantilever to a desired force value, the process is reversed. As the cantilever is withdrawn, adhesion or bonds formed during contact with the surface may cause the cantilever to adhere to the sample some distance past the initial contact point on the approach curve (B).

E:A key measurement of the AFM force curve is the point at which the adhesion is broken and the cantilever comes free from the surface. This can be used to measure the rupture force required to break the bond or adhesion.



One of the first uses of force measurements was to improve the quality of AFM images by monitoring and minimizing the attractive forces between the tip and sample.

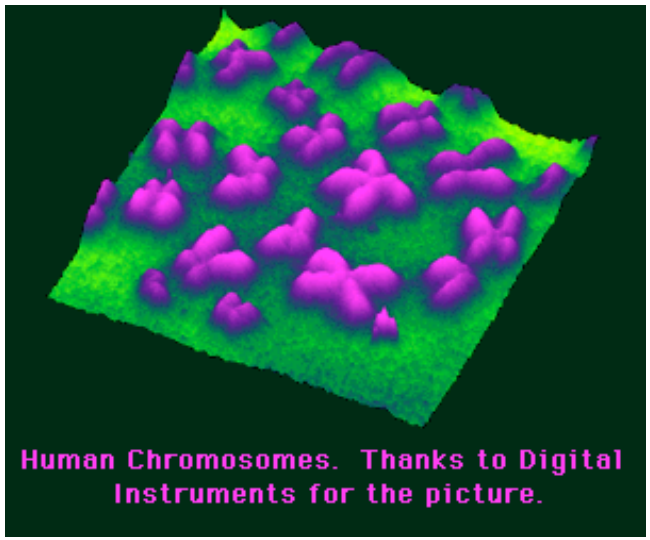
Measuring Fundamental Forces



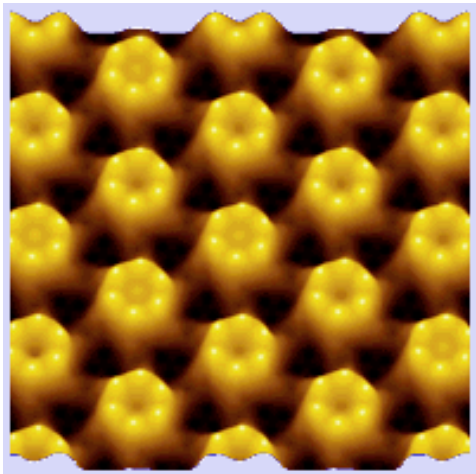
Concern with the fundamental interactions between surfaces extends across physics, chemistry, materials science and a variety of other disciplines. With a force sensitivity on the order of a few piconewtons (pN = 10^{-12} N), AFMs are excellent tools for probing these fundamental force interactions. Force measurements in water revealed the benefits of AFM imaging in this environment due to the lower tip-sample forces. Some of the most interesting force measurements have also been performed with samples under liquids where the environment can be quickly changed to adjust the concentration of various chemical components. In liquids, electrostatic forces between dissolved ions and other charged groups play an important role in determining the forces sensed by an AFM cantilever. The liquid environment has become an important stage for fundamental force measurement because researchers can control many of the details of the probe surface force interaction by adjusting properties of the liquid. Experimentally, the electrostatic tip-sample forces depend strongly on pH and salt concentration. In fact, it is often possible to adjust the pH or salt concentration such that the attractive Van der Waals forces are effectively negated by repulsive electrostatic forces. This has been an important discovery because it can allow tuning of the liquid environment to minimize adhesive tip-sample forces that can damage the sample during imaging.

Applications of AFM

- One of the advantages of AFM is that it can image the non-conducting surfaces. So it was immediately extended to the biological systems, such as analyzing the crystals of amino acids and organic monolayers. Applications of AFM in the biosciences include: DNA and RNA analysis; Protein-nucleic acid complexes; Chromosomes; Cellular membranes; Proteins and peptides; Molecular crystals; Polymers and biomaterials; Ligand-receptor binding. Bio-samples have been investigated on lysine-coated glass and mica substrate, and in buffer solution

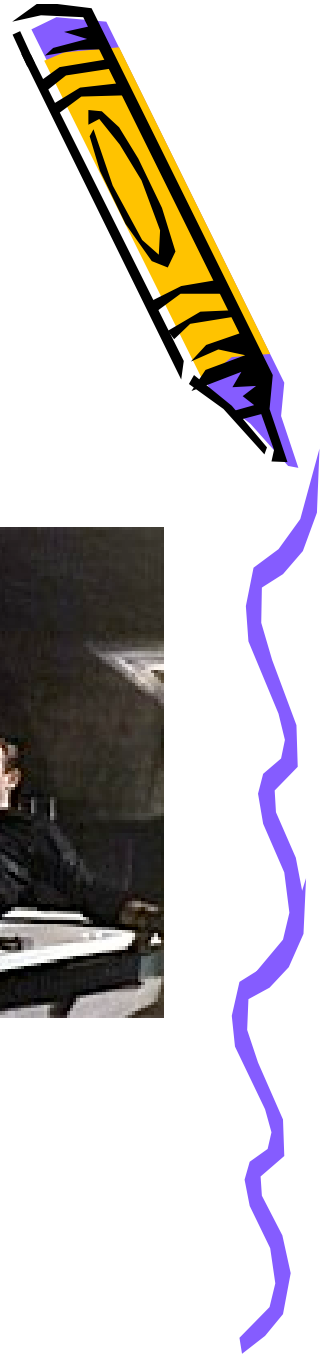


Human Chromosomes. Thanks to Digital Instruments for the picture.

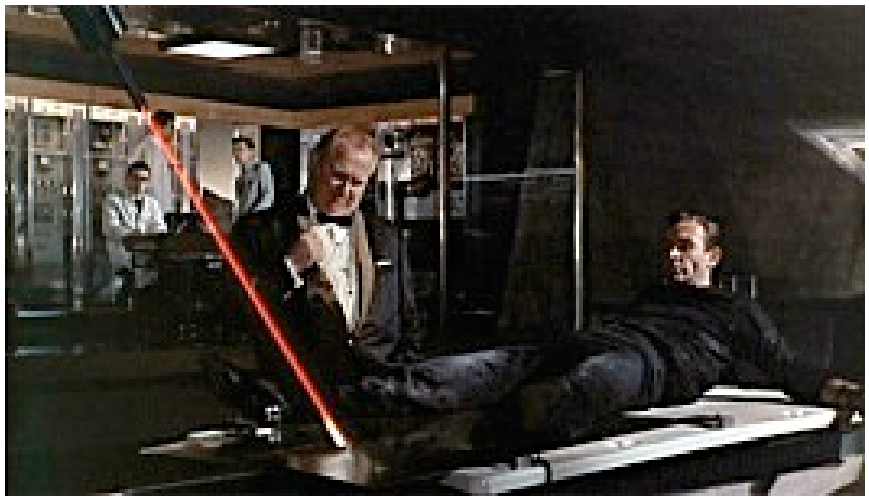


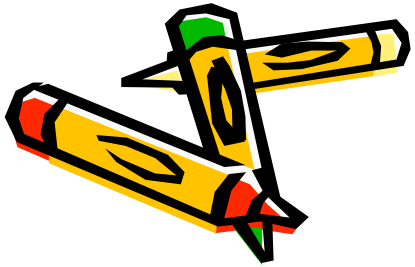
Protein surface layer of D. Radiodurans. Courtesy of Digital Instruments.

Laser Spectroscopy

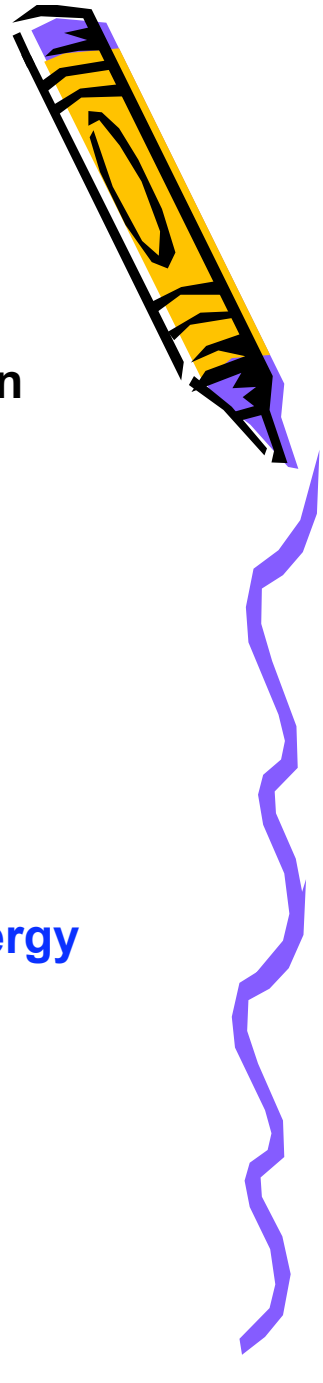


- Lasers are used ubiquitously in physics and chemistry as well as in everyday life. Their impact in chemistry has been nothing less than revolutionary in the areas of spectroscopy, kinetics and dynamics. Domain of electronic transitions





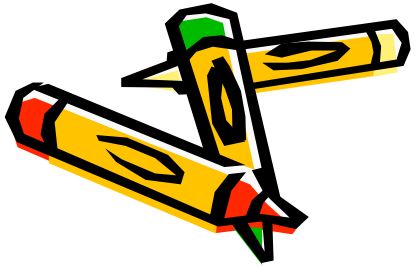
Laser Action – the fundamentals of the Laser



- **The Laser process is based on Stimulated Emission – Light Amplification (by) Stimulated Emission of Radiation.**

- Going to consider:
- 1) The basic processes of light absorption and emission
- 2) The requirements for these to result in intense beams of coherent radiation
- 3)Example of practical lasers

- **Consider a collection of identical quantum systems each of with two energy levels.**
- **There are N_1 systems in level E_1, N_2 in E_2 :**
- **There are three fundamental photo-processes**



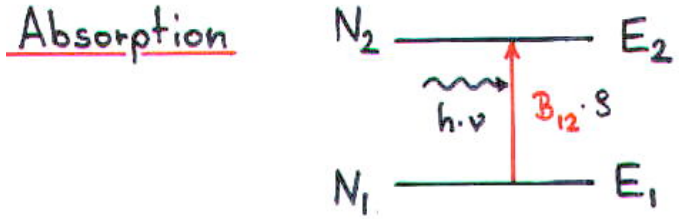
(Stimulated) Absorption

Stimulated Emission

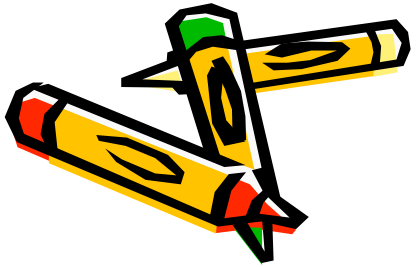
Spontaneous Emission

Laser Action – the fundamentals of the Laser

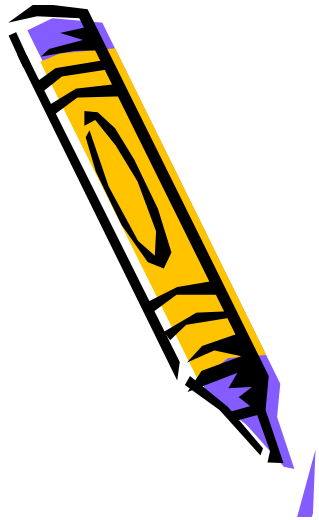
- Absorption requires: $h\nu = E_2 - E_1$
- The rate at which transitions occur depends on the number of molecules in level 1, N_1 ,the density of photons of the correct frequency $\rho(\nu)$, and the probability that a transition takes place $B_{12.}$
-
- Then rate of change of N_1 (same as the transition rate) is:
- **$dN_1 / dt = - N_1 \ \rho(\nu) \ B_{12}$ (-ve as N_1 decreases)**
- [Units are difficult:
- N_1 – number (of molecules) (volume^{-1})
- ∀ $\rho(\nu)$ – number (of photons of freq. ν) J s volume^{-1} – needs additional explanation
- B_{12} – J^{-1} volume s^{-2} – to make the units balance]



Stimulated – as it requires the presence of photons to occur.

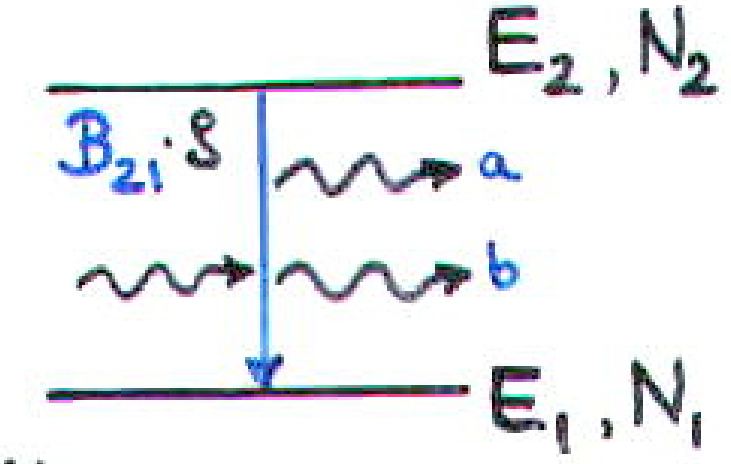


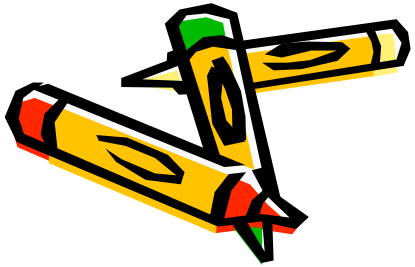
Laser Action – the fundamentals of the Laser



- The opposite process is **Stimulated Emission**:

- The directions of photons a and b is the same.
- $dN_2/dt = - N_2 \rho(\nu) B_{21}$
- Requires presence of photons



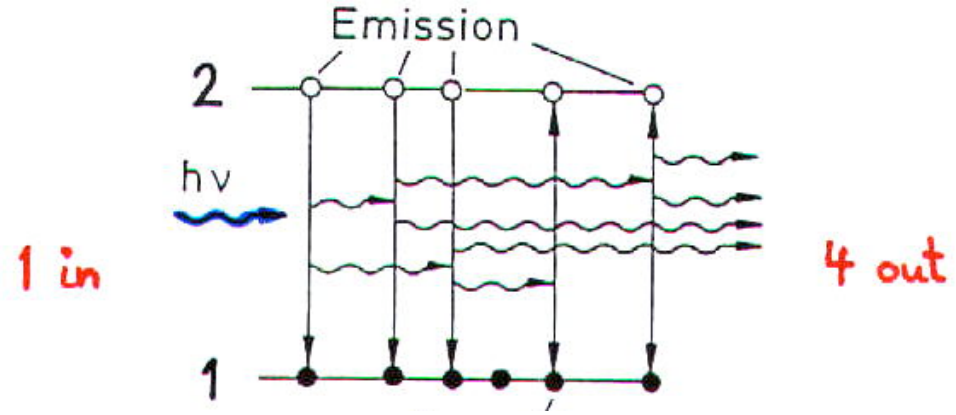


Laser Action – the fundamentals of the Laser

- Spontaneous Emission
- The direction of the emitted photon is random.
- Probability of emission does not depend on photon field
- $d N_2 / dt = - N_2 A_{21}$
- B_{12} , B_{21} and A_{21} are called Einstein Coefficients
- Einstein showed $B_{12} = B_{21}$

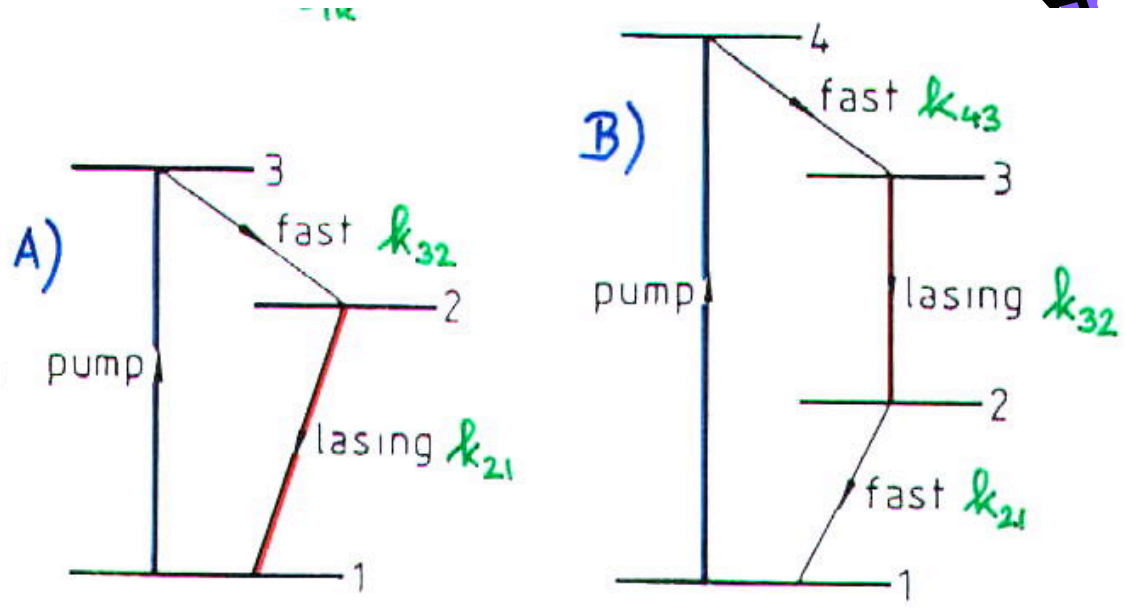
Laser Action – the fundamentals of the Laser

- Basically the laser process involves the Stimulated Emission process – sequential amplification, producing coherent photons.
- This is only a picture. A two level system cannot produce laser radiation.



Laser Action – the fundamentals of the Laser

- In order to achieve laser action have to achieve Population Inversion.
- $N_2 > N_1$ – then the rate of emission will exceed the rate of absorption and there will be a net emission of coherent radiation.
- (For a two level system the limit achievable is $N_2 = N_1$)
- Lasers fall into two types:
- 3 or 4 level lasers



Inversion condition

$N_2 > N_1$

$k_{32} \gg k_{21}$

$N_3 > N_2$

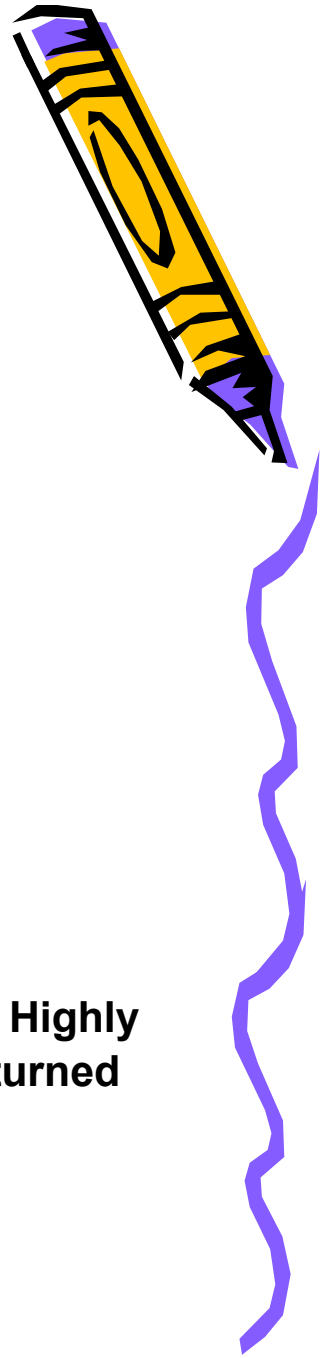
$k_{43} \gg k_{32}$

$k_{21} \gg k_{32}$

Requirements for efficient lasing action

- **For an efficient laser energy must be moved efficiently 1 → 4 → 3 and also 2 → 1.**
- **This allows a population inversion to be established between levels 3 and 2**
- **For the three level laser it is necessary to pump 1 → 3 followed by efficient energy transfer 3 → 2 but the energy is trapped in 2. (2 → 1 very slow.)**
- **Eventually more molecules in the sample are in 2 than are in 1, population inversion has been established and laser action can occur.**

Requirements for laser action

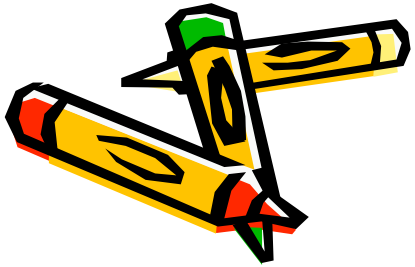


- 1) A pumping mechanism
- 2) A laser medium – gas/solution/solid – that is a three or four level system
- 3) A high density of photons of the correct frequency

- Pumping
  - a) Gas Discharges: dc and pulsed discharges
  - b) Optical pumping: flash(arc) lamps, dc and pulsed; other lasers; …
  - c) Chemical reactions
  - d) Direct electrical pumping

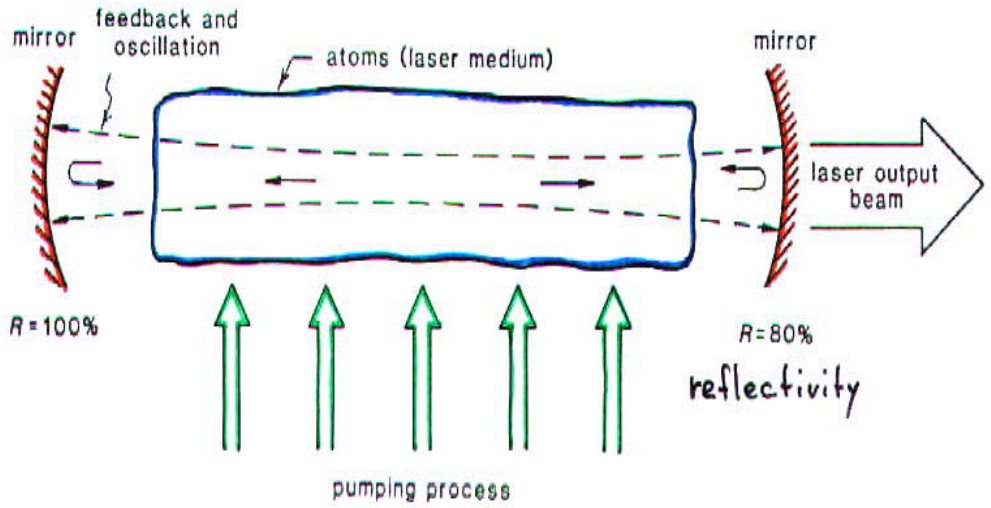
- c and d are unusual.

- To build up large $\rho(\nu)$ – the emitted photons have to retained in the laser medium. Highly reflecting mirrors at opposite ends of the medium. (Or have 'mirrors' that can be turned on/off – Q switching.)



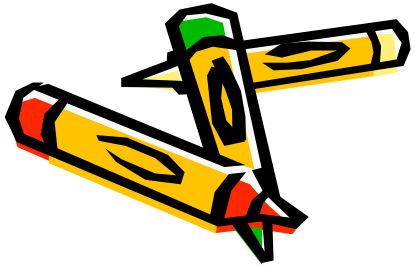
Requirements for laser action

- **In both 3 or 4 level laser medium:**
- **Require efficient pumping to upper lasing level and efficient depletion of lower lasing level to achieve population inversion. ($\Delta N/N$)**
- **After the pump is turned on there is a build up of $\Delta N/N$. At some point – Threshold – stimulated emission dominates spontaneous emission, and:**
- **sudden increase in power**
- **sudden narrowing of range of frequencies**
- **sudden narrowing of spatial distribution and direction**

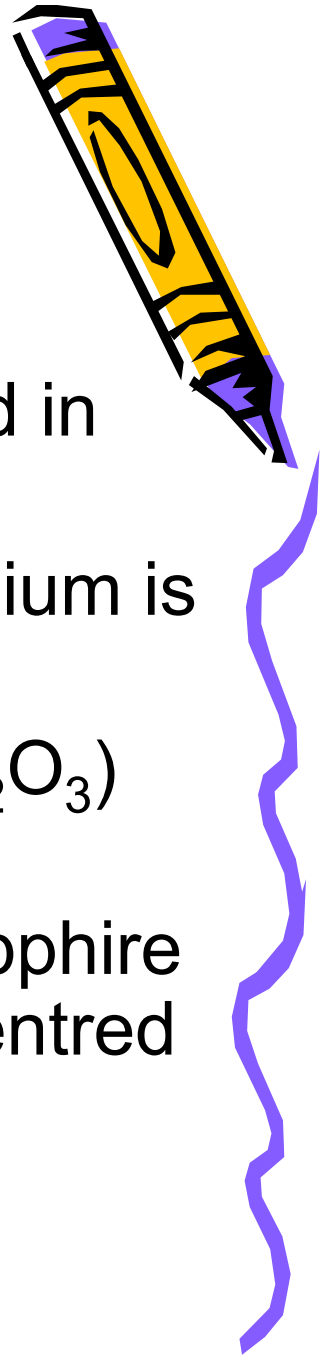


Power and energy of Lasers

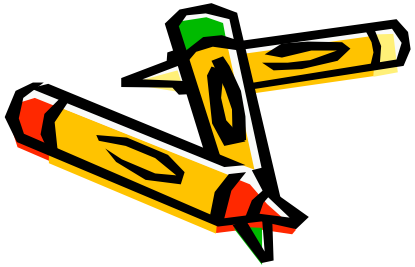
- Power output is energy released in interval divided by duration of interval, units of watts (1W=1 Js^{-1}). Peak power output,P_{peak}, is energy released divided by duration of pulse. Average power output is total energy released by large number of pulses divided by duration time over which total energy measured.
- Laser of 0.1J generates radiation in 3.0 ns pulses at a repetition rate of 10Hz
- P_{peak} = 0.1J / 3.0 * 10^{-9} s = 3.3 * 10^{7} Js^{-1} = 33 Mw
- $P_{average}$= 0.1J x 10 s^{-1} = 1.0 Js^{-1} = 1.0 W



Practical lasers

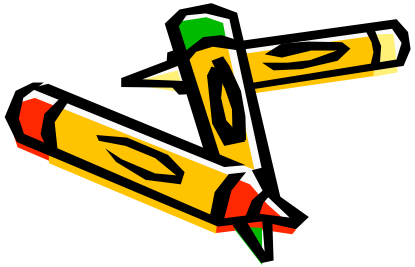


- 4 types:- Solid-state, Gas, Chemical and dye
- Only going to briefly look at solid state lasers and in particular the Titanium Sapphire laser
- A solid state laser is one in which the active medium is in the form of a single crystal or a glass
- Titanium Sapphire laser consists of sapphire (Al_2O_3) doped with Ti^{3+} ions.
- Electronic absorption spectrum of Ti^{3+} ions in sapphire is a characterised by a broad absorption bans centred at around 500nm

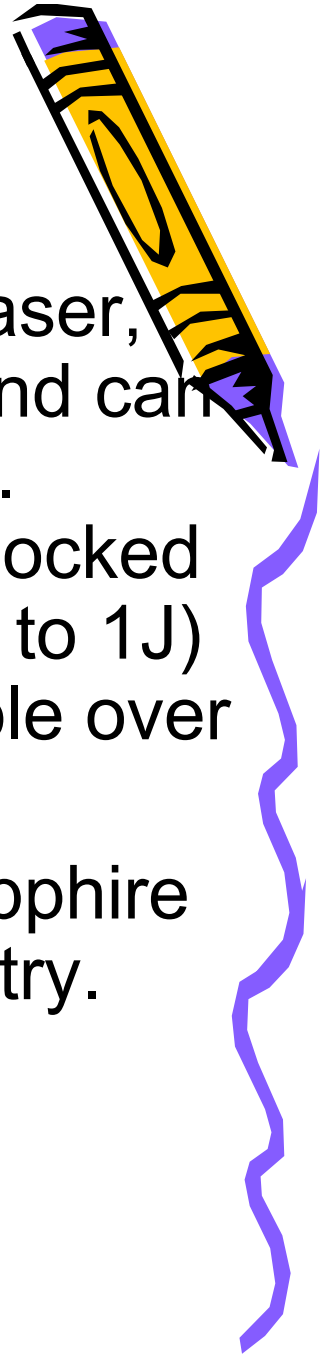


Practical lasers

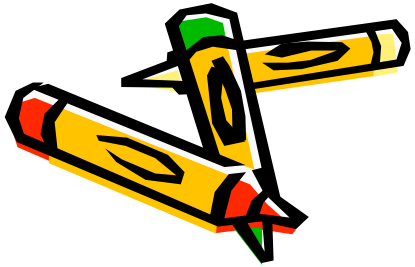
- The broad absorption band arises from vibronically allowed d-d transitions of the Ti^{3+} ion in an octahedral environment provided by oxygen atoms of the sapphire.
- Emission spectrum of Ti^{3+} in sapphire is also broad and laser action occurs over a wide range of λ's.
- Ti:sapphire laser is an example of a **Vibronic laser**, in which laser transitions originate from vibronic transitions in the laser medium



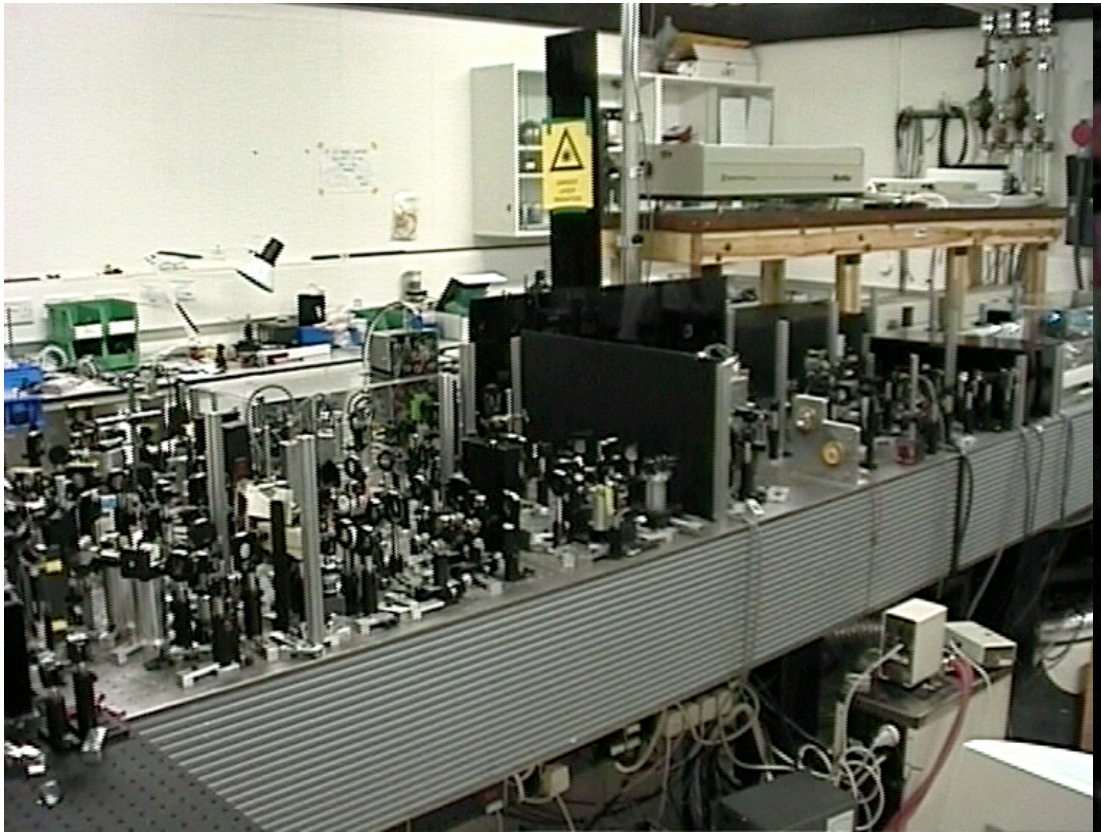
Practical lasers

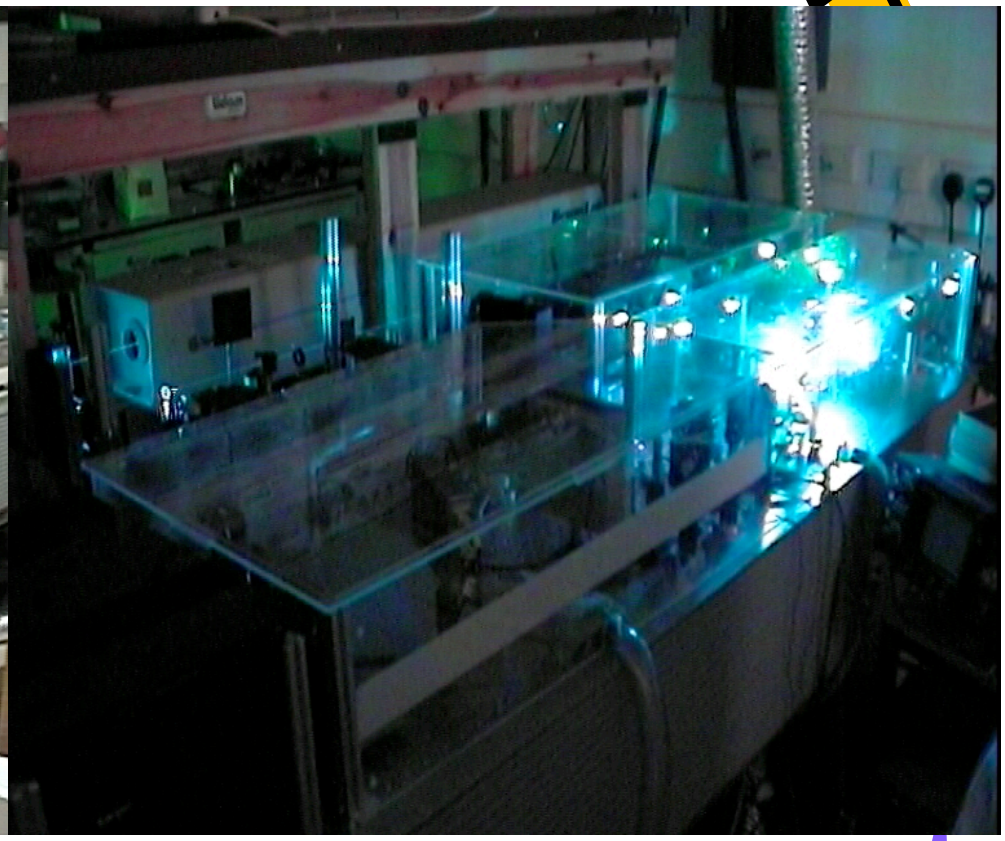


- Ti:sapphire laser is usually pumped by another laser, such as a Nd-YAG laser or an argon-ion laser, and can be operated in both continuous or pulsed modes. Sapphire is a Kerr medium and passively mode-locked Ti:sapphire lasers can produce energetic (20 mJ to 1J) and very short (20-100 fs) pulses, they are tunable over a broad spectrum (700-1000 nm)
- These features illustrate the wide usage of Ti:sapphire lasers in modern spectroscopy and photochemistry.

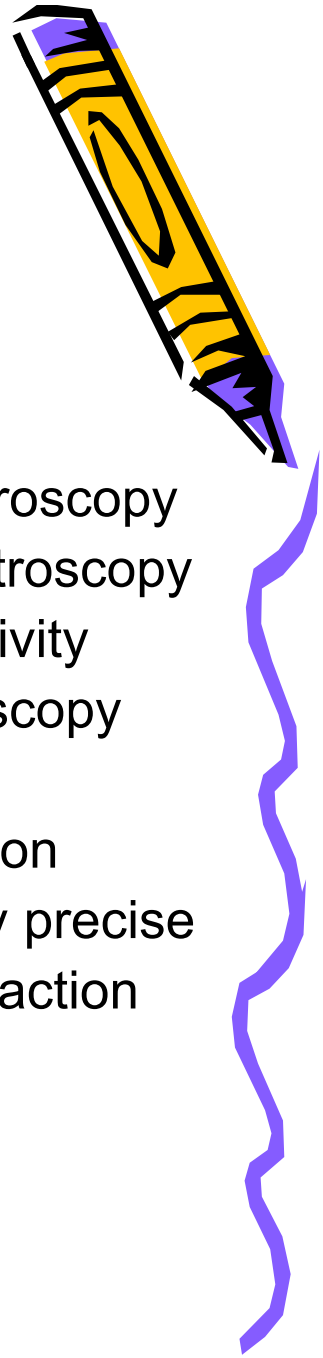


Practical lasers

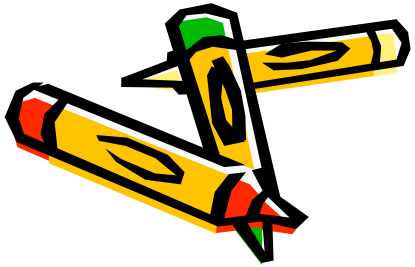




Applications of lasers in chemistry

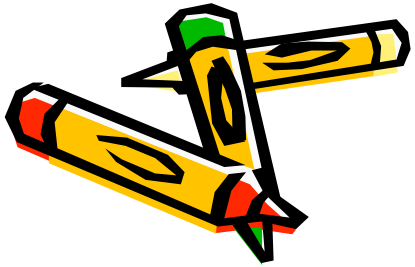


Characteristic	Advantages	Applications
High power	Multiphoton process	Nonlinear spectroscopy
		Saturation spectroscopy
	Low detector noise	Improved sensitivity
	High scattering intensity	Raman spectroscopy
Monochromatic	High resolution	Spectroscopy
	State selection	Isotope separation
		Photochemically precise
		State to state reaction dynamics
Pulsed	Precise timing of excitation	Fast reactions
		Relaxation
		Energy transfer



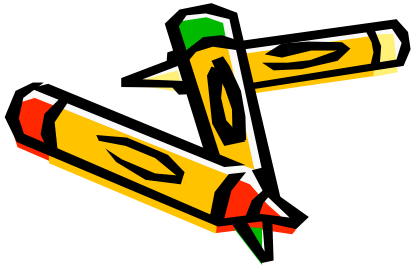
Raman Spectroscopy

- Raman spectroscopy, molecular energy levels are explored by examining the frequencies present in the radiation scattered by molecules. An intense excitation beam increases intensity of scattered radiation, so use of laser sources increases sensitivity of Raman spectroscopy. Well defined beam also implies that the detector can be designed to collect only the radiation that has passed through the sample, and can be screened much more effectively against stray scattered light which can obscure Raman signal
- Monochromaticity of laser radiation is also of great advantage, make possible the observation of scattered light that differs by only fractions of wavenumbers from incident radiation. High resolution useful for observing rotational structure of Raman lines.

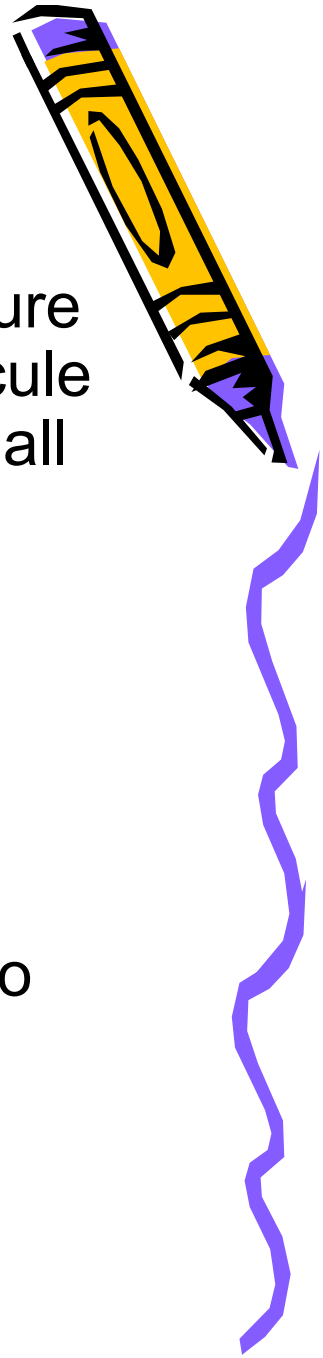


Precision-specified transitions

- Monochromatic nature of laser radiation extremely powerful since it allows us to excite specific states with very high precision. State-specificity for photochemistry means that illumination of a sample may be photochemically precise and hence efficient in stimulating a reaction, since frequency can be tuned exactly to an absorption. Specific excitation of a particular excited state of a molecule may greatly enhance rate of reaction even at low temperatures.



Precision-specified transitions

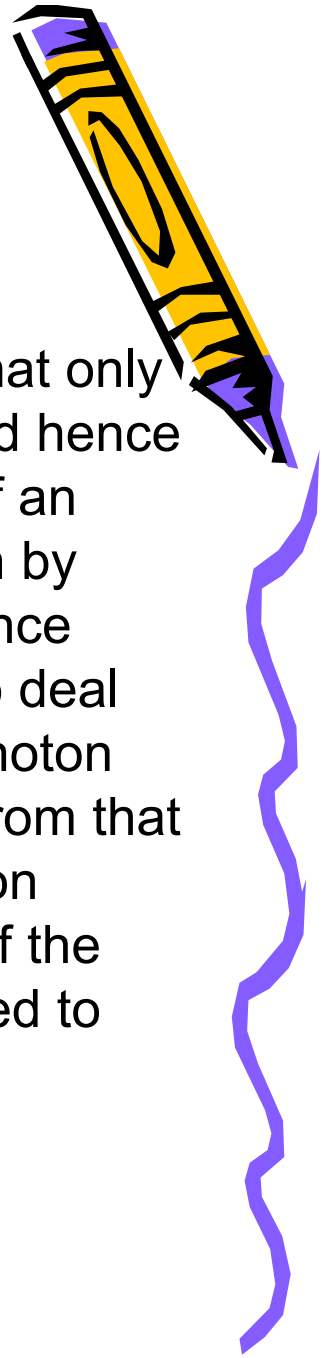


- Rate of a reaction generally increased by raising temperature because energies of various modes of motion of the molecule are enhanced. This enhancement increases the energy of all modes, even those that do not contribute appreciably to reaction rate. A laser can excite the kinetically significant mode, so rate enhancement achieved more efficiently

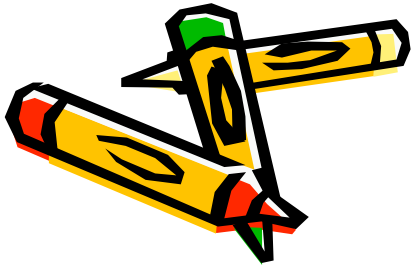
$$BCl_3 + C_6H_6 \text{ ------> } C_6H_5\text{-}BCl_2 + HCl$$

Usually 600^0C in presence of catalyst needed, exposure to CO_2 laser radiation of 10.6 μm results in formation of products at room temperature without using a catalyst,

Isotope separation

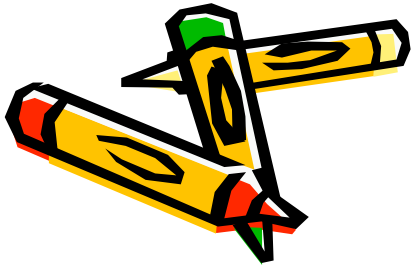


Precision state-selectivity of lasers of considerable potential for isotope separation. Isotope separation possible since two **isotopmers**, species that only differ in their isotopic composition, have slightly different energy levels and hence slightly different adsorption frequencies. Use **photoionization**, ejection of an electron by absorption of electromagnetic radiation. Direct photoionization by absorption of a single photon does not distinguish between isotopmers since upper level belongs to continuum. To distinguish isotopmers necessary to deal with discrete states. At least 2 absorption processes needed. 1^{st} step a photon excites atom to a higher state, 2^{nd} step photon achieves photoionization from that state. Energy separation between two states involved in step 1 depends on nuclear mass. If laser radiation tuned to appropriate frequency only one of the isotopmers will undergo excitation and hence be accessible in step 2. Used to separate ^{235}U from ^{238}U, an important process.

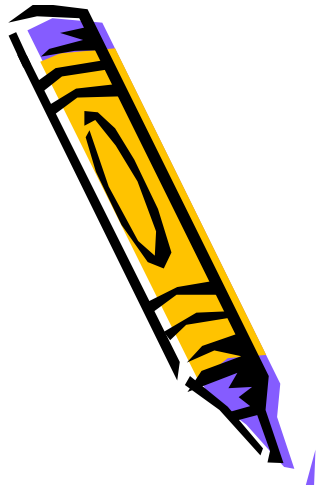


Time resolved spectroscopy

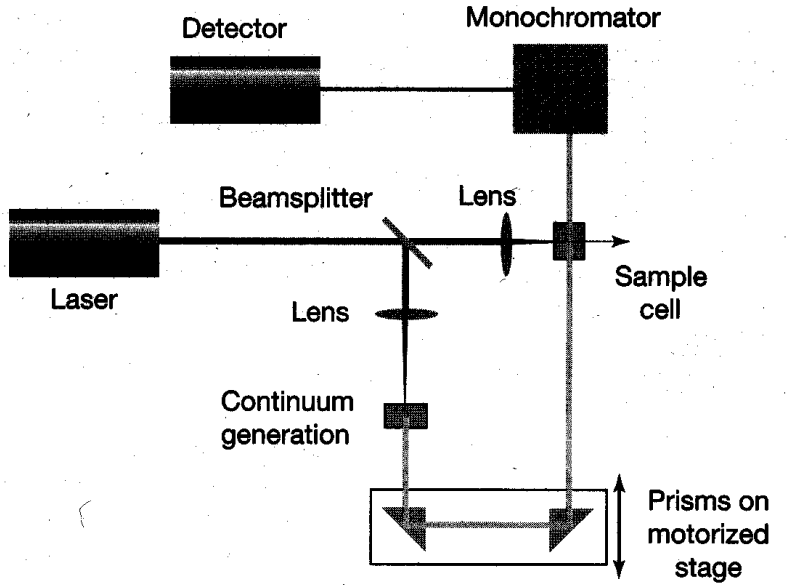
- Mode-locked lasers, i.e. Ti:sapphire, are capable of generating femtosecond pulses which enables the interrogation of the rate at which energy is converted from one mode to another within a molecule. Time resolved spectroscopy can obtain absorption, emission or Raman spectrum of reactants, intermediates, products and even transition states of reactions. Possible to study energy transfer, molecular rotations, vibrations and conversion from one mode of motion to another.

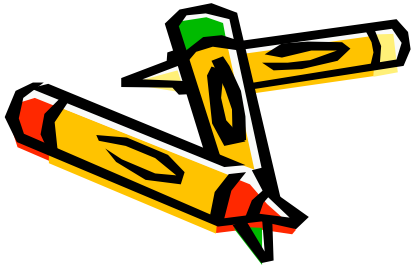


Time resolved spectroscopy

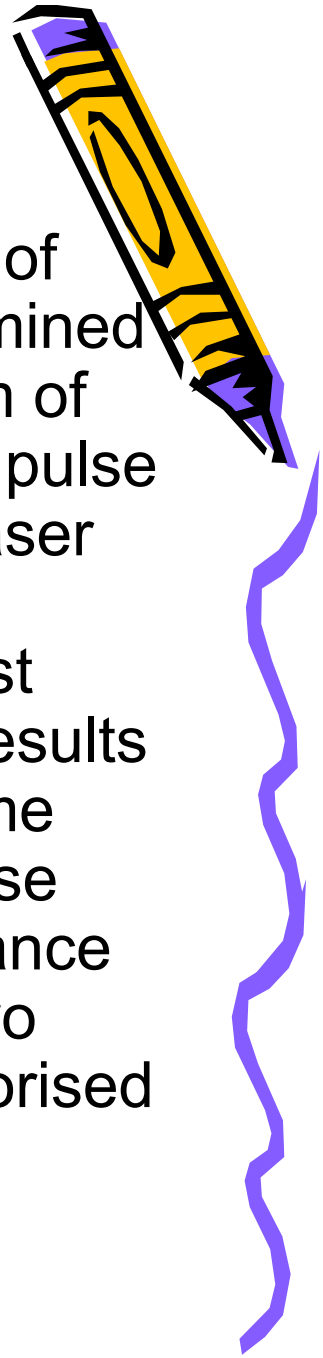


- Strong short laser pulse pumps molecule A to an excited state A^* which can emit a photon or react with another species to B to yield product C
- $A+h\nu$ ---> A^* Absorption
- A^* ----> A Emission
- A^* + B --> [AB] --> C Reaction





Time resolved spectroscopy

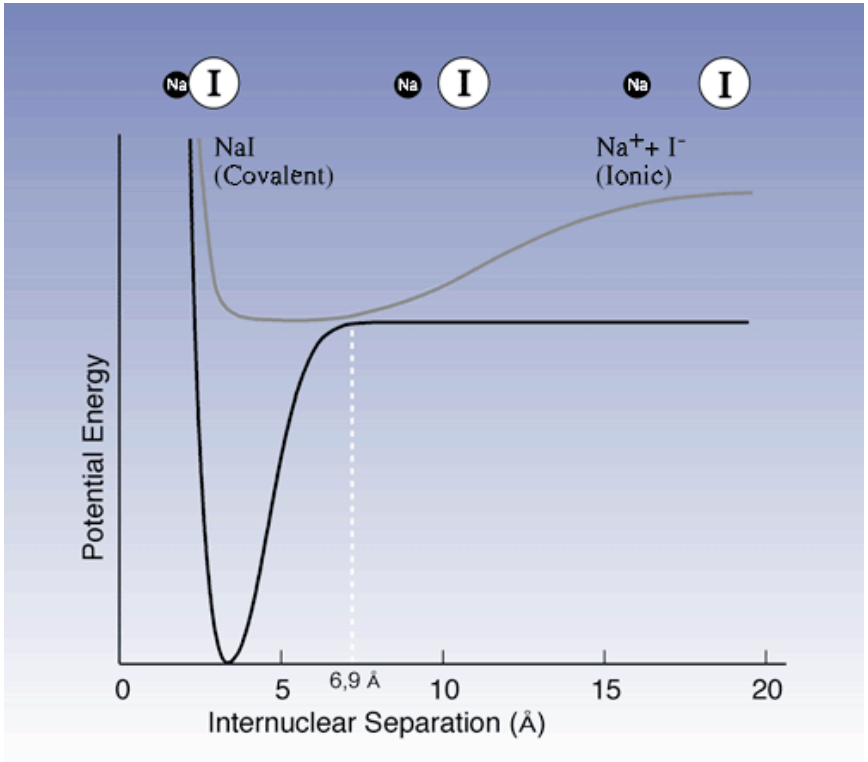


[AB] is either an intermediate or an activated complex. Rates of appearance and disappearance of various species are determined by observing time dependent changes in absorption spectrum of sample during course of reaction. Achieved by passing weak pulse of white light, *probe*, through sample at different times after laser pulse. Pulsed “white” light generated by nonlinear optical phenomenon of **continuum generation** - focusing an ultrafast laser pulse on vessel containing liquid such as H_2O or CCl_4 results in an outgoing beam with wide distribution of frequencies. Time delay between the strong laser pulse and the “white” light pulse introduced by allowing one of the beams to travel longer distance before reaching sample; relative distances travelled by the two beams controlled by directing the “white” light beam to a motorised stage carrying two mirrors

Atomic video camera
Noble prize

In his first experiments Zewail studied the disintegration of iodocyanide: ICN -->I + CN. His team were able to observe a transition state exactly when the I-C bond was about to break: the whole reaction takes place in 200 femtoseconds.

In another important experiment Zewail studied the dissociation of sodium iodide (NaI): NaI --> Na + I. The pump pulse excites the ion pair Na**+** I **-** which has an equilibrium distance of 2.8 Å between nuclei to an activated form [NaI]* which then assumes covalent bonding. However, its properties change when the molecules vibrate; when the nuclei are at their outer turning points, 10-15 Å apart, the electron structure is ionic, while at short distances it is covalent. At a certain point on the vibration cycle, just when the nuclei are 6.9 Å apart, there is a great probability that the molecule will fall back to its ground state or decay into sodium and iodine atoms.



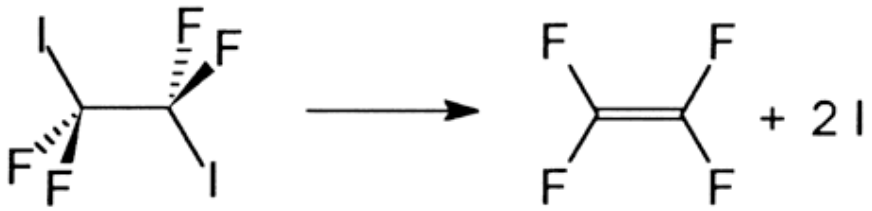
Atomic video camera
Noble prize

Zewail also studied the reaction between hydrogen and carbon dioxide:

$$H + CO_2 \text{ --> } CO + OH$$

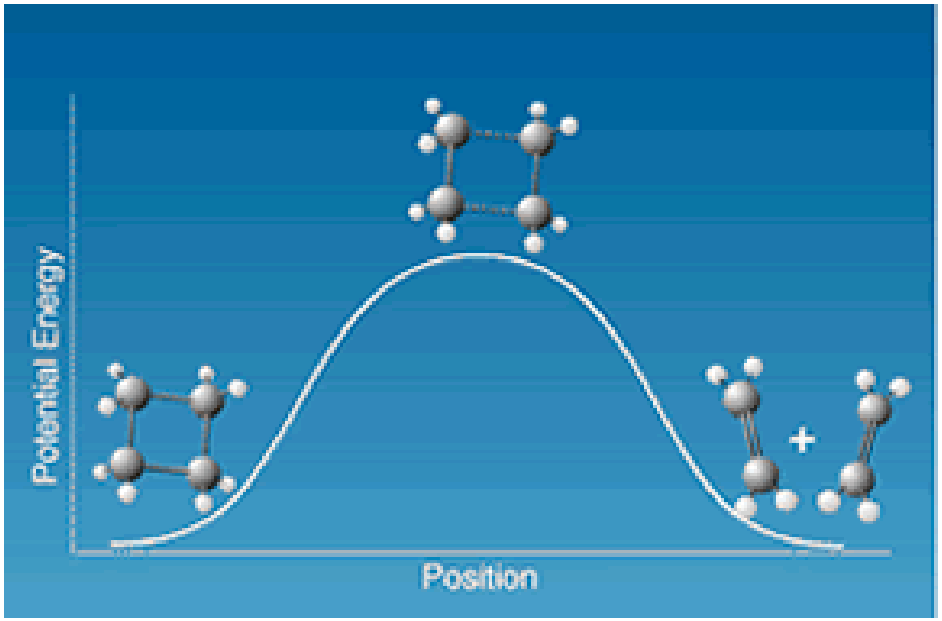
a reaction that takes place in the atmosphere and in combustion. He showed that the reaction crosses a relatively long state of HOCO (1000 fs).

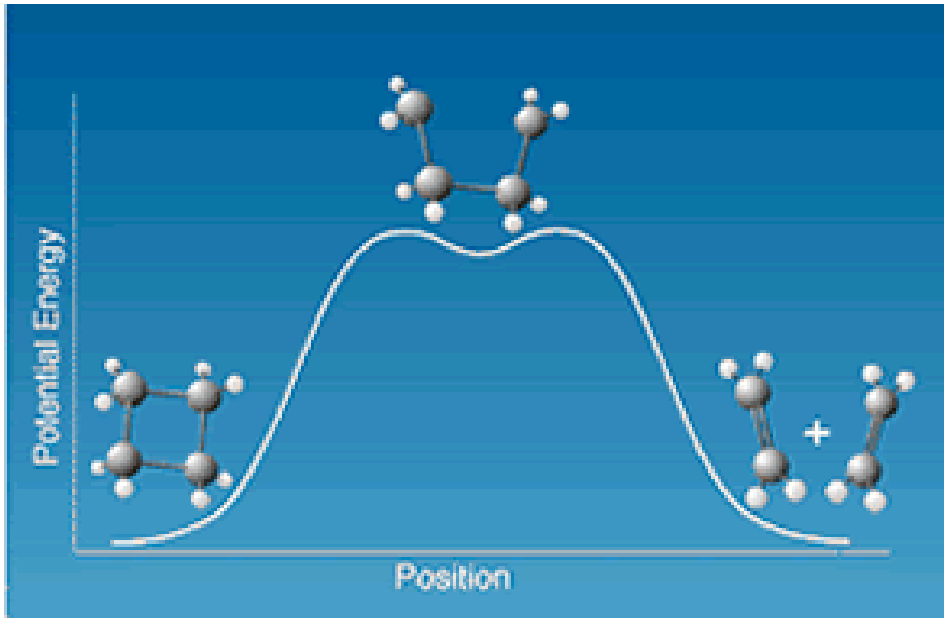
A question that has occupied many chemists is why certain chemical bonds are more reactive than others and what happens if there are two equivalent bonds in one molecule: will they break simultaneously or one at a time? To answer this kind of question Zewail and his co-workers studied the disassociation of tetrafluordiiodethane (CI_2F_4) into tetrafluorethylene (C_2F_4) and two iodine atom



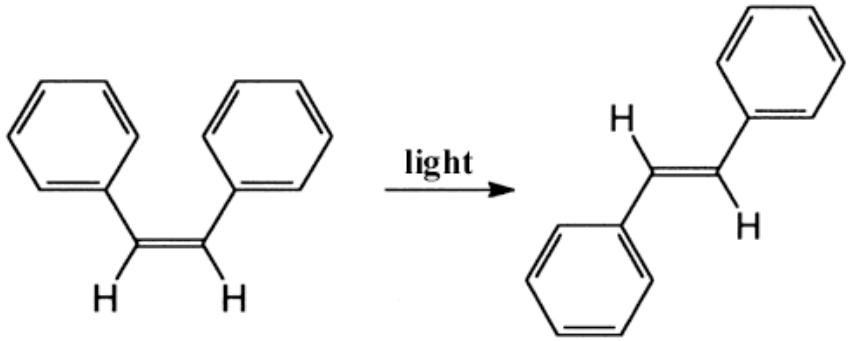
They discovered that the two C-I bonds, despite their equivalence in the original molecule, break one at a time.

A much studied model reaction in organic chemistry is the ring opening of cyclobutane to yield ethylene or the reverse, the combining of two ethylene molecules to form cyclobutane. The reaction may thus go directly via one transition state with a simple activation barrier as shown schematically on the left. Alternatively, it may proceed through a two-stage mechanism (right) so that first one bond breaks and tetramethylene is formed as an intermediate. After crossing another activation barrier the tetramethylene in turn is converted to the final product. Zewail and his co-workers showed with femtosecond spectroscopy that the intermediate product was in fact formed, and had a lifetime of 700 fs.





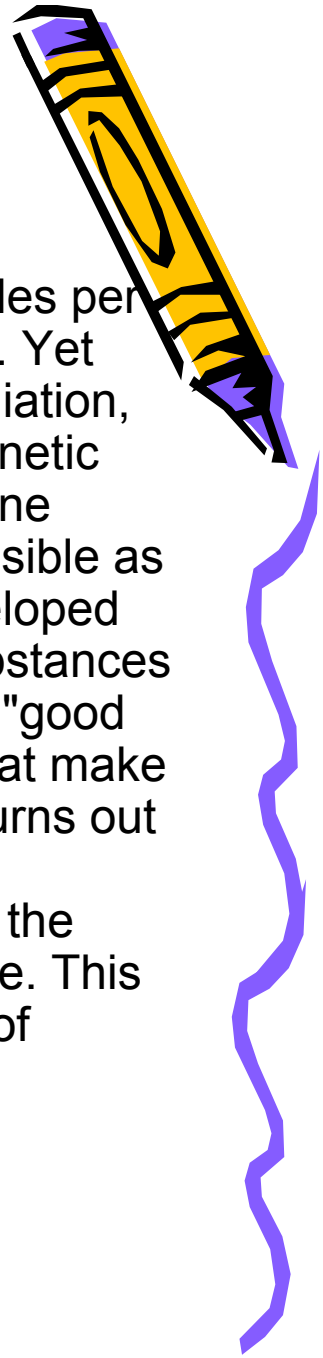
Another type of reaction studied with femtosecond technology is the light-induced conversion of a molecule from one structure to another, *photoisomerisation*. The conversion of the *stilbene* molecule, which includes two benzene rings, between the *cis*- and *trans*- forms was observed by Zewail and his co-workers.They concluded that during the process the two benzene rings turn synchronously in relation to one another.



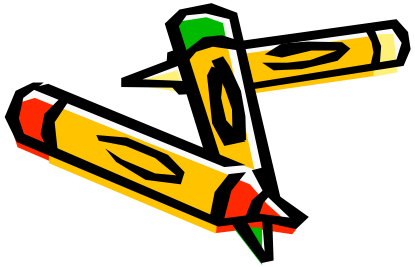
cis-stilbene **trans-stilbene**

Similar behaviour has also been observed for the *retinal* molecule, which is the colour substance in rodopsin, the pigment in the rods of the eye. The primary photochemical step, when we perceive light, is a cis-trans conversion around a double bond in retinal. With femtosecond spectroscopy other researchers have found that the process takes 200 fs and that a certain amount of vibration remains in the product of the reaction. The speed of the reaction suggests that energy from the absorbed photon is not first redistributed but is localised directly to the relevant double bond. This would explain the high efficiency (70%) and hence the eye's good night vision.

Stratospheric Ozone

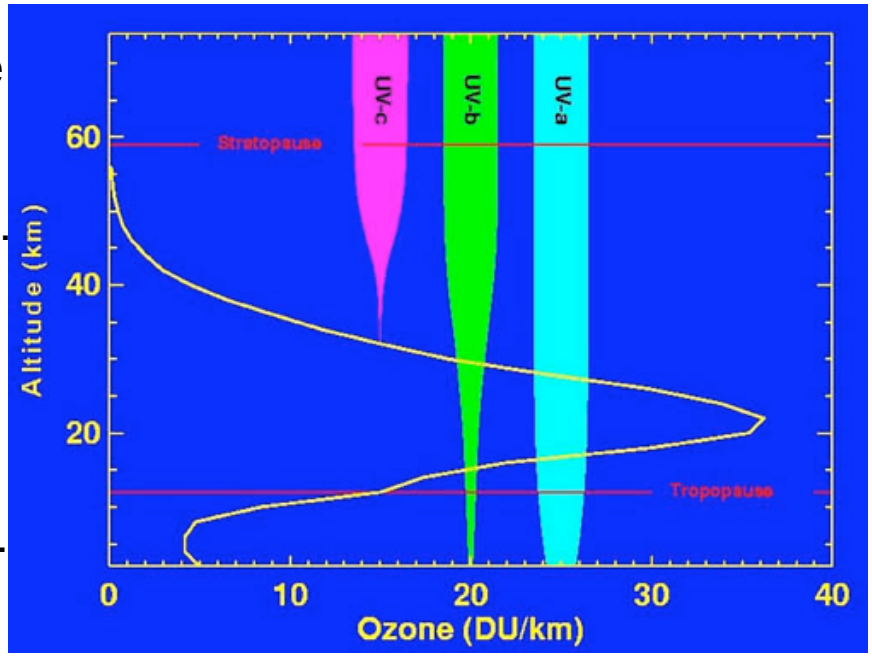


Ozone is a "bad guy" in that breathing it is lethal at dosage levels of a few molecules per million air molecules. This is why ozone at the surface is referred to as a pollutant. Yet ozone high in the atmosphere screens out biologically harmful solar ultraviolet radiation, keeping it from reaching the surface. Such ultraviolet radiation is destructive of genetic cellular material in plants and animals, as well as human beings. Without the "ozone layer" high up in the atmosphere, life on the surface of the Earth would not be possible as we know it.Chlorofluorocarbons (CFCs) are a family of chemical compounds developed back in the 1920's as safe, non-toxic, non-flammable alternative to dangerous substances like ammonia for purposes of refrigeration and spray can propellants. Hence their "good guy" image. Their usage grew enormously over the years. One of the elements that make up CFCs is chlorine. Very little chlorine exists naturally in the atmosphere. But it turns out that CFCs are an excellent way of introducing chlorine into the ozone layer. The ultraviolet radiation at this altitude breaks down CFCs, freeing the chlorine. Under the proper conditions, this chlorine has the potential to destroy large amounts of ozone. This has indeed been observed, especially over Antarctica. As a consequence, levels of genetically harmful ultraviolet radiation have increased.



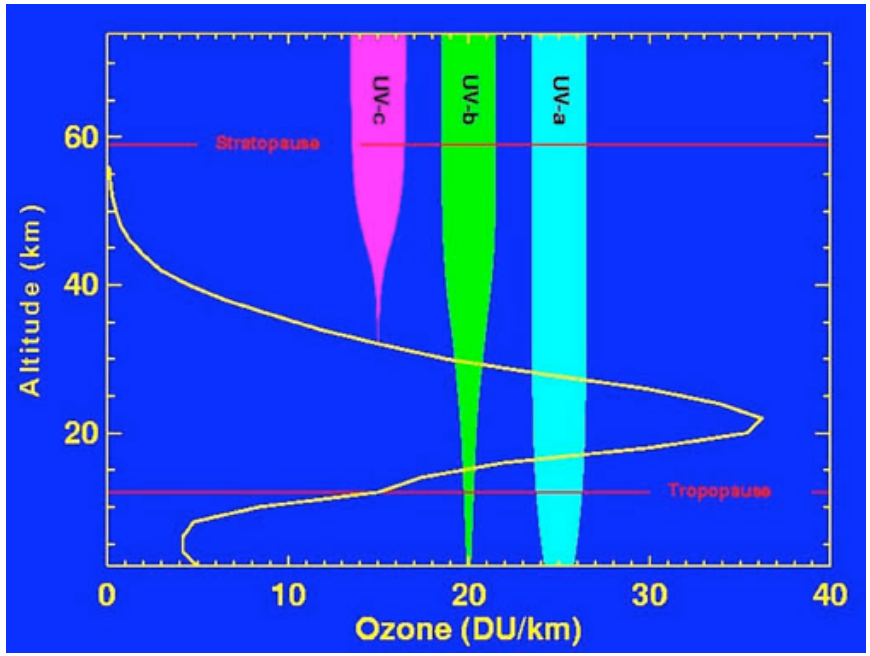
Atmospheric Chemistry
Stratospheric Ozone

A typical vertical profile of ozone in the midlatitudes of the northern hemisphere. The stratosphere lies between the tropopause and stratopause (marked in red). Superimposed on the figure are plots of UV radiation as a function of altitude for UV-a (320-400 nm, cyan), UV-b (280-320 nm, green), and UV-c (200-280 nm, magenta). The width of the bar indicates the amount of energy as a function of altitude. The UV-c energy decreases dramatically as ozone increases because of the strong absorption in the 200-280 nm wavelength band. The UV-b is also strongly absorbed, but a small fraction reaches the surface. The UV-a is only weakly absorbed by ozone, with some scattering of radiation near the surface

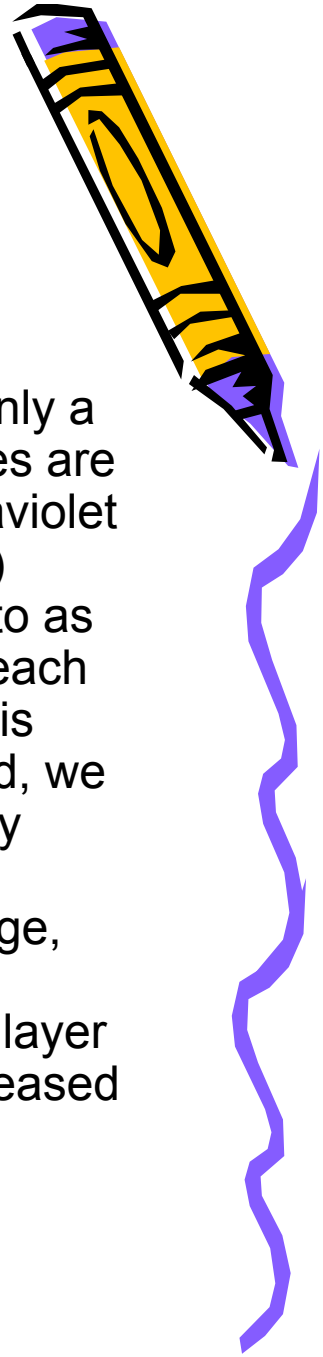


Atmospheric Chemistry
Stratospheric Ozone

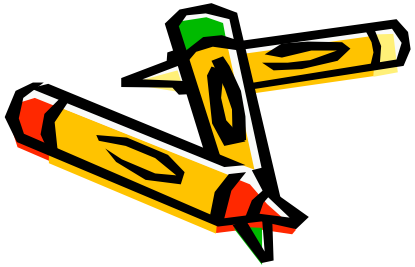
About 90% of the ozone in our atmosphere is contained in the stratosphere, the region from about 10 to 50-km (32,000 to 164,000 feet) above Earth's surface. Ten percent of the ozone is contained in the troposphere, the lowest part of our atmosphere where all of our weather takes place. Measurements taken from instruments on the ground, flown on balloons, and operating in space show that ozone concentrations are greatest between about 15 and 30 km. The yellow curve shows how ozone amount varies with altitude.



Atmospheric Chemistry
Stratospheric Ozone

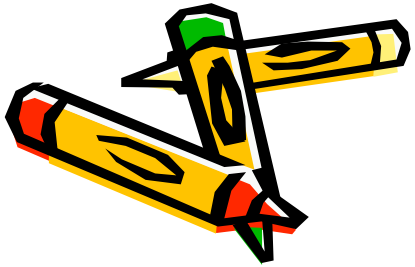


The ozone concentrations shown in the figure are very small, typically only a few molecules O_3 per million molecules of air. But these ozone molecules are vitally important to life because they absorb the biologically harmful ultraviolet radiation from the Sun. There are three different types of ultraviolet (UV) radiation, based on the wavelength of the radiation. These are referred to as UV-a, UV-b, and UV-c. Figure also shows how far into the atmosphere each of these three types of UV radiation penetrates. We see that UV-c (red) is entirely screened out by ozone around 35 km altitude. On the other hand, we see that most UV-a (blue) reaches the surface, but it is not as genetically damaging, so we don't worry about it too much. It is the UV-b (green) radiation that can cause sunburn and that can also cause genetic damage, resulting in things like skin cancer, if exposure to it is prolonged. Ozone screens out most UV-b, but some reaches the surface. Were the ozone layer to decrease, more UV-b radiation would reach the surface, causing increased genetic damage to living things.



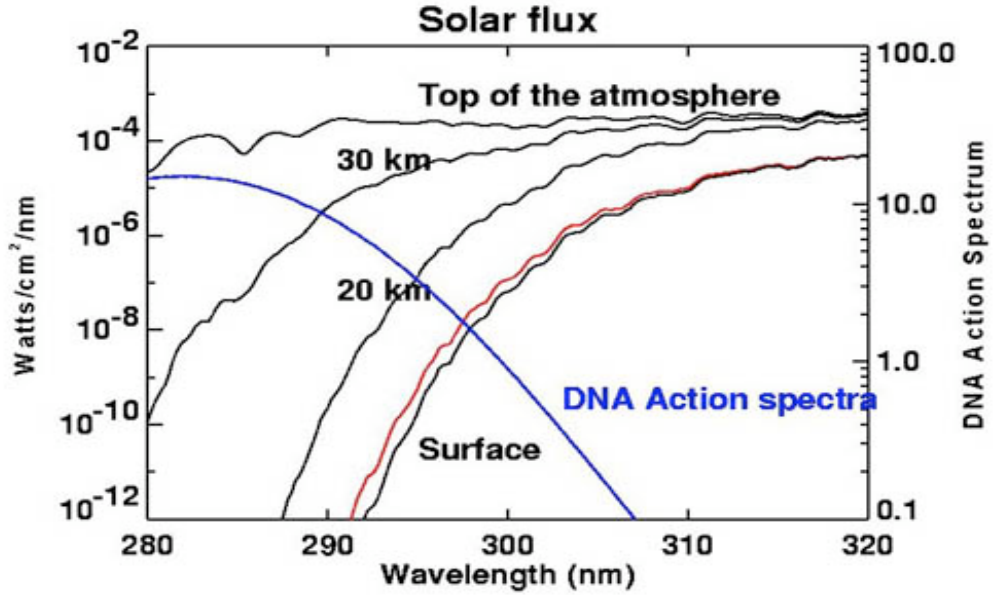
Atmospheric Chemistry
Tropospheric Ozone

Because most of the ozone in our atmosphere is contained in the stratosphere, we refer to this region as the stratospheric ozone layer. In contrast to beneficial stratospheric ozone, tropospheric ozone is a pollutant found in high concentrations in smog. Though it too absorbs UV radiation, breathing it in high levels is unhealthy, even toxic. The high reactivity of ozone results in damage to the living tissue of plants and animals. This damage by heavy tropospheric ozone pollution is often manifested as eye and lung irritation. Tropospheric ozone is mainly produced during the daytime in polluted regions such as urban areas.



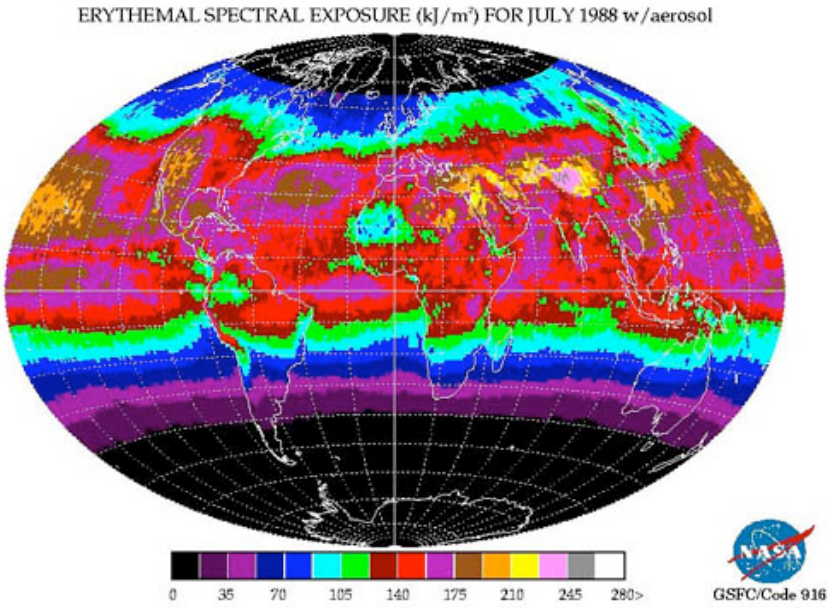
Atmospheric Chemistry
Stratospheric Ozone

To appreciate how important this ultraviolet radiation screening is, we can consider a characteristic of radiation damage called an action spectrum. An action spectrum gives us a measure of the relative effectiveness of radiation in generating a certain biological response over a range of wavelengths. This response might be erythema (sunburn), changes in plant growth, or changes in molecular DNA. The blue line shows the action spectrum for DNA. It represents the probability of DNA damage by UV radiation at various wavelengths. Fortunately, where DNA is easily damaged (where there is a high probability), ozone strongly absorbs UV. At the longer wavelengths where ozone absorbs weakly, DNA damage is less likely. The red line shows the calculated UV spectrum at Earth's surface if there was a 10% decrease in ozone. In response to this decrease in protective ozone, the amount of DNA damaging UV increases, in this case, by about 22%.



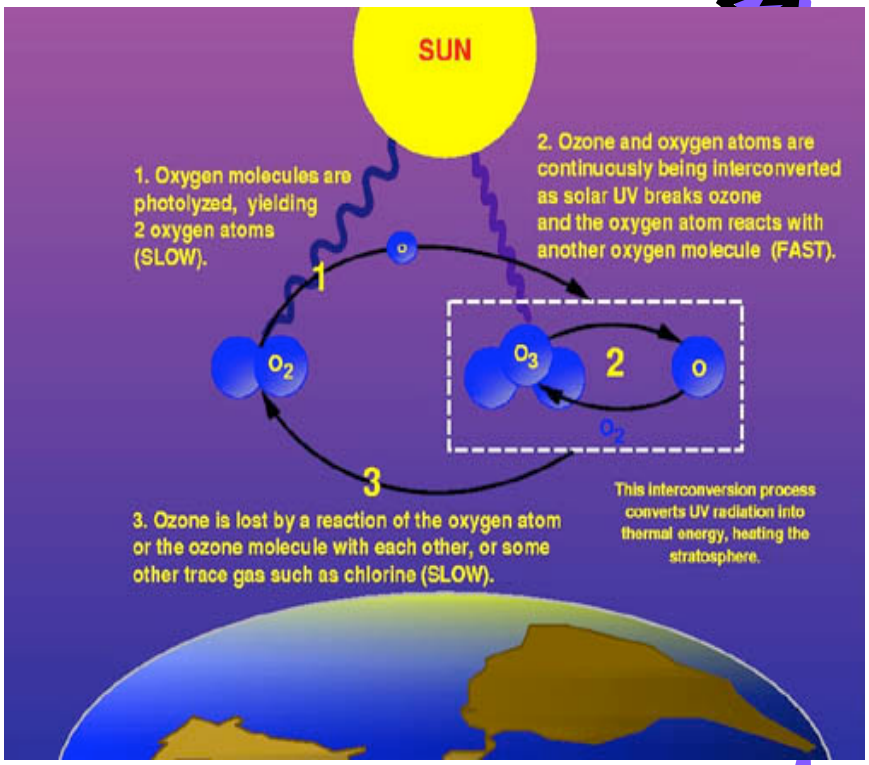
Atmospheric Chemistry
Stratospheric Ozone

Image is derived from satellite observations of the solar UV reflected off Earth's atmosphere detected by the NASA Total Ozone Mapping Spectrometer (TOMS). Intense sunburn-causing UV is shown by the red-orange colors, while lesser values are shown by the blue-purple colors (as indicated by the color scale at bottom of the figure). Tropical regions with low ozone and the Sun high overhead have very intense exposure. High latitude regions with higher ozone amounts and the Sun lower in the sky have rather weak exposures. Higher altitudes in the Rockies and Himalayas also have higher exposure because the column of air that radiation passes through is shorter. Clouds also decrease the UV that is incident on Earth's surface (so cloudiness does have its benefits), though it is possible to get sunburned on a cloudy day.



Schematic Diagram of the Life Cycle of an Ozone Molecule

Illustration of the life cycle of an ozone molecule. In step 1, the oxygen molecule is photolyzed by extreme UV creating two oxygen atoms. In step 2, ozone is photolyzed by UV into and oxygen atom and an oxygen molecule, with a subsequent reaction of this oxygen atom with another oxygen molecule to reform ozone. In step 3, ozone can react with a chlorine atom (among others) to form ClO and O2. The ClO can subsequently react with an oxygen atom to form another oxygen molecule and a Cl atom. This "catalytic reaction" of step 3 results in the conversion of an O3 and an O atom into two oxygen molecules (O2) without affecting the original Cl atom.

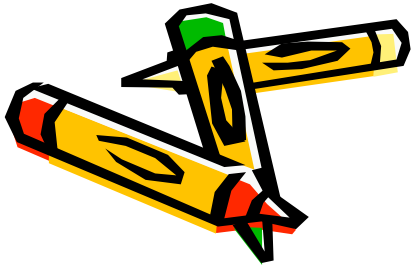


Chapman Cycle for Ozone Production

Ozone photochemistry is driven by the interaction of the Sun's radiation with various gases in the atmosphere, particularly oxygen. The understanding of the basics of ozone photochemistry began with Chapman (1930), who hypothesized that UV radiation was responsible for ozone production and proceeded to lay the foundation of stratospheric photochemistry: the Chapman reactions. He proposed that atomic oxygen is formed by the splitting (dissociation) of O_2 by high energy ultraviolet photons (i.e., packets of light energy with wavelengths shorter than 242 nm) via

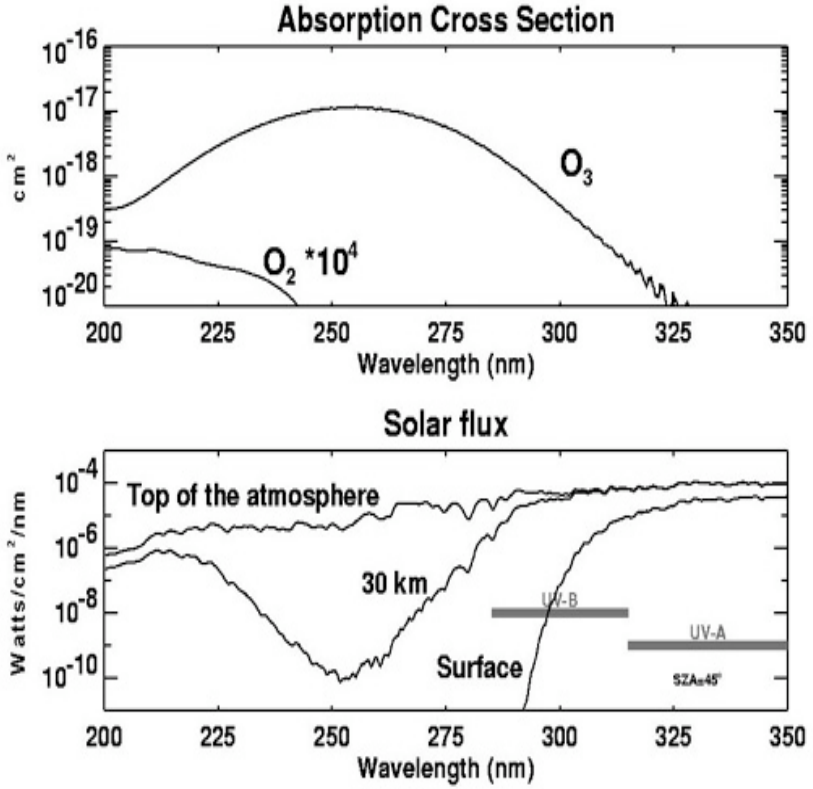
$$O_2 + hc/\lambda \rightarrow O + O$$

Where h is the Planck constant, c is the speed of light, and λ is the wavelength of the photon, given in nm



Chapman Cycle for Ozone Production

The top panel displays the absorption cross section for oxygen multiplied by 10,000. The cross-section is proportional to the probability that a photon from the Sun will be absorbed by an oxygen molecule. While this probability increases for the shorter, more energetic photons, the amount of UV radiation with wavelength shorter than 242 nm reaching into the atmosphere falls dramatically with decreasing altitude.The bottom of panel shows the amount of solar energy per unit area (the flux) of different wavelengths reaching to three different altitudes: the top of the atmosphere, 30 km, and the surface. The amount of very energetic UV (< 242 nm) radiation falls off sharply. Thus, the splitting apart or photolysis of oxygen molecules by solar radiation is relatively slow in the lower and middle stratosphere because the photons of sufficient energy have already been absorbed by molecular oxygen in the upper stratosphere in the Chapman reaction given above. Few such photons are able to penetrate deeply into the atmosphere.

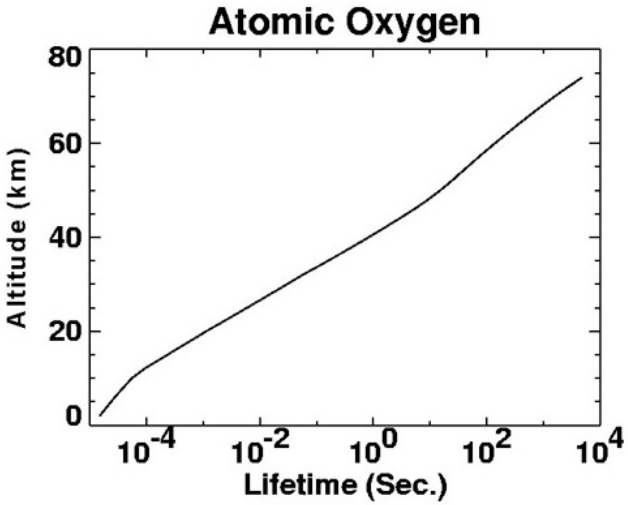


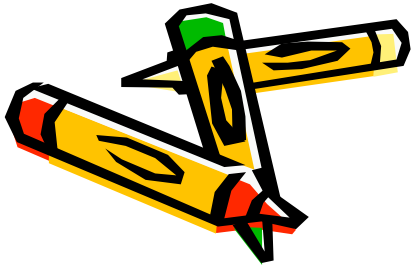
Chapman Cycle for Ozone Production

Oxygen atoms are highly reactive, and quickly react with oxygen molecules to form ozone via

$$O_2 + O + M \rightarrow O_3 + M$$

The M represents any other molecule (most probably N_2 or O_2 since these two molecules comprise 99% of the atmosphere). The third neutral body (M) is needed for the energy balance of the reaction. This particular reaction proceeds at a very fast rate. Figure shows the calculated lifetime of these oxygen atoms as a function of altitude. The lifetime is defined as the time required for the abundance of oxygen atoms (O) to decrease by about 63% (known by most scientists as the e-folding timescale). The lifetime is very short in the stratosphere, typically less than 1 second. Hence, oxygen atoms almost immediately form ozone after they are dissociated.



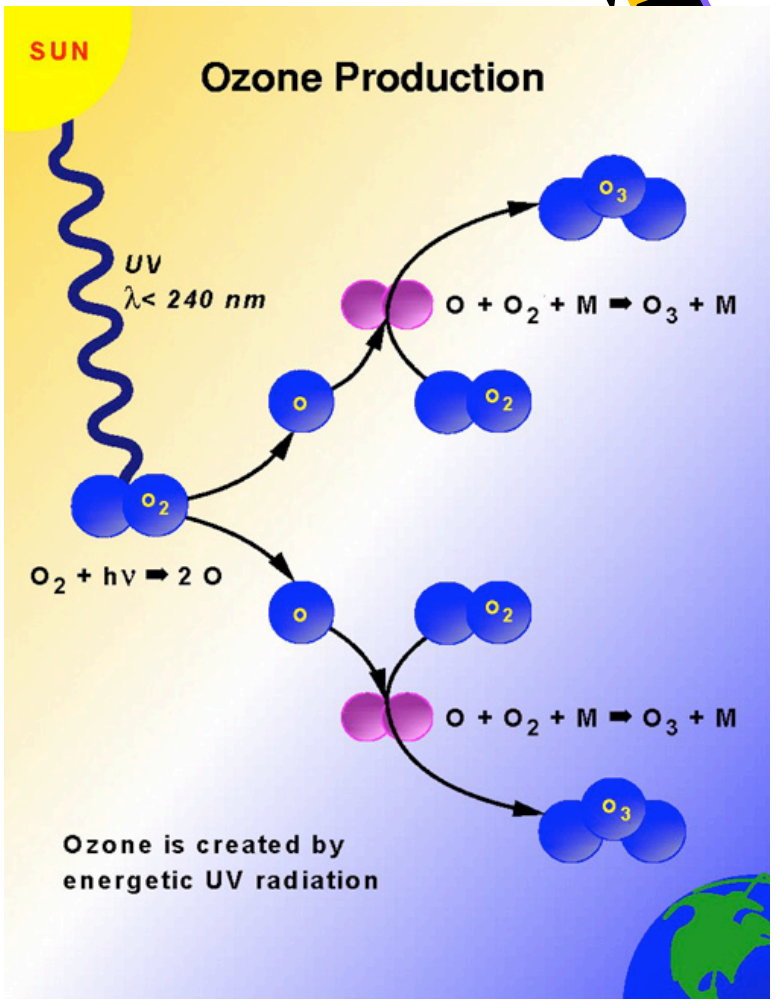


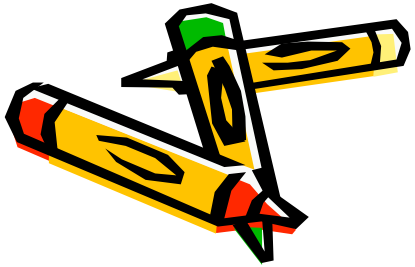
Chapman Cycle for Ozone Production

The ozone molecule is dissociated by these UV photons into O and O_2 via the reaction

$$O_3 + hc/\lambda \rightarrow O_2 + O$$

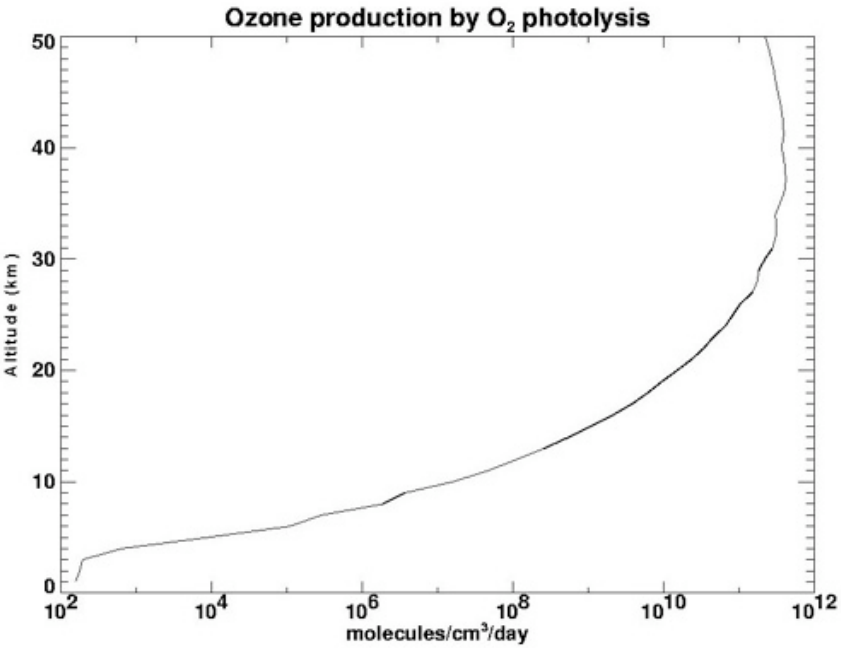
Because O atoms have such short lifetimes, they quickly reform ozone after dissociation, converting the energy of the photons at these wavelengths into thermal energy (note: this thermal energy is the energy which is given to the M atom in the previous equation).The process of ozone photochemical production is summarized in the figure. Ozone is formed when an energetic ultraviolet photon splits an oxygen molecule (O_2). These oxygen atoms quickly react with other oxygen molecules to form ozone. The M molecule shown as the two atom magenta colored molecule carries off the excess energy.



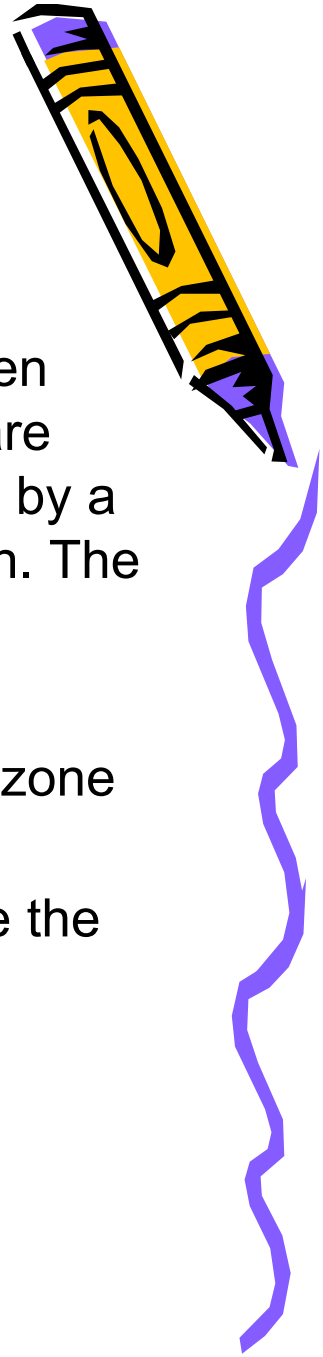


Chapman Cycle for Ozone Production

The production of ozone is estimated by calculating the photolysis of O_2 and assuming the two resulting oxygen atoms will each form an ozone molecule. A vertical profile of this production is shown in the figure. Note that the x-axis scale increases by a factor of 10 for each tick mark. Most of the ozone production occurs in the tropical upper stratosphere and mesosphere. The total mass of ozone produced per day over the globe is about 400 million metric tons! The global mass of ozone is relatively constant at about 3 billion metric tons, meaning the Sun produces about 12% of the ozone layer each day.



Chapman Cycle for Ozone Loss



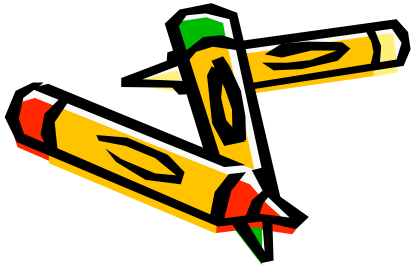
The Chapman cycle for ozone production by solar UV photolysis of oxygen would produce amounts of ozone much greater in the atmosphere than are actually observed. Hence, Chapman also hypothesized that ozone is lost by a reaction with the free oxygen atoms. This ozone loss balances production. The basic loss reaction is

$$O_3 + O \dashrightarrow 2O_2$$

This reaction should be relatively slow in most of our atmosphere since ozone concentrations as a total share of the atmosphere are quite small.

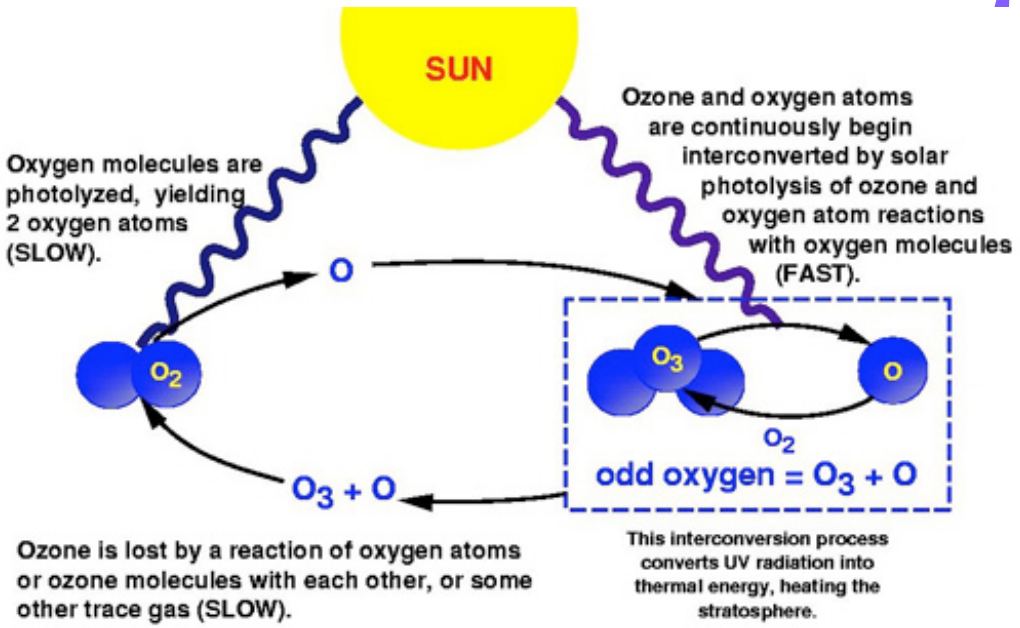
In the ozone loss reaction given above, the reactants are O_2 and O, while the products are the two O_2 molecules. Mathematically,

the decrease of ozone molecules = $k[O_3][O]$

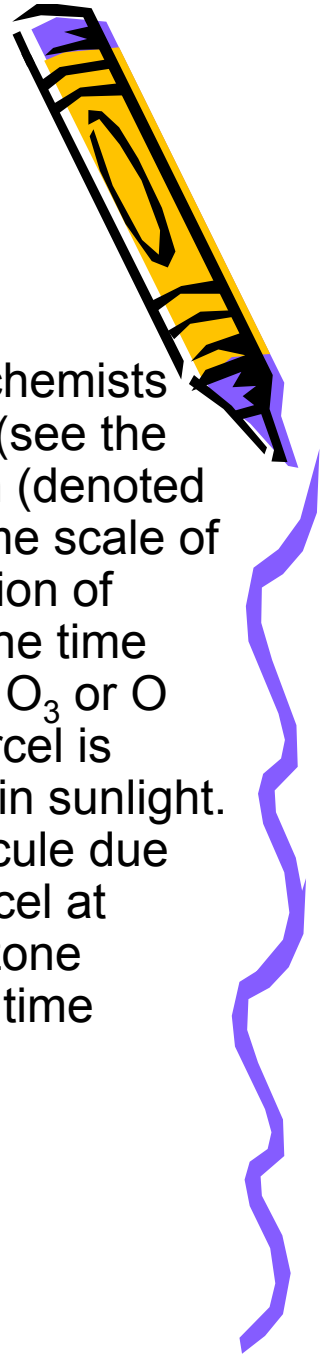


Chapman Ozone Life Cycle

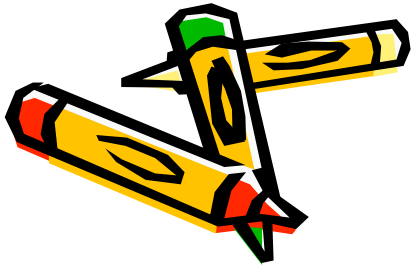
In Chapman's model, this loss process balanced the photochemical production from the photolysis of oxygen molecules. The figure illustrates the Chapman life cycle of ozone. We can conceptualize a balance of production and loss, such that the production is a fixed number that depends on the solar output and overhead screening of UV (top pathway), while the loss process is due to the oxygen atoms and ozone reacting with one another (bottom pathway).



Chapman Ozone Life Cycle

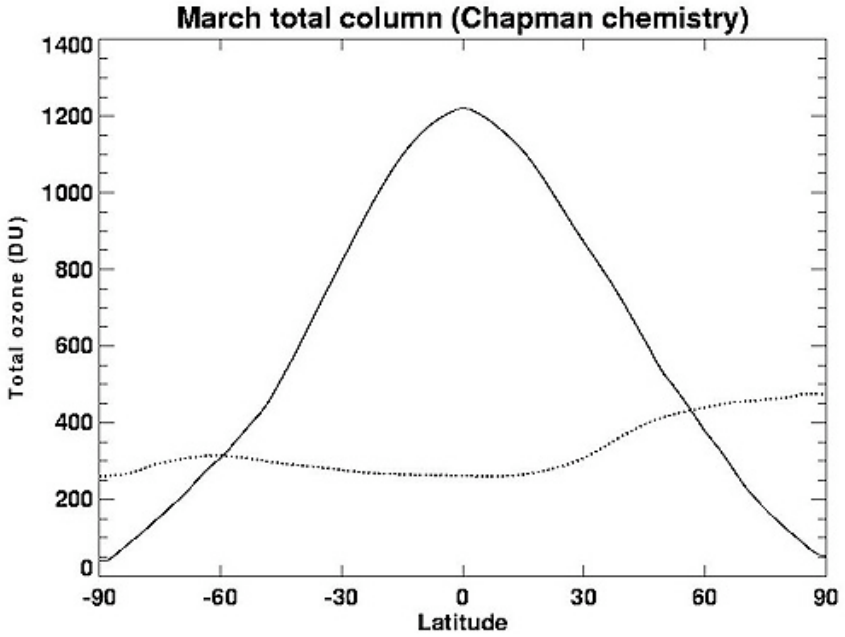


Because oxygen and ozone molecules are rapidly interconverted, atmospheric chemists regard the sum of ozone and oxygen atoms as a "family" known as odd oxygen (see the dashed box on the right hand side of previous figure). The source of odd oxygen (denoted by Ox) is the photolysis of oxygen molecules (a relatively slow process with a time scale of many weeks at 30-km over the equator), and the loss of odd oxygen is the reaction of ozone and oxygen atoms (also a slow process with a comparable time scale). The time between creation and destruction of O_x is much longer than the lifetime of either O_3 or O individually because of this rapid interconversion. All the ozone in a given air parcel is destroyed many times over during the course of a single day when the parcel is in sunlight. Indeed, at an altitude of 30 km above the equator, the lifetime of an ozone molecule due only to UV photolysis is less than 1 hour. However, ozone is reformed in the parcel at almost exactly the same rate through the reaction between O and O_2. Hence, ozone concentrations in the middle stratosphere change only very slowly over the long time scales (weeks to months) of production and loss.



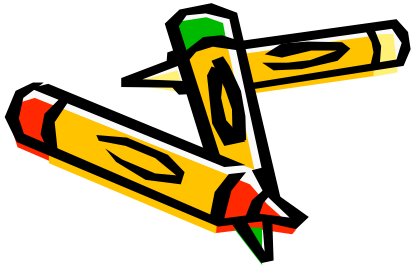
CATALYTIC LOSS AND LIFE CYCLE OF A POLLUTANT

Chapman chemistry does not give the full story behind the atmospheric ozone budget. Simple Chapman chemistry results in ozone amounts much greater than what are actually observed in the stratosphere. Figure displays the total column ozone estimated using Chapman chemistry for March 21, 1993, conditions (solid line) with the actual satellite instrument measurements (dotted line). The measurements were made by the Total Ozone Mapping Spectrometer (TOMS) instrument.



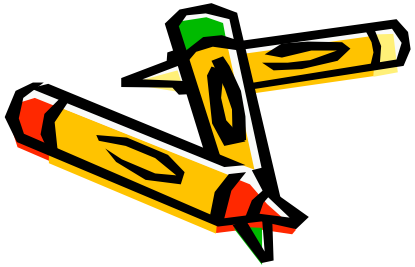
CATALYTIC LOSS AND LIFE CYCLE OF A POLLUTANT

Chapman estimates are much too high in the tropics, and too low in the polar regions. The TOMS-derived global average for column ozone is about 300 Dobson Units (DU). The Chapman production and loss cycle produces a global average of about 790 DU. There is another mechanism at work in addition to the Chapman cycle that reduces the equilibrium amount of ozone. Reactions of O_x with other trace gases alter the ozone budget.. We will examine the effects of these other trace gases, such as hydrogen, nitrogen, chlorine, and bromine, on ozone. Understanding catalytic loss processes is essential to understanding the observed distribution of stratospheric ozone. Several catalytic cycles are important in ozone chemistry.



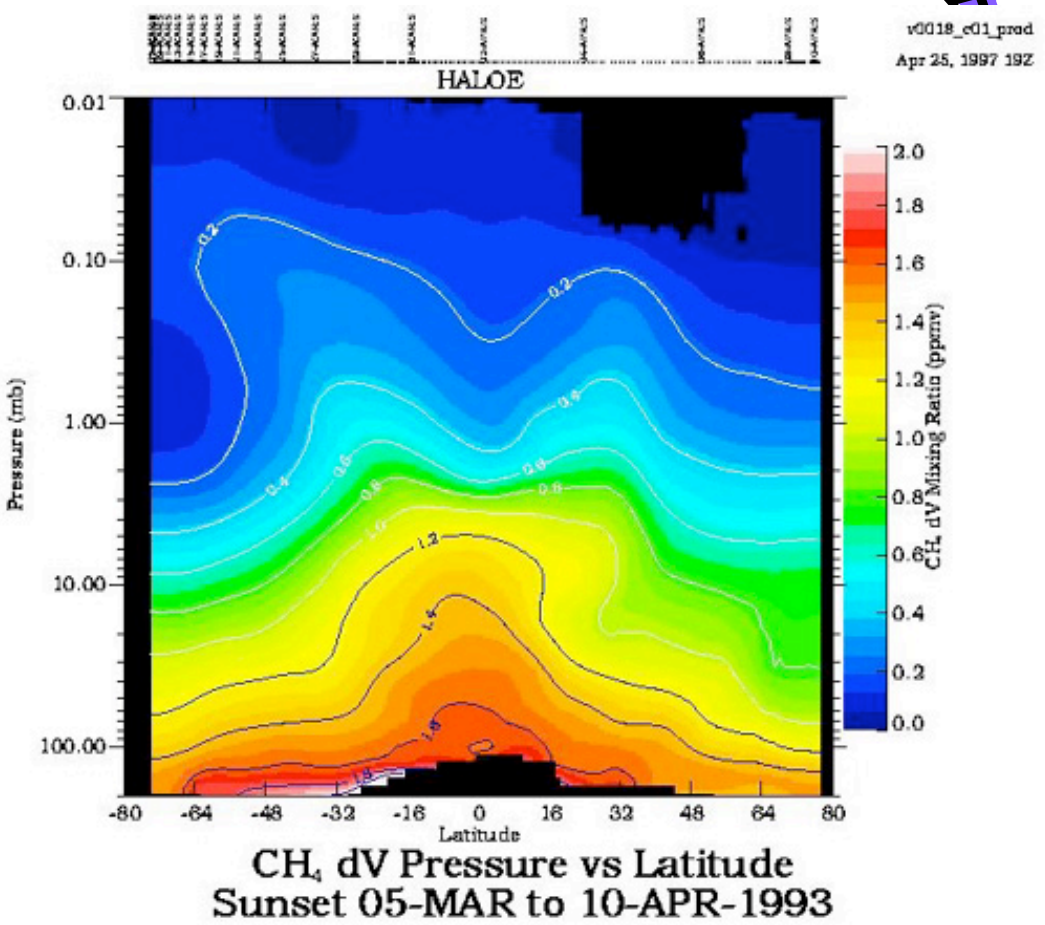
Hydrogen catalytic loss

Examine the impact of reactive hydrogen species (known as HOx, which consists of the hydroxyl radical, OH, and the hydroperoxy radical, HO_2) on ozone chemistry. Hydrogen is transported into the stratosphere in the form of methane (CH_4) and water vapor (H_2O) molecules. Both of these molecules have large sources in the troposphere



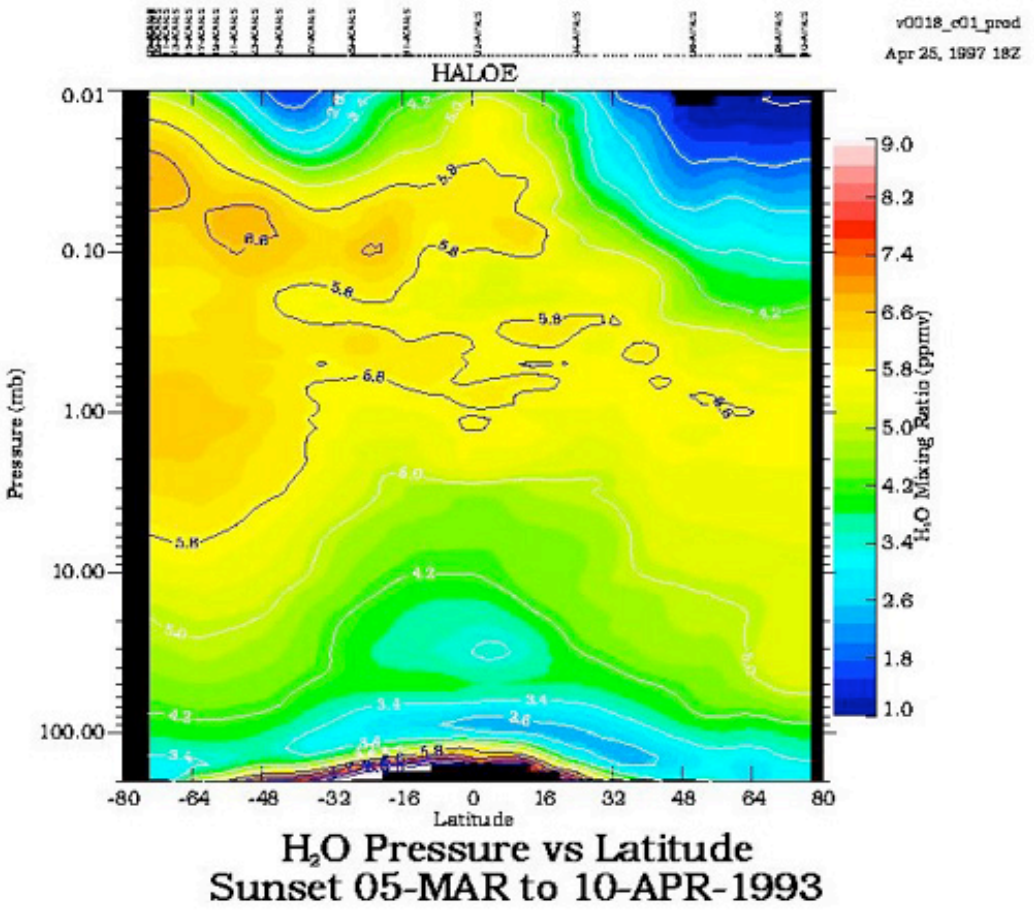
Methane distribution

A typical methane distribution is shown in the figure with data from the Halogen Occulation Experiment (HALOE) instrument aboard the Upper Atmospheric Research Satellite (UARS) taken March 5 to April 10, 1993. The figure shows that methane amounts are largest in the troposphere and decrease steadily through the stratosphere.The source of methane in Earth's atmosphere can be traced to its release at the surface through a variety of sources: wood combustion, coal mining, oil and gas drilling and refining, landfills, wetland rice cultivation, crop residue burning, industrial activity, and digestive action by grazing animals (i.e., cow flatulence).

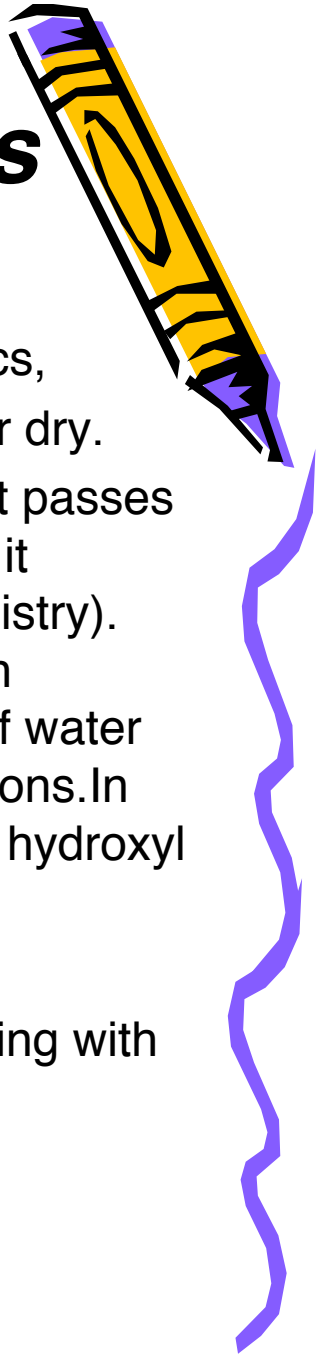


Water Vapour distribution

Figure shows a typical water vapor distribution, again using data from HALOE taken during March and early April 1993. We see the same tropical lifting action where the water vapor mixing ratio contours are bowed upwards, but the amounts quickly fall off in the lower stratosphere. Unlike methane, though, water vapor actually begins to increase above the lower stratosphere, with elevated values in the mesosphere. The explanation for the difference in behavior of these two trace species is connected to both the chemistry and temperature structure of the atmosphere



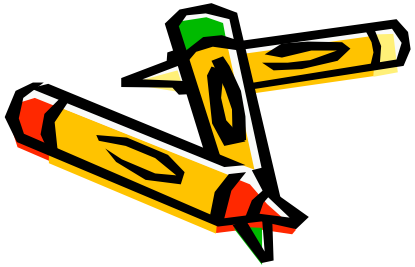
Methane photodissociation reactions



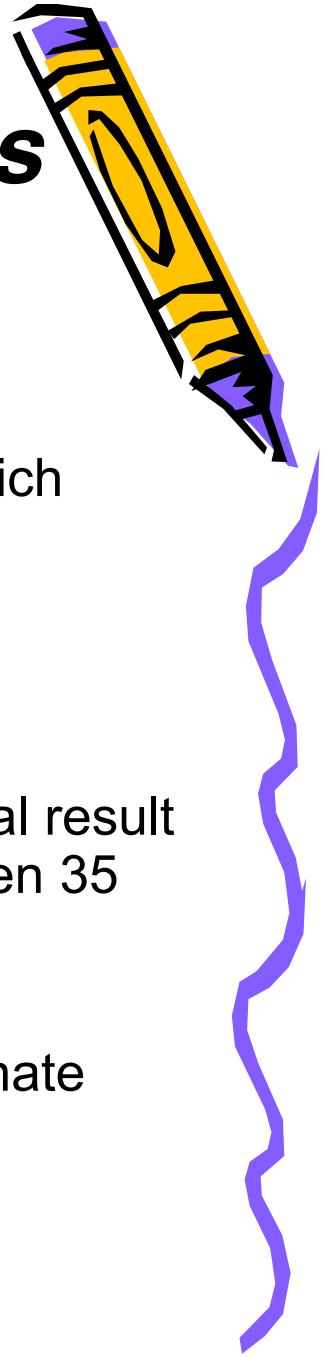
The tropopause is the very cold boundary between the troposphere and the stratosphere. As moist air is lofted upward through the tropopause in the tropics, water vapor is frozen out. Air entering the stratosphere, consequently, is rather dry. On the other hand, methane remains unaffected by the cold temperatures as it passes through this boundary. Only when methane reaches the upper stratosphere is it depleted via oxidation reactions with OH (a very important player in HO_x chemistry). These reactions lead to the production of water vapor molecules. Indeed, each methane molecule eventually is converted to (almost exactly) two molecules of water vapor in the middle to upper stratosphere via the following two oxidation reactions.In the first reaction, methane is converted into water vapor by a reaction with the hydroxyl radical OH.

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

The second reaction involves a series of steps that begins with methane reacting with the singlet D oxygen atom, denoted O(1D).



Methane photodissociation reactions



The reaction is

$$CH_4 + O(1D) \rightarrow CH_3 + OH$$

The result is a hydroxyl radical and a leftover methyl radical (CH_3), which quickly reacts via

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

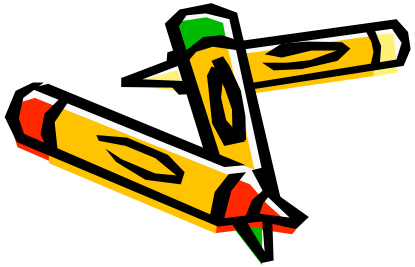
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

Eventually, reactions of HCHO (formaldehyde) with the hydroxyl radical result in the production of another water vapor molecule in the region between 35 and 45-km

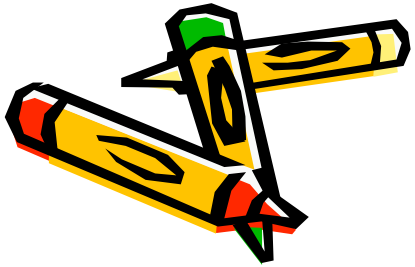
$$HCHO + OH \rightarrow CHO + H_2O$$

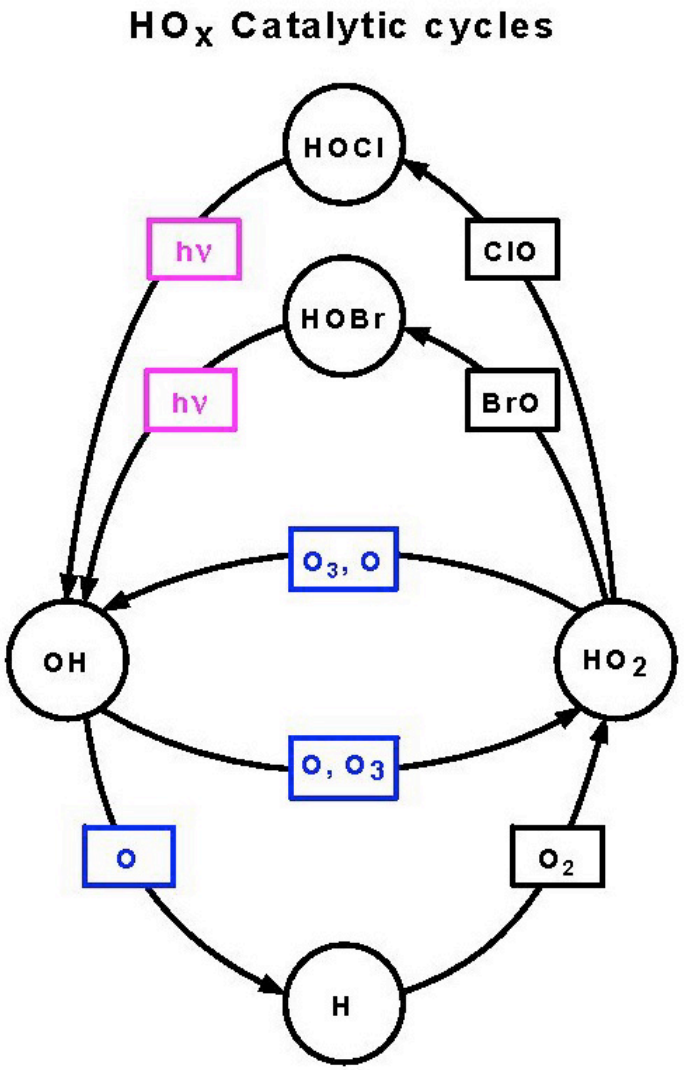
Above about 65 km, photodissociation of methane becomes the dominate mechanism for methane loss



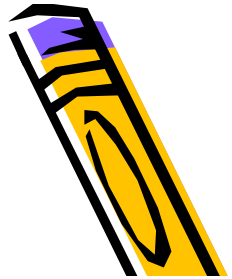
HO_x catalytic cycles

The importance of these two species, methane and water vapor, in ozone chemistry is that they transport and release hydrogen into the stratosphere. The activated hydrogen that is released can then participate in the destruction of odd oxygen, i.e., ozone, through a variety of catalytic cycles. These reactive hydrogen (HOX) cycles are summarized by the figure. The open circles show the predominant species in which hydrogen exists in the stratosphere. We have not included H2 (molecular hydrogen), H2O (water vapor), and CH4 (methane) since they are not involved in the fast stratospheric hydrogen photochemistry balance. The arrows with superimposed boxes are reaction pathways





HO_x catalytic cycles



Each water vapor molecule can be transformed into two molecules of HO_X (reactive hydrogen) through reaction with O atoms via a reaction of water vapor with the singlet D oxygen atom.

$H_2O + O(1D) \rightarrow 2\ OH$

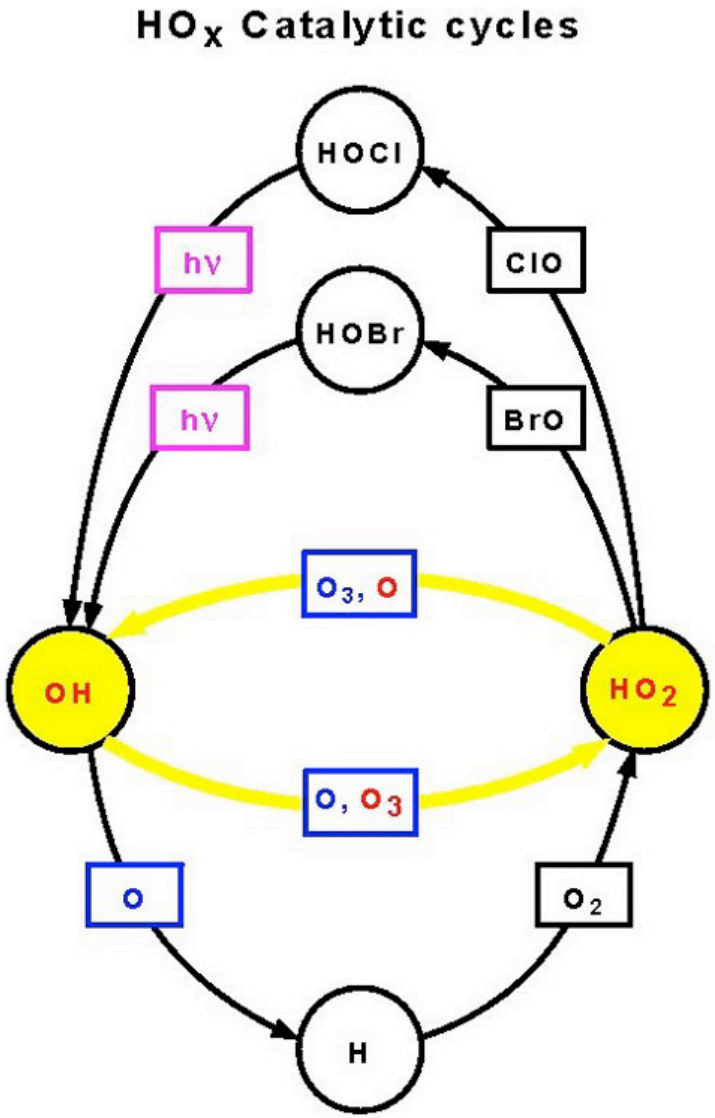
Recall that HOX = OH + HO_2. In this case, the reactive hydrogen exists in the form of two liberated OH (hydroxyl radical) molecules which become the catalyst in a pair of reactions with odd oxygen (O_X) that result in a net loss of O_X, by which we mean a net loss of both ozone molecules and free oxygen atoms.

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

NET: $O_3 + O \rightarrow 2\ O_2$

The sum of reactive hydrogen, OH + HO_2, is conserved by this cycle.



HO_x catalytic cycles

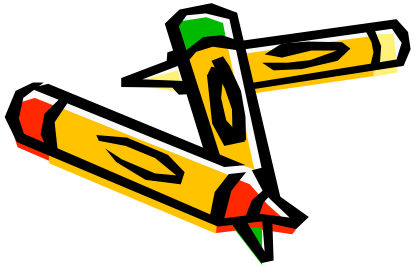
This catalytic cycle involving HO_x will only be disrupted if HO_X is lost through another mechanism. Several reactions can remove HO_x from this cycle

$$OH + HO_2 \rightarrow H_2O + O_2$$

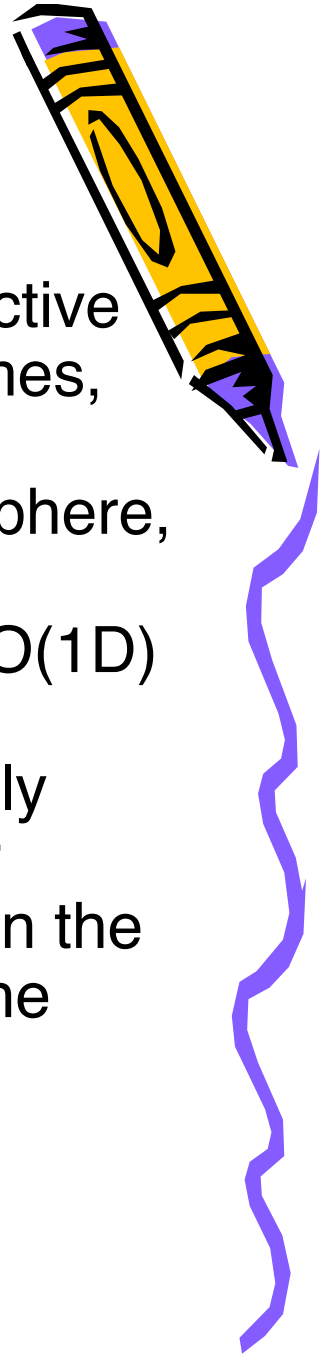
$$OH + NO_2 + M \rightarrow HNO_3 + M$$

$$HO_2 + NO_2 + M \rightarrow HNO_4 + M$$

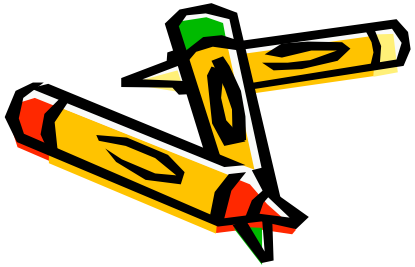
The hydrogen species on the righthand side of these reactions (i.e., H_2O, HNO_3, and HNO_4) are known as reservoir species, which are chemical compounds that store (like a reservoir) a particularly species in a nonreactive form. These species act as stores of hydrogen, locking up or **sequestering** HO_x and preventing its participation in the catalytic cycle outlined above. H_2O, HNO_3 and HNO_4 react very slowly with odd oxygen. When HO_x is tied up in one of the reservoir species, therefore, it is not important in the loss of odd oxygen.



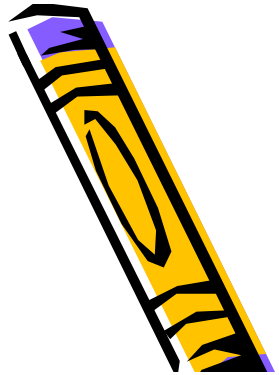
HO_x catalytic cycles



Since reservoir species are relatively inert (compared to reactive species like OH and HO_2), they tend to have very long lifetimes, and the less reactive they are, the longer are their lifetimes. Eventually, reservoir species are transported into the troposphere, removing HO_x from the stratosphere altogether. H_2O can be converted back into reactive hydrogen via the reaction with O(1D) outlined above. HNO_3 (nitric acid), on the other hand, under normal conditions in the stratosphere, releases its HO_x mainly through photolysis. The photolysis of the nitric acid reservoir species is discussed in the section on NO_x catalytic cycles. In the upper stratosphere, where O atoms are relatively plentiful, the HOx catalytic cycle outlined above is fairly effective



HO_x catalytic cycles



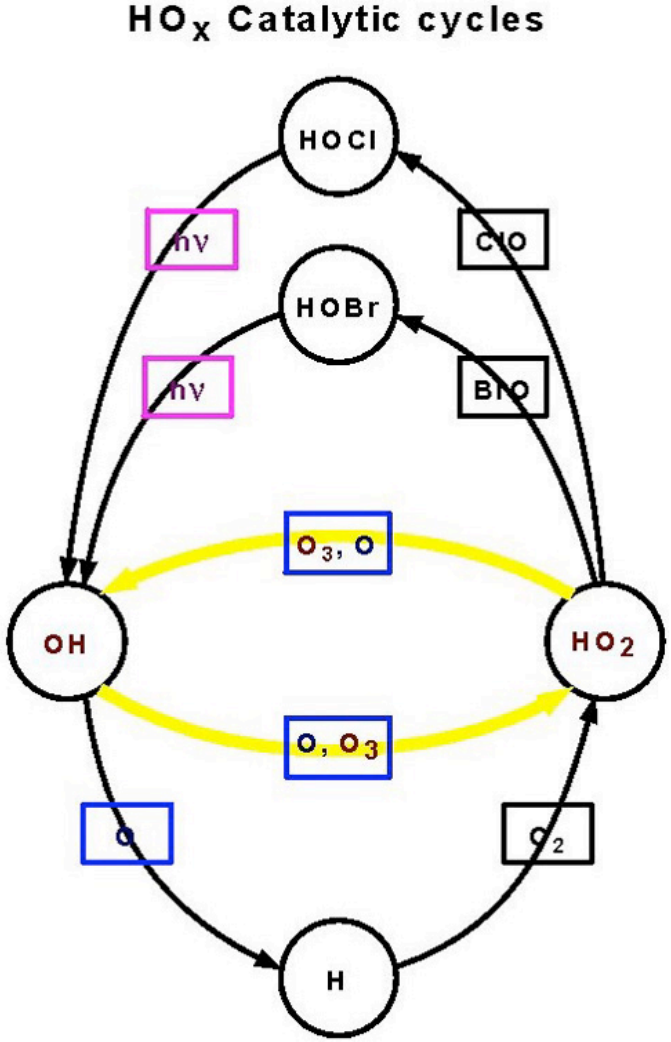
In the lower stratosphere, however, a different catalytic cycle involving HO_x is responsible for O_x loss.

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O_3 \rightarrow OH + O_2 + O_2$

NET: $2O_3 \rightarrow 3O_2$

Again, notice that HO_x ($OH + HO_2$) is neither produced nor destroyed by this cycle, but merely acts as a catalyst for converting two molecules of ozone into three molecules of O_2. The importance of this reaction is that it does not require free O atoms for the reaction. Again, notice that HOx (OH + HO2) is neither produced nor destroyed by this cycle, but merely acts as a catalyst for converting two molecules of ozone into three molecules of O2. The importance of this reaction is that it does not require free O atoms for the reaction



HO_x catalytic cycles

Two other reactions are important for O_X loss in the upper stratosphere. The first one involves a free H (hydrogen) atom as an intermediate compound.Two O atoms are converted into a single diatomic oxygen molecule.

H + O2 + M --> HO2 + M

HO2 + O --> OH + O2

OH + O --> H + O2

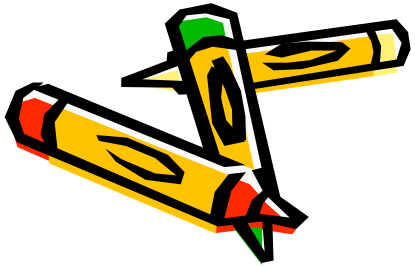
NET: 2O --> O2

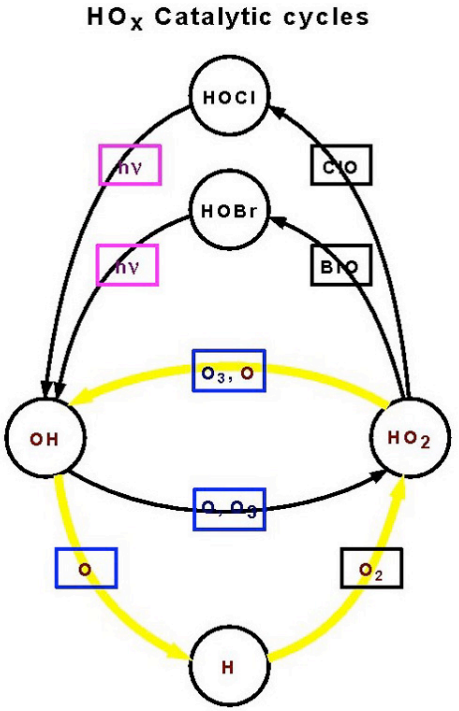
The second reaction involves HOx and the loss of two odd oxygens (an ozone molecule and an oxygen atom).The two odd oxygens are converted into two diatomic oxygen molecules

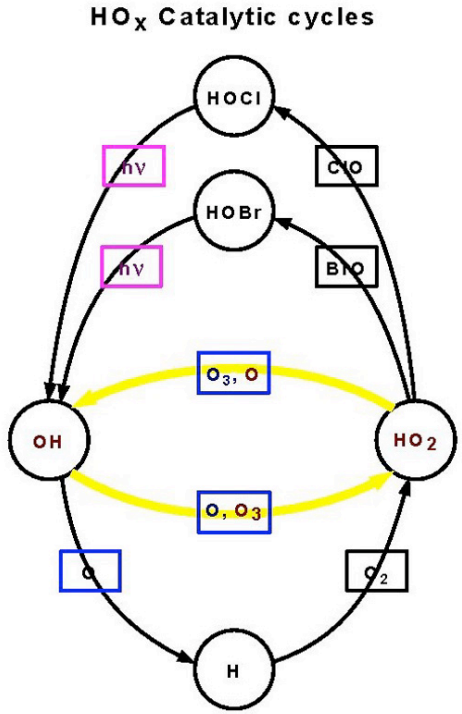
OH + O3 --> HO2 + O2

HO2 + O --> OH + O2

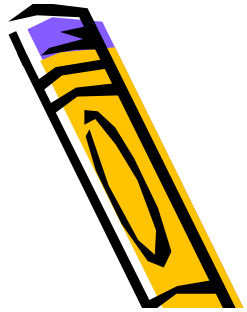
NET: O3 + O --> 2 O2







HO_x catalytic cycles



Finally, yet another pair of catalytic cycles is important in the lower stratosphere. These cycles involve interaction with the chlorine or bromine cycles. These cycles are the most complicated of the catalytic cycles we've looked at so far, but yield the same result: catalytic destruction of odd oxygen. In these reactions, Z can be either chlorine (Cl) or bromine (Br):

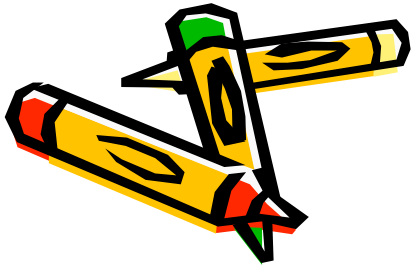
$$ZO + HO_2 \rightarrow HOZ + O_2$$

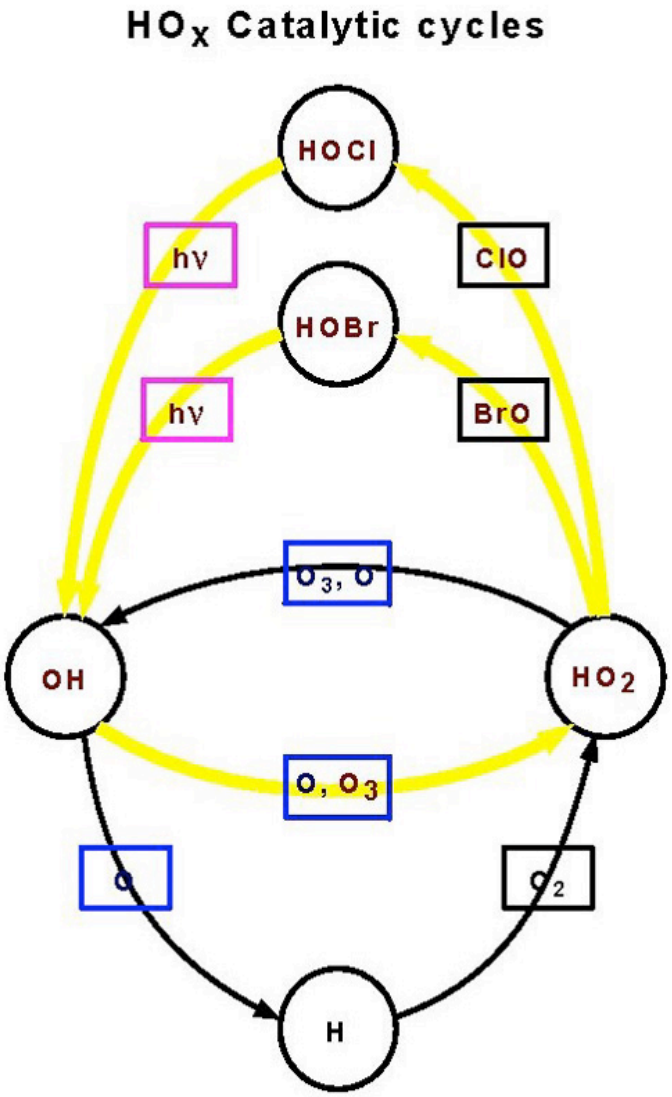
$$HOZ + hc/\lambda \rightarrow OH + Z$$

$$OH + O_3 \rightarrow HO_2 + O_2$$

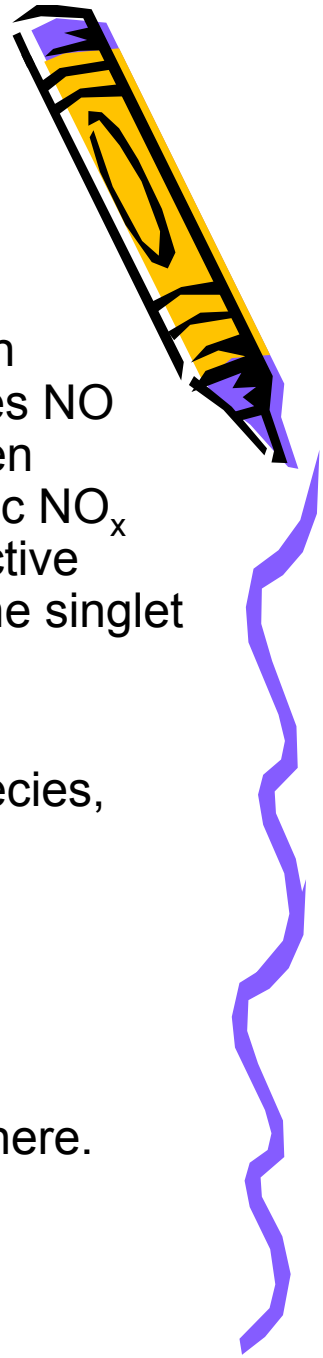
$$Z + O_3 \rightarrow ZO + O_2$$

$$\text{NET: } 2\ O_3 \rightarrow 3\ O_2$$





NO_x catalytic cycles



The loss of odd oxygen can also occur through catalytic cycles involving nitrogen species in the form of reactive nitrogen. Reactive nitrogen, denoted NO_x, includes NO (nitric oxide) and NO_2 (nitrogen dioxide). Like reactive hydrogen, reactive nitrogen species have their origins in the troposphere. Approximately 90% of stratospheric NO_x comes from tropospheric N_2O (nitrous oxide, also known as laughing gas). Reactive nitrogen species are formed from N_2O via the reaction of nitrogen dioxide with the singlet D oxygen atom to form two molecules of nitric acid.

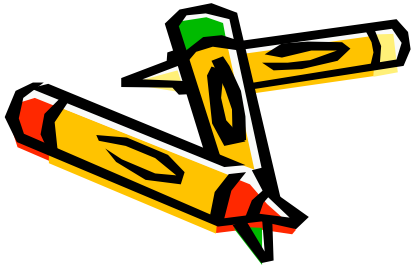
$$N_2O + O(1D) \rightarrow 2\ NO$$

This reaction transfers nitrogen from the inert species, N_2O, into the reactive species, NO.

Another way that N_2O is lost is via photolysis. An energetic UV photon is able to dissociate N_2O into molecular nitrogen, N_2, and the singlet D oxygen atom.

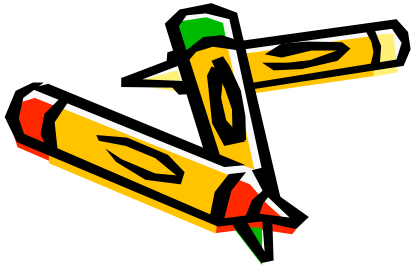
$$N_2O + hc/\lambda \rightarrow N_2 + O(1D)$$

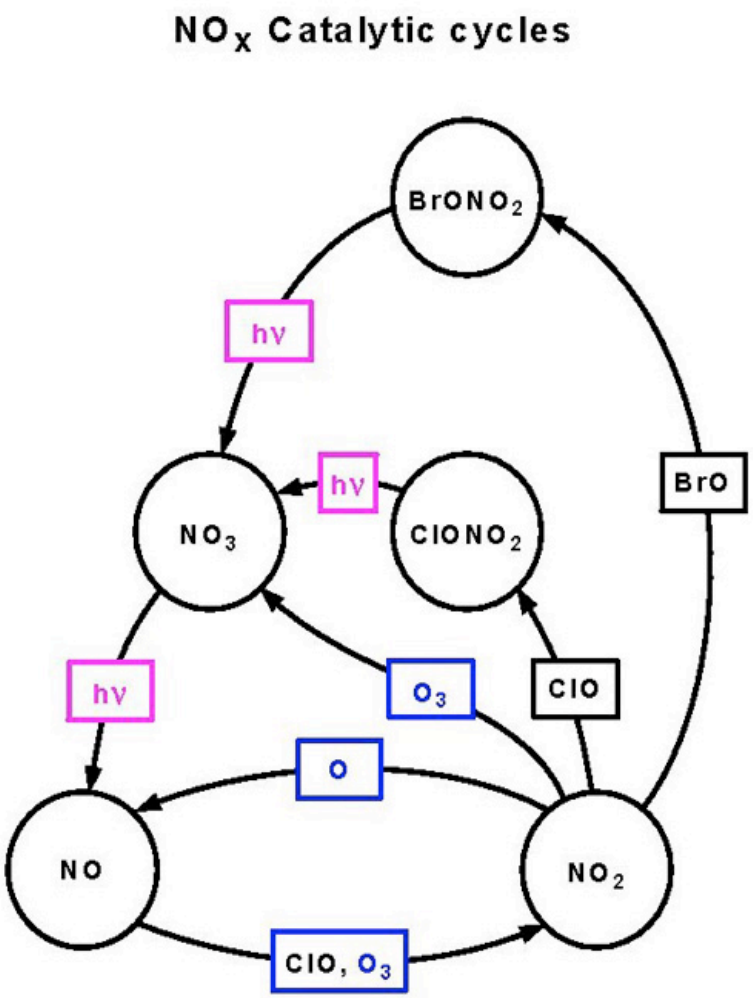
Since N2 is a very long-lived, nonreactive species, it does not contribute to photochemical processes, even though is the most abundant gas in the atmosphere.



NO_x catalytic cycles

Sources of N_2O at the ground include oceans, forest soils, combustion, biomass burning, and fertilizers. The amount of nitrogen generated annually by these processes are estimated to be in the 4.4 to 10.5 teragrams (Tg). (One Tg=10^{12} or one trillion grams.) Some of the chemical processes of these nitrogen oxides are illustrated , which shows the NO_X catalytic cycles.The circles show many of the nitrogen containing species in the stratosphere. We have not included N_2, since it is not involved in stratospheric nitrogen photochemistry, nor have we included N_2O, since it is the prime source of NO. The reaction pathways are shown as dark arrows with superimposed boxes.





NO_x catalytic cycles

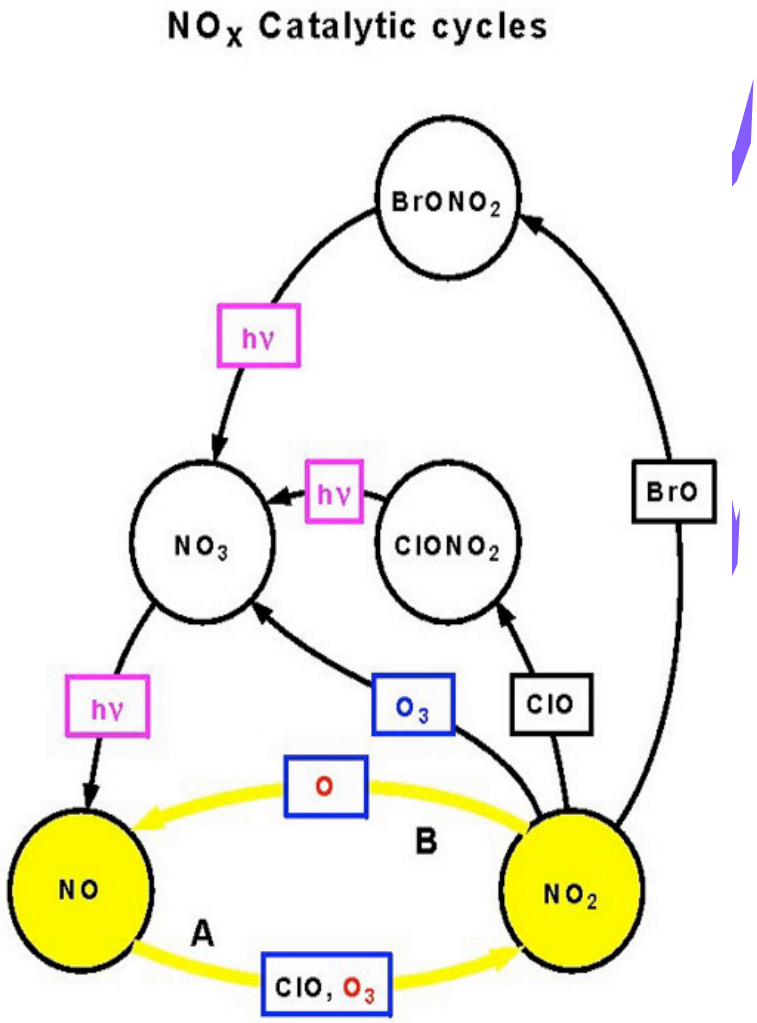
The reactive forms of nitrogen drive their own catalytic cycle, analogous to the HO_X cycles. The reactions are represented by the red and yellow highlights. In step A (lower yellow line), NO reacts with O_3 (indicated by the red O_3 in the blue box on the lower yellow line) to form NO_2 and O_2. The NO_2 then reacts with O to reform NO (upper yellow line). In the process, both an ozone and oxygen molecule are destroyed (i.e., two O_X molecules), while the NO is reformed

$$NO + O_3 \rightarrow NO_2 + O_2$$

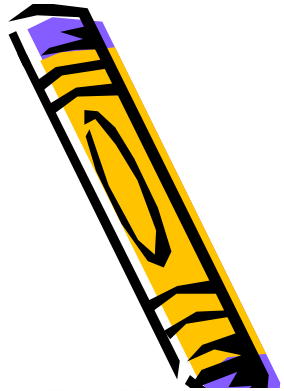
$$NO_2 + O \rightarrow NO + O_2$$

$$\text{NET: } O_3 + O \rightarrow 2\ O_2$$

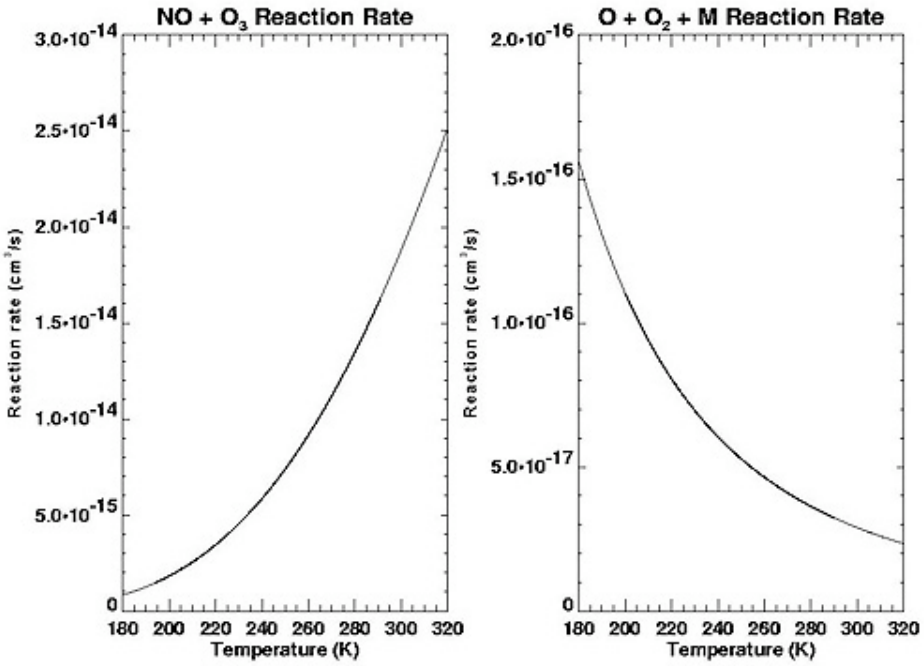
The catalytic cycle results in the loss of two odd oxygen without loss of the catalytic NO_X species.

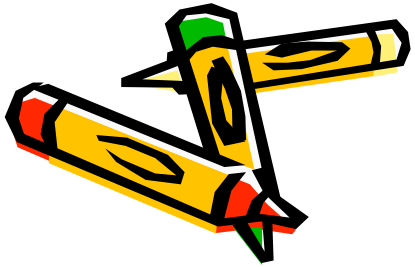


Temperature dependence of NO_X catalytic reactions

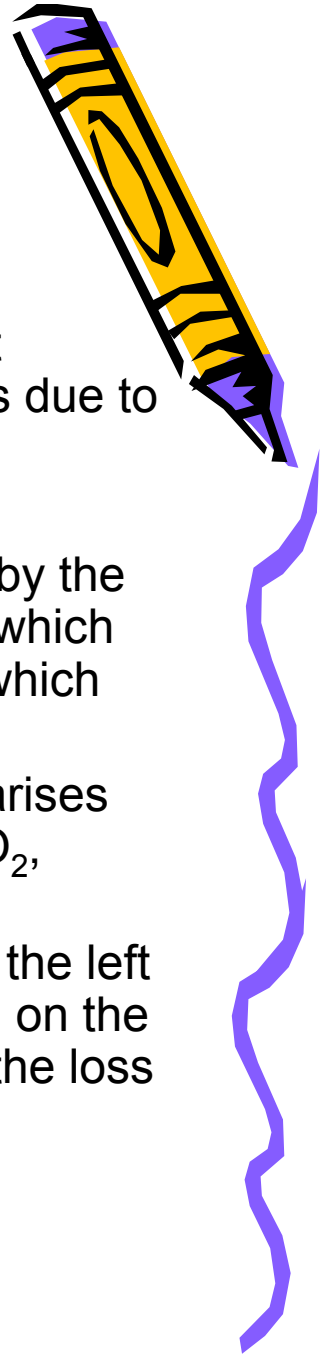


Temperature dependence for NOx species is particularly strong. Left side, shows the reaction rate of $NO+O_3$ --> NO_2+O_2 (cm3/sec/molecule) as a function of temperature over a range of temperatures characteristic of the stratosphere. Note that the $NO+O_3$ rate increases very steeply as the temperature increases. This steep increase is associated with the faster speeds and energies that molecules acquire at higher temperatures. The right panel shows the reaction rate of $O+O_2+M$-->O_3+M (cm3/sec/molecule) as a function of temperature over a range of temperatures characteristic of a 2 mb pressure (about 40 km in altitude). In this reaction, the rate decreases as temperature increases





Temperature dependence of NO_X catalytic reactions



(1) Change in O_X due to NO_x catalytic loss and photochemical production Our first equation arises from the fact that the change of O_x (i.e., ozone and free oxygen) is due to a balance between NO_x catalytic loss and photochemical production.

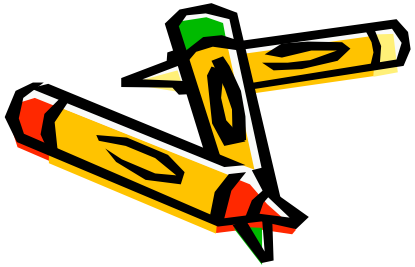
$$k1\ [NO]\ [O_3] + k2\ [NO_2]\ [O] = J1\ [NO_2] + 2\ J2\ [O_2]$$

first term on the left is ozone loss by the NO + O_3 reaction, second term is O loss by the NO_2 + O reaction, 1st term on the right is the photolysis of NO_2 by solar radiation which produces an O atom and an NO molecule, while last term is the photolysis of O_2 which produces two oxygen atoms.

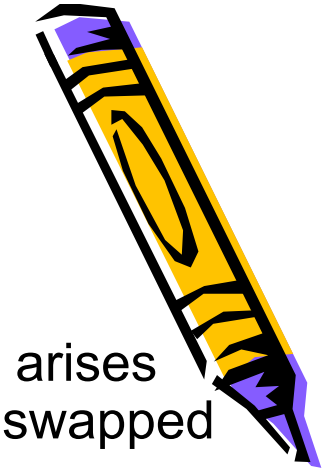
(2) Swapping back and forth of NO_X between NO and NO_2 The second equation arises from the fact that NOX is constantly being swapped back and forth from NO to NO_2,

$$k1\ [NO]\ [O_3] = k2\ [NO_2]\ [O] + J1\ [NO_2]$$

This shows us that the production of NO_2 is equal to the loss of NO_2. The term on the left hand side of the equation is NO_2 production by the NO+O_3 reaction. The first term on the right hand side is the loss of NO_2 by the NO_2+O reaction, and the second term is the loss of NO_2 by photolysis.



Temperature dependence of NO_X catalytic reactions



(3) Swapping back and forth of O_x between O and O_3 The third equation arises because odd oxygen, O_x, like reactive nitrogen, NO_x, is constantly being swapped back and forth from free oxygen, O, to ozone, O_3.

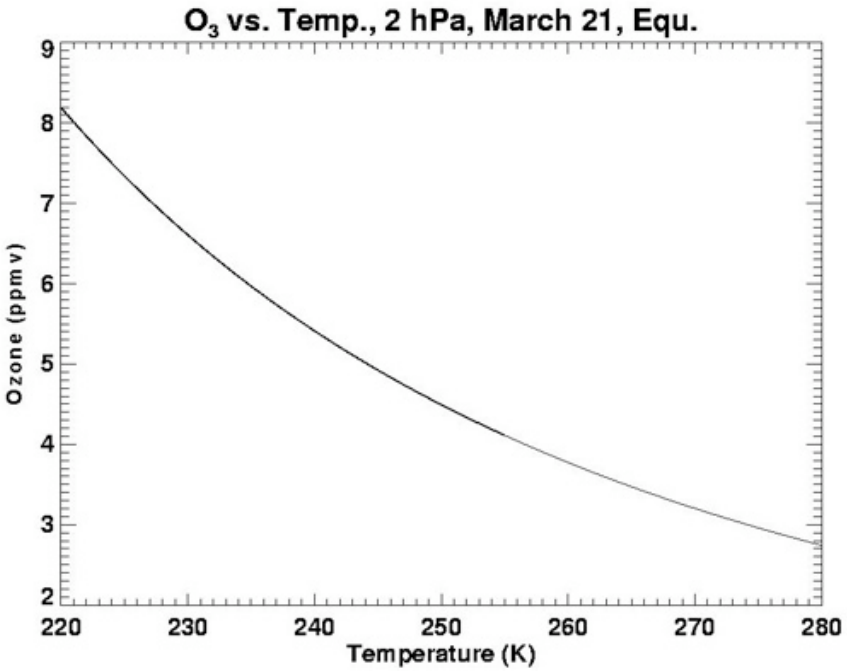
$$k3\ [O]\ [O_2]\ [M] = J3\ [O_3]$$

The first term is the ozone production by the $O+O_2+M$ termolecular reaction, while the term on the right hand side is the photolysis of ozone

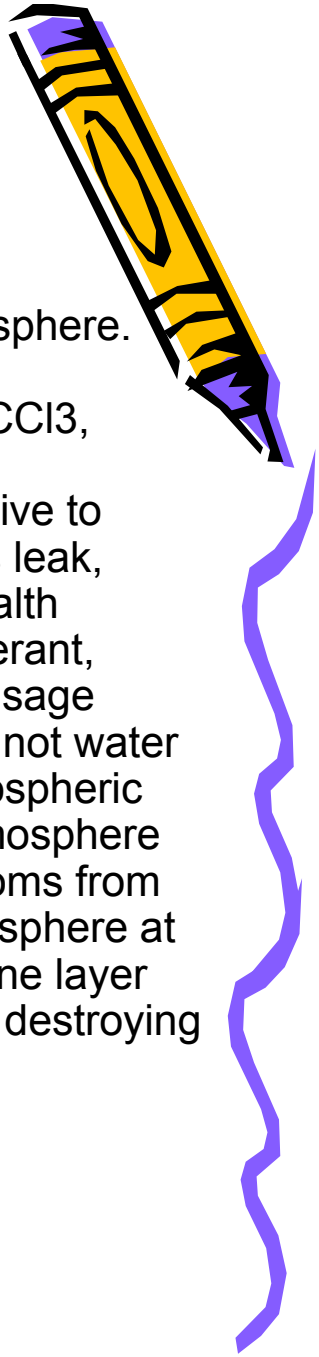
We can combine the three equations above to solve for the ozone concentration as a function of temperature and NOx. This is a relatively complicated expression. However, Figure on nextg slide shows the graphical results of such a calculation by making a few assumptions. We first assume a NOx concentration of 2.0 x109 molecules/cm3. We then perform the calculation at the Equator on March 21, when the Sun is directly overhead. We then assume a pressure level of 2 mb (about 40 km altitude). We then are able to derive an ozone-versus-temperature plot where ozone is a function of temperature

Temperature dependence of NO_X catalytic reactions

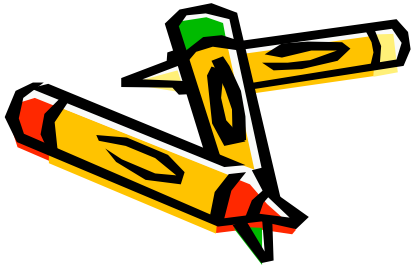
We see in the figure that ozone amounts decrease with increasing temperature. The decrease is a result of the temperature dependence of the $NO+O_3$ reaction which is strongly temperature dependent. As temperatures increase, this reaction speeds up, destroying ozone faster, and reducing the ambient amount of ozone. This reaction rate temperature dependence explains the observed ozone-temperature relationship in the upper stratosphere, and illustrates the impact of temperature dependent reaction rates on the stratosphere.



Chlorine Sources



As with the nitrogen and hydrogen species, the sources of chlorine are also in the troposphere. Chlorine atoms are bound up in the various manmade chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) molecules, including F-11, f12, f113, f114, CCl4, CH3CCl3, CH3Cl, HCFC-22. These molecules can be transported across the tropopause into the stratosphere. CFCs were developed in the 1920s as a safe, nontoxic refrigerant alternative to ammonia. That is, both CFCs and ammonia make good coolants. However, when CFCs leak, there are no adverse health consequences, while when ammonia leaks, undesirable health consequences, even death, can occur.In addition to their characteristic as a good refrigerant, CFCs are cheap to manufacture, nonflammable, and insoluble.They gained enormous usage worldwide from the 1940s to the 1980s.Because CFCs have very long lifetimes and are not water soluble, they can be transported upward into the stratosphere. Indeed, the current stratospheric chlorine content arises mostly from CFCs. This represents a dramatic change to the atmosphere by human activity. While natural sources of chlorine exist, it is the release of chlorine atoms from the photolysis of CFC molecules that provide most of the observed chlorine in the stratosphere at the present time. In the upper stratosphere, the high energy UV radiation above the ozone layer can break the CFC bonds, and releasing chlorine to participate in its own catalytic cycle destroying odd oxygen

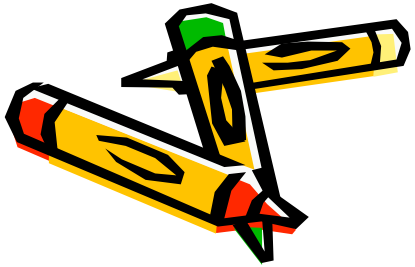


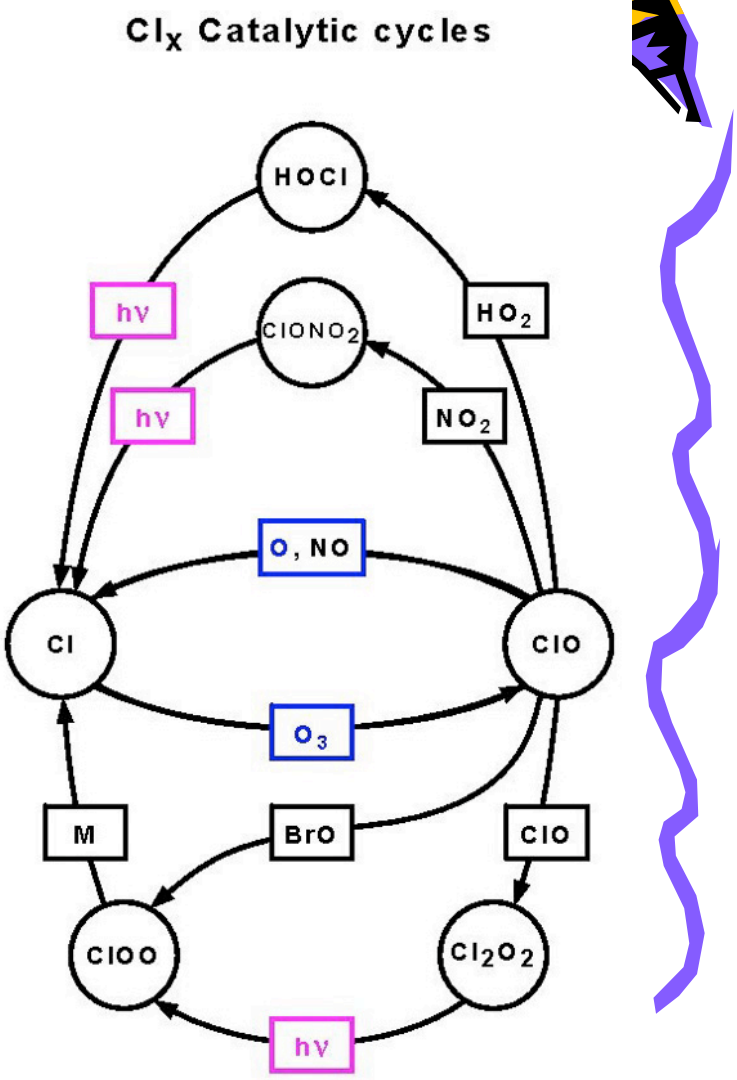
Cl_X catalytic reactions

The chemical reactions of different chlorine-containing molecules are illustrated in the figure. The circles show the predominant short-lived species that form the chlorine containing family in the stratosphere. We have not included CFCs on the graph because of there relatively long lifetimes. The reaction pathways are drawn as black arrows with superimposed boxes. For example, Cl (left, middle circle) can react with O_3 to form ClO (chlorine monoxide) and O_2.

$$Cl + O_3 \text{ --> } ClO + O_2$$

On the figure, we see this represented by the line with the O_3 blue box superimposed on the line. The O_2 is not represented, because it is not a chlorine species. All of the reactions which lead to ozone loss (i.e., O_X loss) are colored in blue, while photolysis reactions are colored in magenta.





Cl_X catalytic reactions

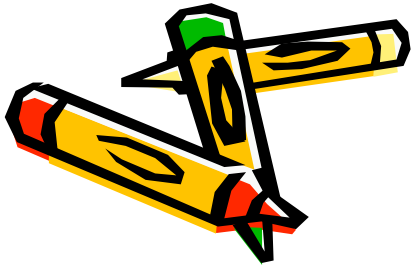
A principal loss of ozone in the upper stratosphere is the Cl/ClO reaction, represented in the figure, and written as

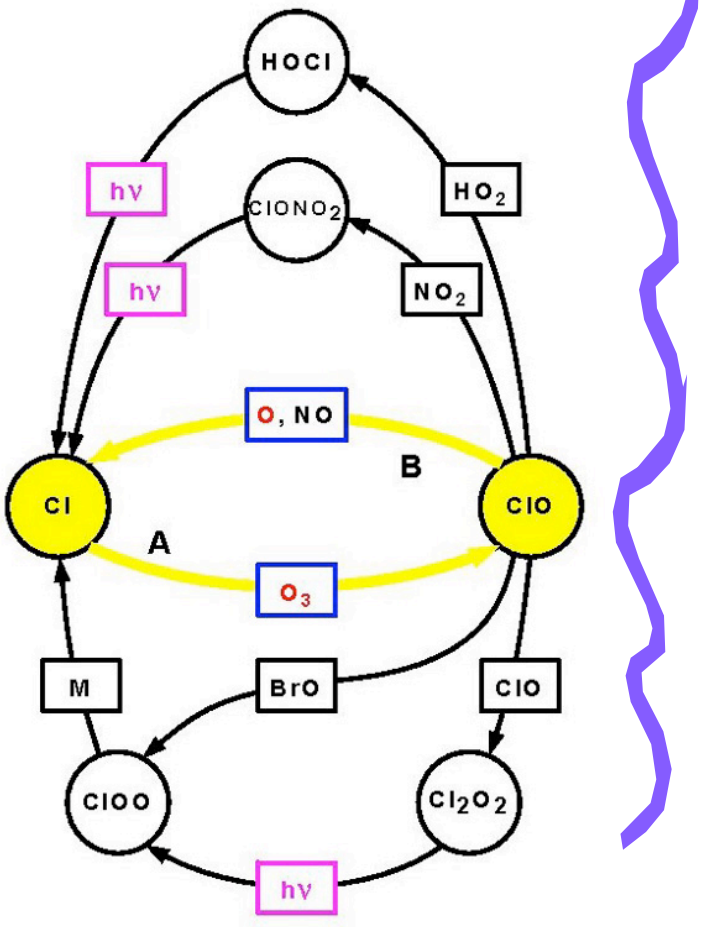
$Cl + O_3 \rightarrow ClO + O_2$ (A)

$ClO + O \rightarrow Cl + O_2$ (B)

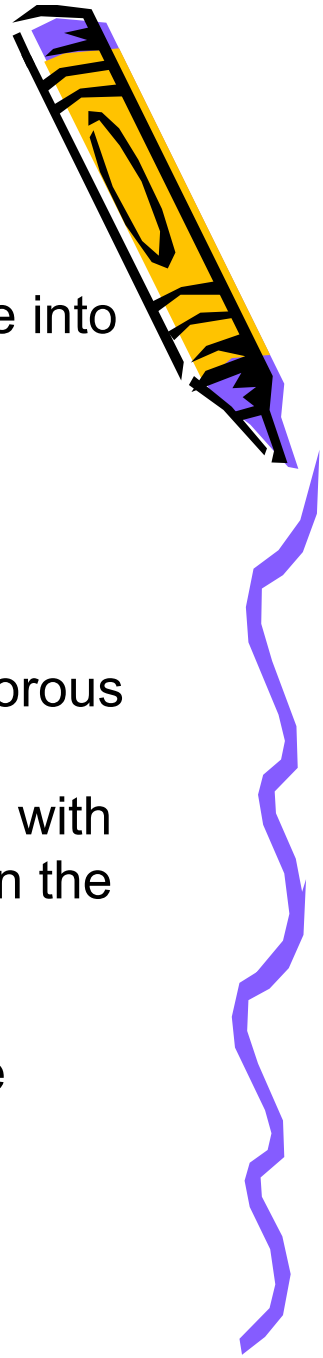
NET: $O_3 + O \rightarrow 2\ O_2$

Here the reactive chlorine compounds are Cl and ClO, denoted Cl_X. The net reaction is to convert two odd oxygens, an ozone molecule and an oxygen atom, into two molecules of diatomic oxygen. Since there is little free oxygen in the lower stratosphere, this reaction is not the principal loss mechanism for polar lower stratospheric ozone.





Cl_X catalytic reactions



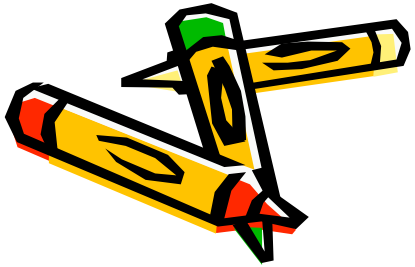
As in NO_X case, several reactions exist that transform reactive chlorine into reservoir species.

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + HO_2 \rightarrow HOCl + O_2$

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

The chlorine reservoir species HCl (hydrochloric acid), HOCl (hypochlorous acid), and $ClONO_2$ (chlorine nitrate) are characterized by a variety of lifetimes, determined by their photolysis rates. HCl is the longest lived, with a lifetime on the order of weeks. HOCl is the shortest, with a lifetime on the order of hours, as HOCl quickly photolyzes in sunlight.In the lower stratosphere, several other catalytic cycles involving chlorine have important effects on the ozone balance. Yet another cycle involves the photolysis of NO_3 and $ClONO_2$



Cl_X catalytic reactions

$ClONO_2 + h\upsilon \rightarrow Cl + NO_3$

$NO_3 + h\upsilon \rightarrow NO + O_2$

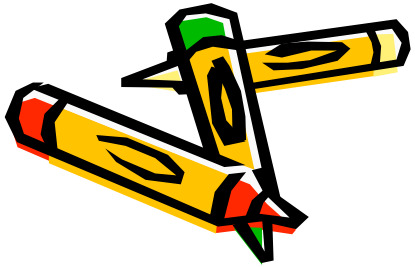
$NO + O_3 \rightarrow NO2 + O_2$

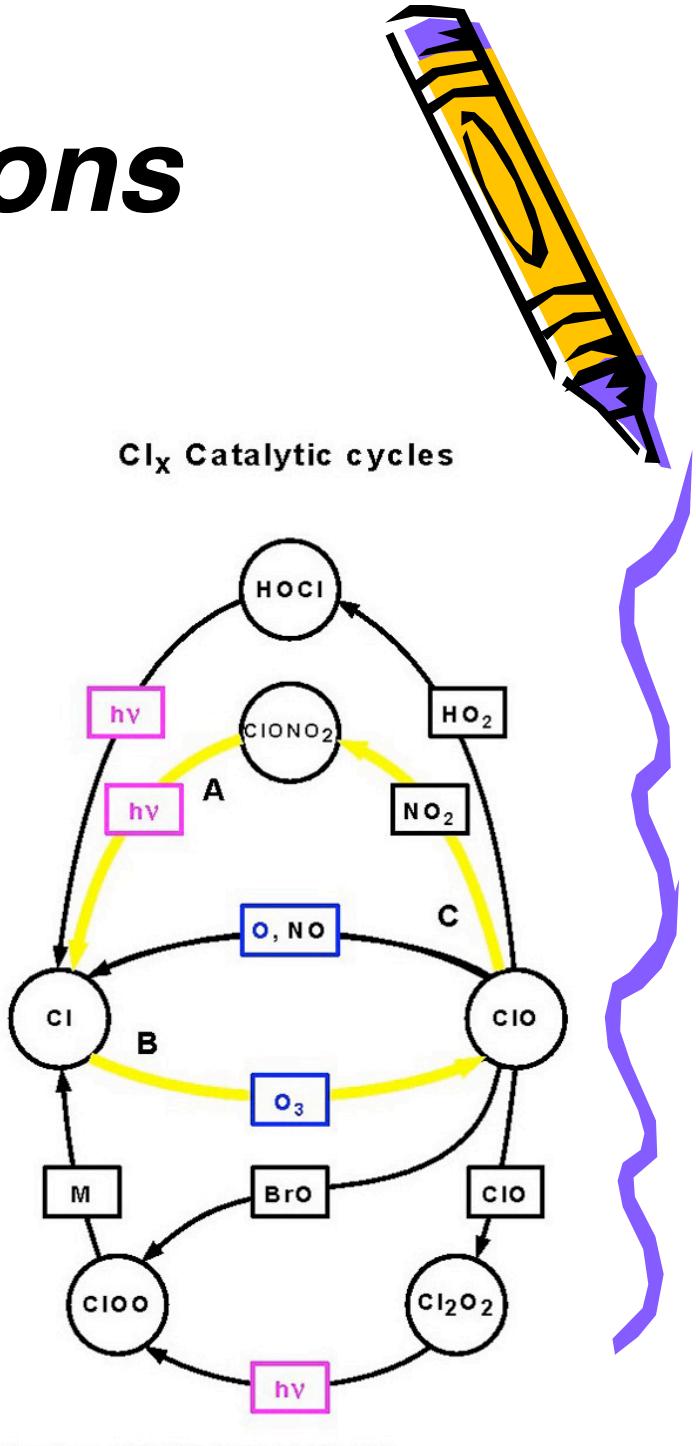
$Cl + O_3 \rightarrow ClO + O_2$

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

NET: $2O_3 \rightarrow 3O_2$

The three-body reaction of ClO with NO_2 and some other molecule M deactivates the reactive chlorine species ClO into nonreactive chlorine species $ClONO_2$. The net effect of this set of reactions involving both reactive and nonreactive forms of chlorine and nitrogen is to convert two molecules of ozone into three molecules of diatomic oxygen.





Bromine sources

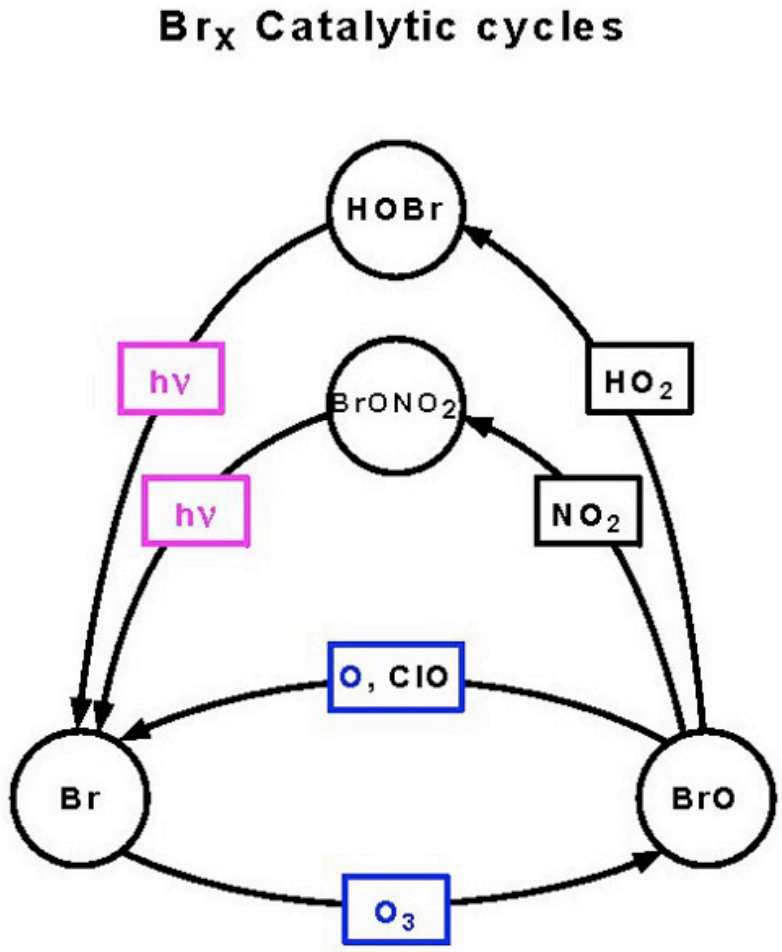
Bromine is another molecule effective for ozone destruction. Bromine accounts for significant ozone loss (about 20-40%) inside the Antarctic ozone hole. The sources of bromine are both anthropogenic and natural. Methyl bromide (CH_3Br) is produced in the troposphere, but it is also the predominant source of bromine in the stratosphere. Methyl bromide is produced by biological processes on both land and in the ocean. Methyl bromide is also used as a fumigant for agricultural purposes, and is released via biomass burning and from cars using leaded fuel. Two other major sources of bromine are Halon-1211 ($CBrClF_2$) and Halon-1301 ($CBrF_3$), used as fire suppressants.The losses of methyl bromide occur through reactions with water, the hydroxyl radical, chlorine ions, and photolysis by ultraviolet radiation. There are probably also losses via biological processes, but these are uncertain. Methyl bromide has a long lifetime, which allows some of it to be lifted out of the troposphere and into the stratosphere.Halons 1211 and 1301 are only destroyed by UV photolysis at wavelengths shorter than 280 nm. Hence, the halons can only be photolyzed in both the upper and lower stratosphere. They have very long lifetimes, since it takes quite a while for a molecule to reach these altitudes.

BrX catalytic reactions

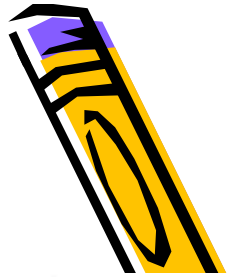
Reactive bromine exists in the form of bromine (Br) and bromine monoxide (BrO). Nonreactive bromine species include hypobromous acid (HOBr) and bromine nitrate ($BrONO_2$). These are typically not referred to as "reservoir species" because they are very easily photolyzed, even by visible light, and hence have very short lifetimes. This means that they do not lock up reactive bromine in the same way that $ClONO_2$ locks up reactive chlorine, and so bromine species in the stratosphere tend to exist in reactive forms. The open circles show these main bromine species in the stratosphere, all of which are relatively short-lived. We have not included methyl bromide or any halons, since their lifetimes are long. The reaction pathways are shown as black arrows with superimposed boxes. One such pathway involves the reaction of Br (left, bottom circle) with ozone (O_3) to form BrO and O_2. The reaction is written

$$Br + O_3 \rightarrow BrO + O_2$$

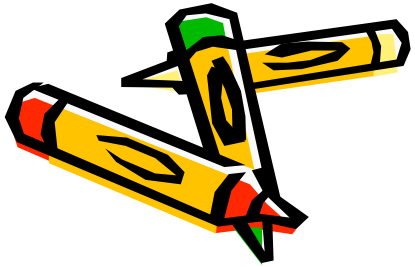
we see this represented by the black arrow with the superimposed O_3 blue box. O_2 is not represented, because it is not a bromine species.

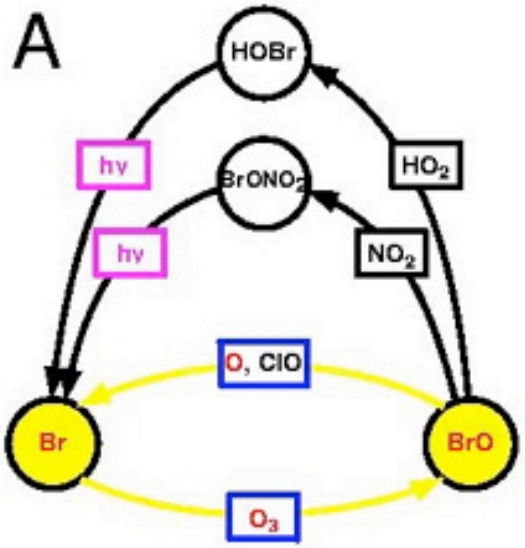


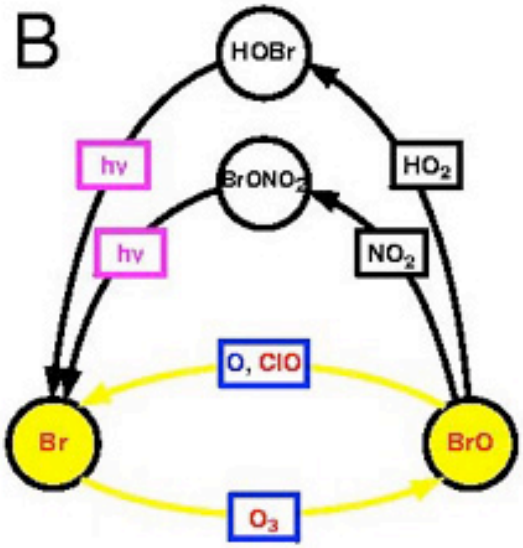
BrX catalytic reactions

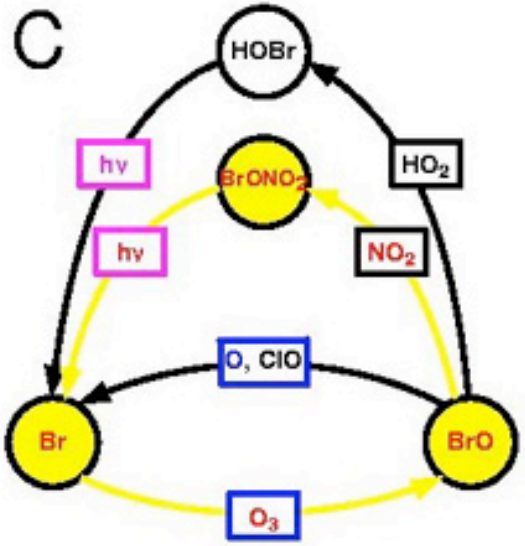


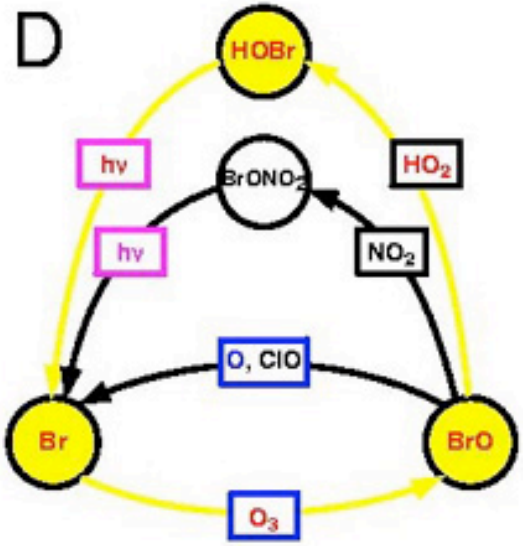
There are four distinct catalytic cycles for ozone loss. These reaction cycles are illustrated (A, B, C, and D). The principle reactants are highlighted in red. The reaction pathways are shown by the yellow arrows. The yellow shaded circles show the principle bromine reactants.



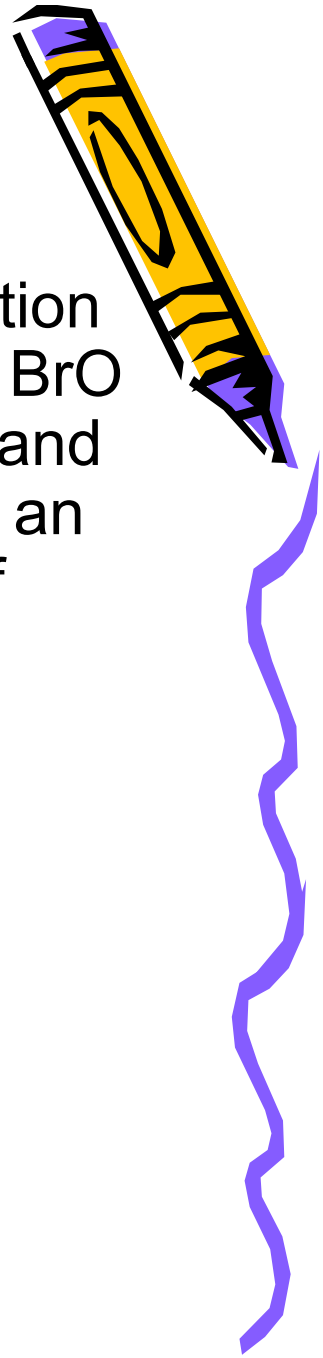








BrX catalytic reactions

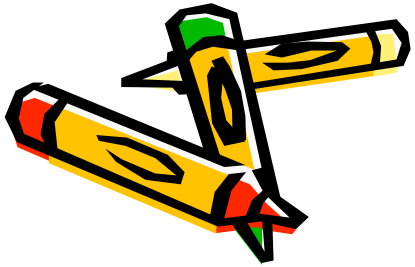


(A) Br_x - O_x Reaction Cycle -- In this cycle, a two-step reaction occurs between reactive bromine and odd oxygen. First, a BrO molecule reacts with a free O atom to form a free Br atom and a diatomic oxygen molecule. Next, the Br atom reacts with an O_3 molecule to reform the BrO molecule and a molecule of diatomic oxygen. The net reaction is to convert two odd oxygen species, an O atom and an O_3 molecule, into two diatomic oxygen molecules. The reactions are

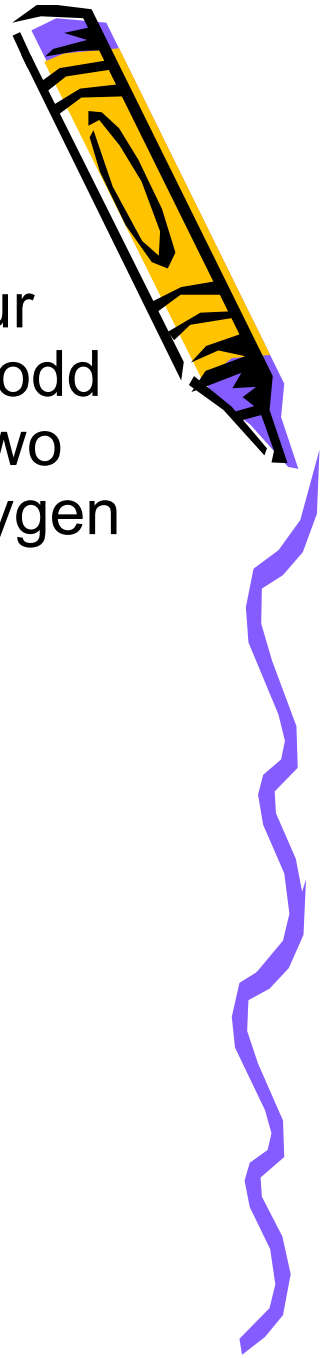
$$BrO + O \rightarrow Br + O_2$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$\text{NET: } O + O_3 \rightarrow 2\ O_2 \qquad \text{(A)}$$



BrX catalytic reactions



(B) Br_x - Cl_x - O_x Reaction Cycle -- In this second cycle, four reactions occur involving reactive Br_x and Cl_x species and odd oxygen, in the form of ozone. The net result is to convert two O_3 molecules into three O_2 molecules. That is, two odd oxygen species are lost. The reactions are

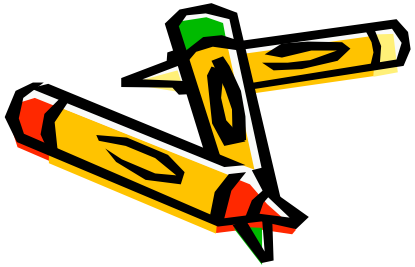
$BrO + ClO \rightarrow Br + ClOO$

$ClOO + M \rightarrow Cl + O_2 + M$

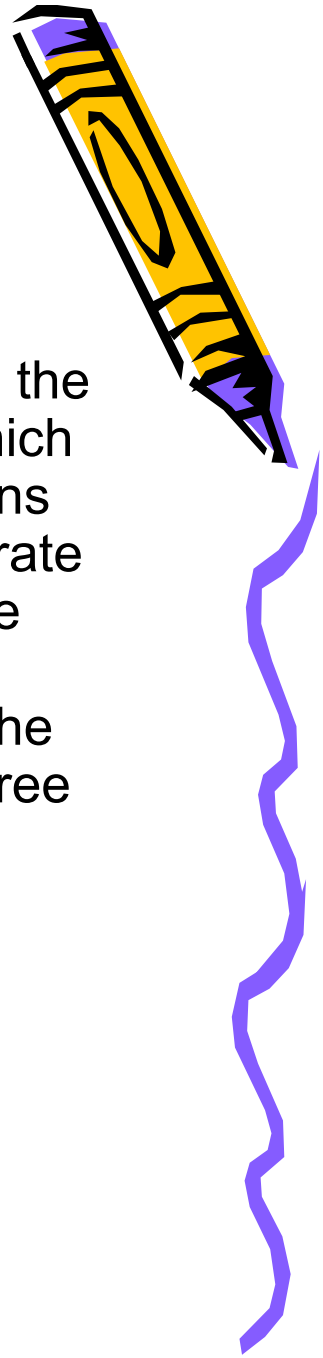
$Cl + O_3 \rightarrow ClO + O_2$

$Br + O_3 \rightarrow BrO + O_2$

NET: $2\ O_3 \rightarrow 3\ O_2$ (B)



BrX catalytic reactions



(C) Br_x - NO_x - O_x Reaction Cycle -- In this third cycle, there are five reactions among reactive Br_x and NO_x species and O_x (odd oxygen) in the form of O_3 . Also involved is nonreactive bromine nitrate ($BrONO_2$), which is photolyzed by less energetic near-UV and visible light. These photons are less energetic than UV photons, and hence they are able to penetrate into the lower stratosphere, since ozone higher up screens out only the more energetic UV photons. Bromine thus exists mostly in its reactive forms in the lower stratosphere. The net change is as in (B), namely, the conversion of two molecules of an odd oxygen species (ozone) into three molecules of O_2. These reactions are

$$BrO + NO_2 + M \rightarrow BrONO_2 + M$$

$$BrONO_2 + h\upsilon \rightarrow Br + NO_3$$

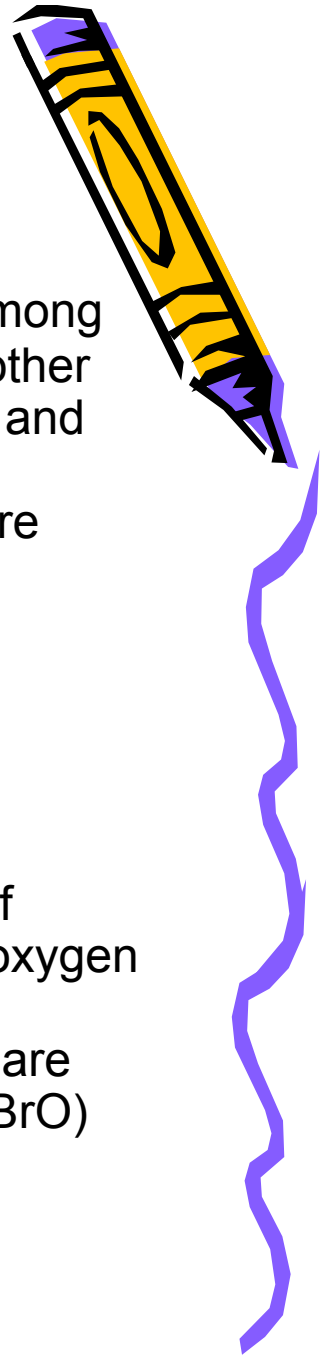
$$NO_3 + h\upsilon \rightarrow NO + O_2$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$\text{NET: } 2\ O_3 \rightarrow 3\ O_2 \qquad \text{(C)}$$

BrX catalytic reactions



(D) Br_x - HO_x - O_x Reaction Cycle -- In this fourth cycle, there are four reactions among reactive Br_X and HO_x species and O_x, again in the form of O_3. Also involved is another nonreactive form of bromine (HOBr), which is also quickly photolyzed by near-UV and visible light. The net change is as in (B) and (C) above: the conversion of two O_3 molecules into three O_2 molecules, representing the loss of O_x. These reactions are

$$BrO + HO_2 \rightarrow HOBr + O_2$$

$$HOBr + h\upsilon \rightarrow OH + Br$$

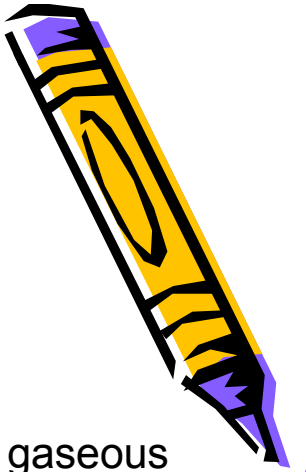
$$OH + O_3 \rightarrow HO_2 + O_2$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$\text{NET: } 2\ O_3 \rightarrow 3\ O_2$$

(D)These chains of reactions make bromine one of the most efficient destroyers of ozone for two reasons. First, catalytic cycles (B), (C), and (D) do not require free oxygen atoms to destroy ozone, meaning that these reactions can occur in the lower stratosphere where there are few O atoms available. Second, HOBr and $BrONO_2$ are very easily photolyzed, so that bromine typically exists as reactive species (Br or BrO) rather than as nonreactive species ($BrONO_2$ and HOBr).

HETEROGENEOUS CHEMISTRY



Heterogeneous chemical reactions are crucial to understanding the chemical balance of the stratosphere. A heterogeneous reaction is a chemical process that involves solid, liquid, and gaseous phases (hence, it is a multiphase process). Heterogeneous chemistry occurs on or in condensed particles (such as liquid water droplets or solid ice particles) that are in contact with gaseous molecules. Such multiphase processes include adsorption (i.e. adhesion of a thin layer of molecules to a surface) or absorption of molecules onto particles. This is followed by chemical reactions on the particle surfaces or within the particles themselves. They are the physical mechanism behind the Antarctic ozone hole phenomenon.Chemical reactions on the surfaces of particles take place via a chain of processes. First, the reactant species must make contact with the particles by kinetic motion. Second, the reactants are absorbed onto the surface of the particle by either physical or chemical bonding, where they then diffuse into the body of the particle or remain on the surface. Third, the reactants meet on (or in) the particle, chemically forming different products. These products will then diffuse into the particle, remain on the surface, or be desorbed (emitted) from the particle.This complex chain of events is represented as the product of a number of parameters, including the concentrations of the reactants, the total particle surface area in a given volume of air, a so-called "sticking coefficient" (representing the probability that a molecule will actually stick to a particle after a collision), temperature (representing the speed or kinetic energy of the molecules in the air parcel), and the particle type.

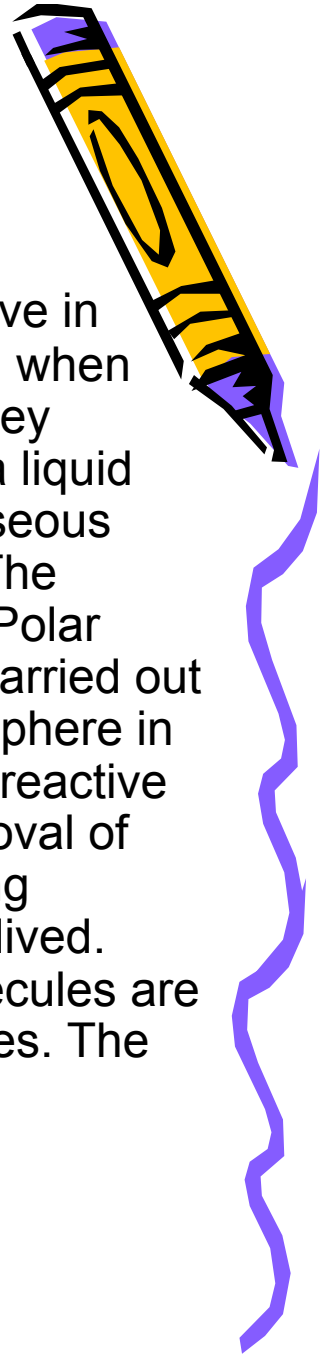
HETEROGENEOUS CHEMISTRY

There are 5 basic heterogeneous reactions necessary to understand stratospheric chemistry. The five reactions are given below.

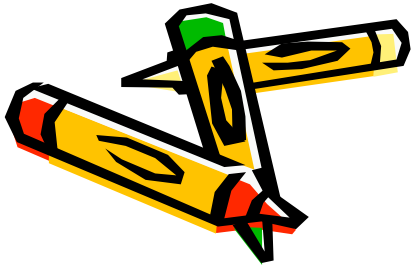
$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (1)$$
$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (2)$$
$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \quad (3)$$
$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad (4)$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O \quad (5)$$

Rates for these reactions depend on a number of factors, including particle type (via the sticking coefficient), particle surface area, and temperature. Reaction 4 does not have a temperature dependent sticking coefficient, and is therefore important wherever and whenever we find particles in the stratosphere (e.g., after volcanic eruptions). In fact, the nitrogen chemistry of the middle latitude stratosphere cannot be explained without including reaction 4. Because the other reaction rates increase dramatically in cold temperatures, they are extremely important to an understanding of the ozone budget of the polar stratosphere.

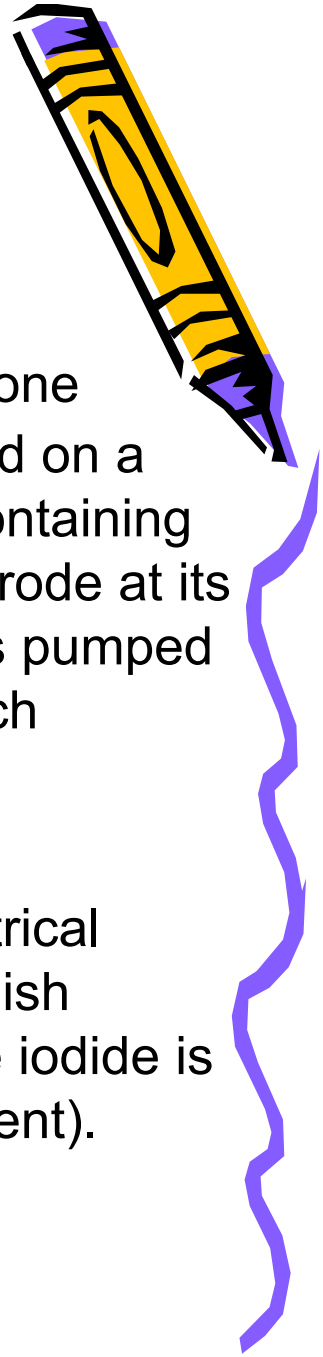
HETEROGENEOUS CHEMISTRY



Molecules such as HCl and $ClONO_2$, as shown in reaction 1, are mostly nonreactive in their gaseous state, which is why they act as chlorine reservoir species. However, when these molecules are dissolved in liquids such as sulphuric acid-water solutions, they become highly reactive with one another. The absorption of HCl and $ClONO_2$ on a liquid sulphate aerosol particle in the stratosphere results in the release of Cl_2 into a gaseous form (desorption) and the retention of a HNO_3 molecule with the aerosol particle.The nonreactive HNO_3 formed remains in a solid (frozen) state on the surfaces of the Polar Stratospheric Clouds (PSCs). As the PSCs undergo sedimentation, the HNO_3 is carried out of the stratosphere. This process leads to the removal of nitrogen from the stratosphere in a process called denoxification. Since HNO_3 photolysis results in the formation of reactive NO_2, which in turn reacts with ClO to form the reservoir $ClONO_2$ species, the removal of nitrogen from the stratosphere means that there is more reactive, ozone destroying ClO.The chlorine species Cl_2 and HOCl created in reactions 1, 2, and 5 are short lived. They are quickly photolyzed by sunlight even in visible wavelengths. The Cl_2 molecules are photolyzed into two chlorine atoms, which then participate in the Cl_X catalytic cycles. The HOCl photolysis liberates ClO, another Cl_X species that destroys ozone.



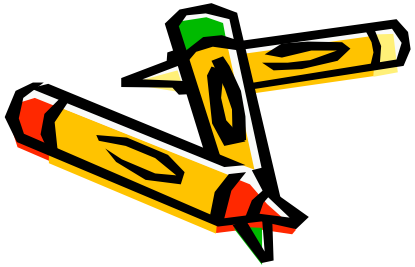
Ozone and Atmospheric Chemistry Measurements



An example of an in-situ measurement technique used to measure ozone vertical profiles involves an ozonesonde, which is an instrument carried on a weather balloon. The ozone sensor consists of two small chambers containing solutions of potassium iodide (KI). Each chamber has a platinum electrode at its base and the electrodes are connected by an ion bridge (a wire). Air is pumped into one chamber and the ozone reacts with the potassium iodide which produces iodine (I2) by the equation

$$2KI + O3 + H2O \rightarrow 2KOH + I2 + O2$$

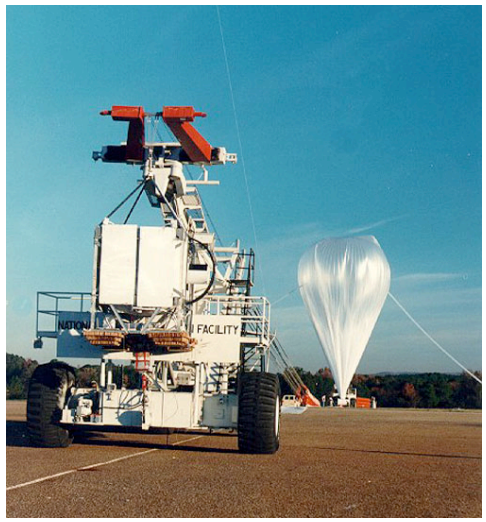
When the iodide changes to iodine, the two cells are no longer in electrical equilibrium. Electrons flow from one cell to another in order to reestablish equilibrium. As the amount of ozone in the air increases, the faster the iodide is changed to iodine and the more electrons flow between the cells (current).



Ozone and Atmospheric Chemistry Measurements

The amount of current that flows between the chambers is measured and sent to the ground receiving station. The ozone amount can be derived by the simple equation

$$P_{ozone} = C \cdot i \cdot Tp \cdot t$$



where P_{ozone} = ozone partial pressure (in nanobars);

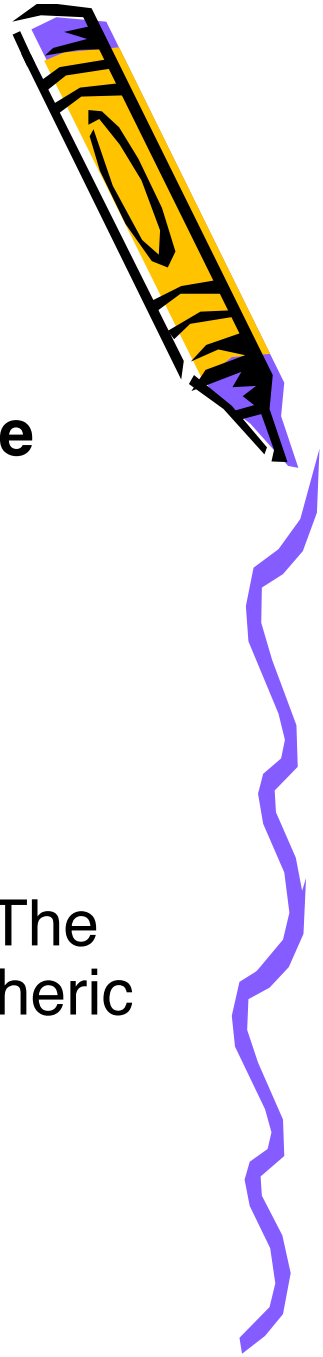
C= constant

i = current

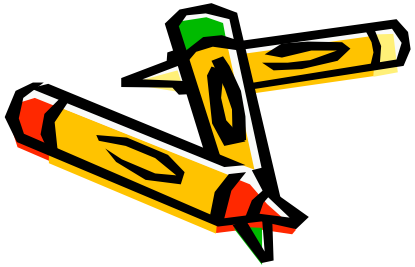
Tp = pump temperature

t = amount of time to force 100 milli-litres of air through the system.

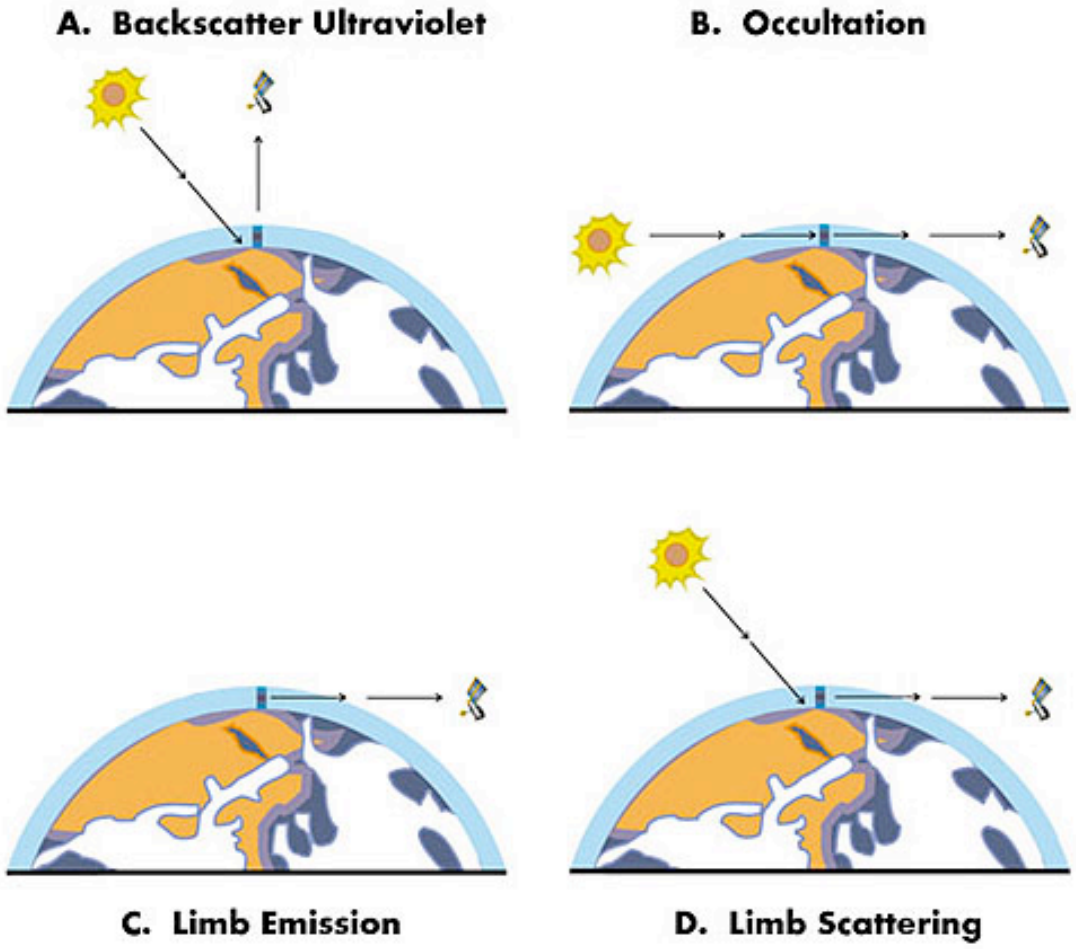
Ozone and Atmospheric Chemistry Measurements



- **Passive Remote Sensing Techniques Using Satellite Platforms**
- (1) the backscatter ultraviolet (BUV) technique
- (2) the occultation technique
- (3) the limb emission technique
- (4) the limb scattering technique.
- Each technique involves a different viewing geometry. The viewing geometry affects the measurements of atmospheric radiation

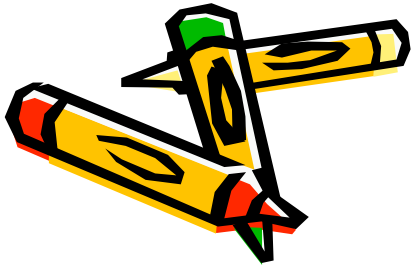


Ozone and Atmospheric Chemistry Measurements



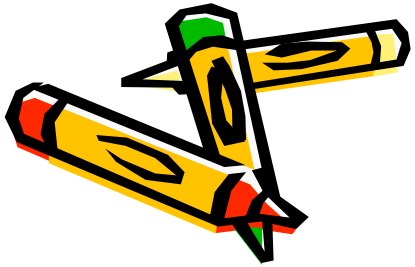
Ozone and Atmospheric Chemistry Measurements

- In the backscatter ultraviolet (BUV) technique, measurements are made of solar ultraviolet (UV) light entering the atmosphere (referred to as the irradiance) at a particular wavelength and of the solar UV that is either reflected from the surface or scattered back from the atmosphere (referred to as the radiance) at the same wavelength



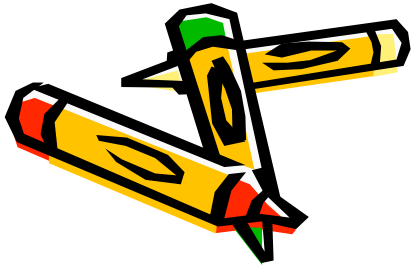
Ozone and Atmospheric Chemistry Measurements

- Another method for measuring the ozone vertical profile from a satellite platform is the occultation technique. Occultation instruments measure solar, lunar, and even stellar radiation directly though the limb of the atmosphere during satellite Sun, Moon, and star rise and set events (depending on which celestial radiator is being used by the satellite instrument). By measuring the amount of absorption of radiation through the atmosphere at different wavelengths (e.g. UV, visible, infrared), occultation instruments can infer the vertical profiles of a number of trace constituents, including ozone

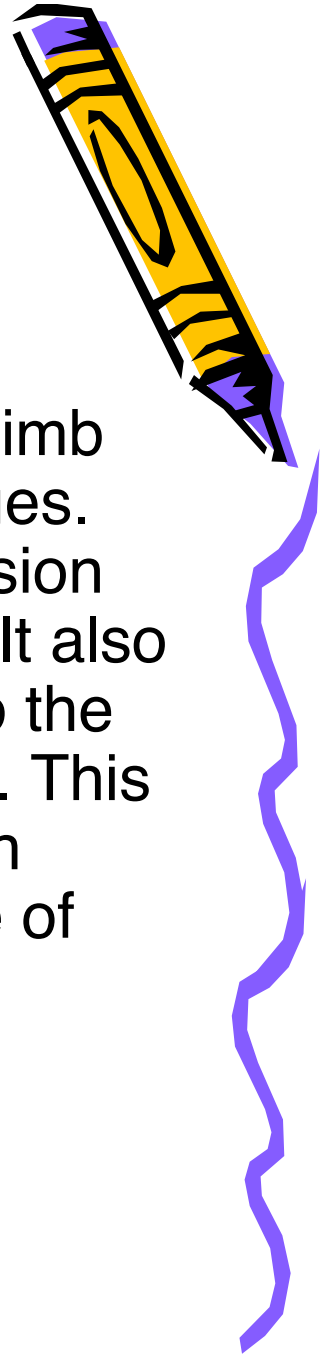


Ozone and Atmospheric Chemistry Measurements

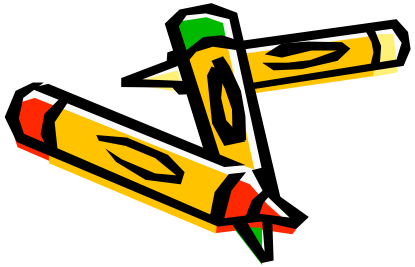
- A third technique for remote sensing measurements of ozone from a satellite platform is the limb emission technique. Instruments based upon the limb emission technique infer ozone amounts from measurements of longwave radiation (infrared or microwave) thermally emitted in the atmosphere along the line of sight of the instrument. The altitude to which the instrument can see is called the tangent altitude. In theory, the instrument could look all the way to the surface, but below a certain altitude (under 10 km), clouds interfere with the emitted longwave radiation.



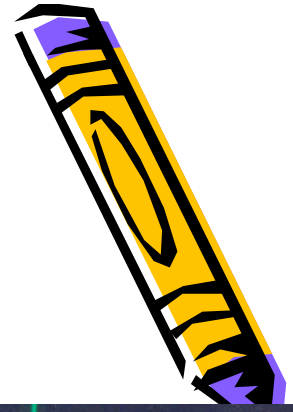
Ozone and Atmospheric Chemistry Measurements



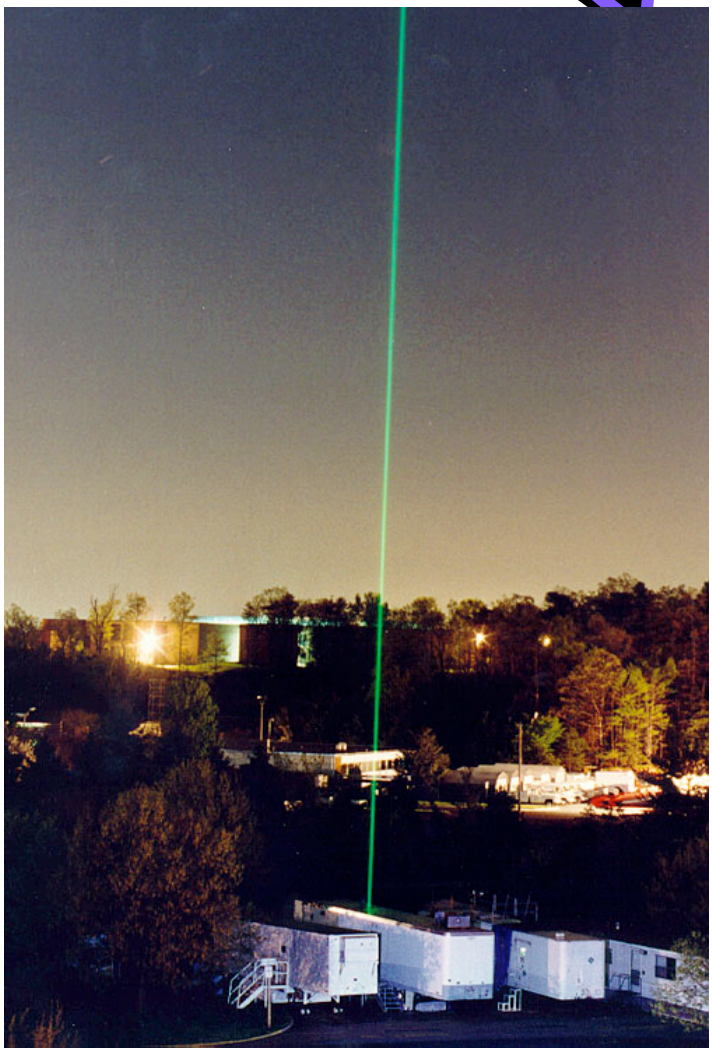
- The final technique for passive remote sensing is called limb scattering. It employs aspects of the other three techniques. The viewing geometry is similar to that of both limb emission and occultation, which provides good vertical resolution. It also measures scattered solar radiation in a manner similar to the BUV measurement, but the light source is in Earth's limb. This allows for coverage through the entire atmosphere, which provides for good column measurements similar to those of BUV instruments like TOMS.

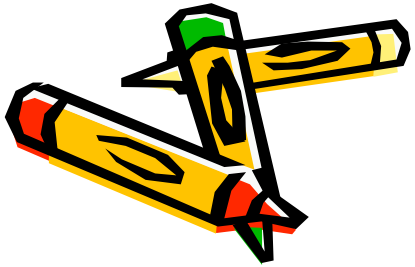


Ozone and Atmospheric Chemistry Measurements



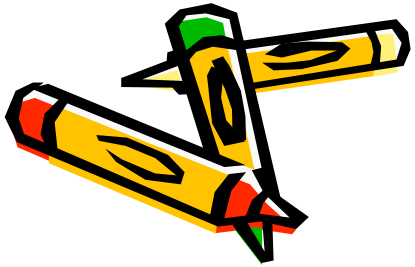
- There are also ground based techniques that use backscattered radiation to remotely measure properties of the atmosphere. LIDARS (light detection and ranging) are active remote sensing instruments which infer temperature, density, and trace constituent concentration profiles from measurements of backscattered laser light





Ozone and Atmospheric Chemistry Measurements

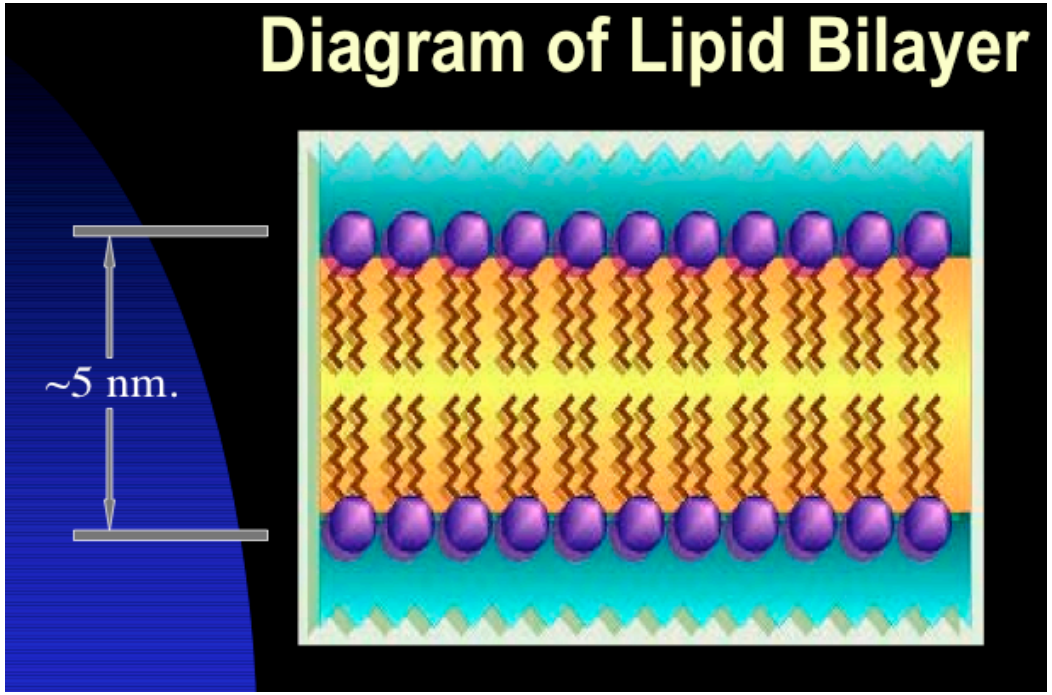
- Measurements of ozone profiles use the differential absorption lidar (DIAL) technique. This technique consists of transmitting an intense beam of light into the atmosphere, where it is scattered by interactions with aerosol particles and air molecules. Some fraction of the light is scattered in the backward direction and can be collected by a telescope located near the transmitting laser. The signal is then collected by a detector. It is stored as a function of time of the transmitted laser pulse. The time duration between transmission of the laser pulse and its detection can be converted directly into a geometric altitude, provided the beam is transmitted vertically



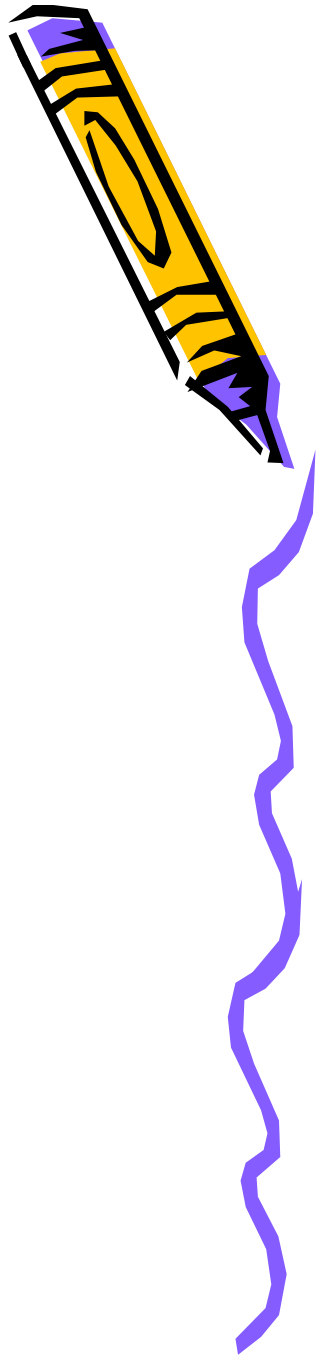
ATP Synthesis: Molecules in Motion

- Controlled transport of molecules and ions across biological membranes is at the heart of a number of key cellular processes:
  - transfer of glucose into red blood cells
  - synthesis of ATP by oxidative phosphorylation

  How does transport occur?



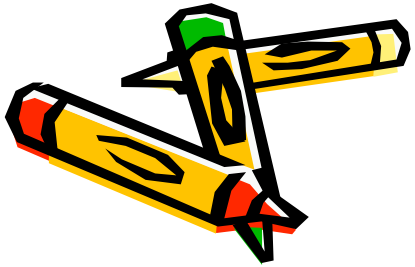
ATP Synthesis: Molecules in Motion



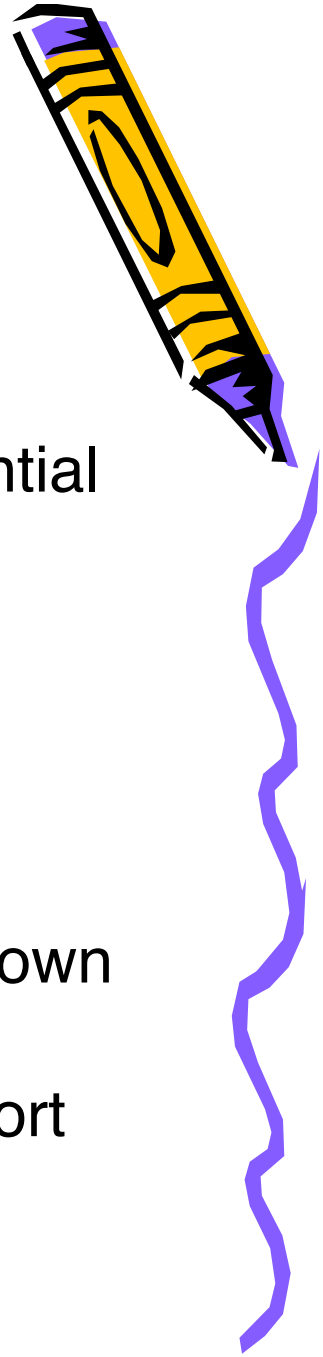
- Thermodynamic tendency to transport species A through bilayer partially determined by activity gradient across membrane

$$\Delta G_m = G_{m,in} - G_{m,out} = RT \ln \frac{a_{in}}{a_{out}}$$

- If $a_{in} < a_{out}$ then transport of neutral or charged ion will be thermodynamically favourable



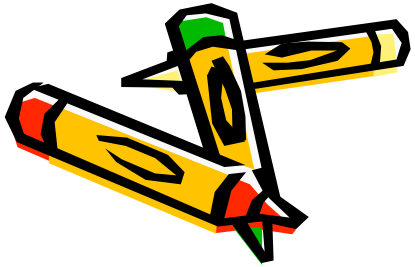
ATP Synthesis: Molecules in Motion



- If A is an ion then you also have to consider Coulomb repulsions on each side of bilayer which gives rise to potential difference

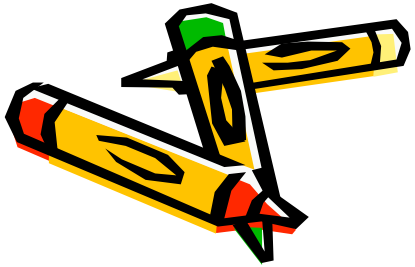
$$\Delta G_m = RT \ln \frac{a_{in}}{a_{out}} + zF\Delta\phi$$

- Z is ion charge number and F is Faraday's constant
- This indicates Passive Transport as species A is moving down a concentration gradient
- Possible to move species against gradient - Active Transport

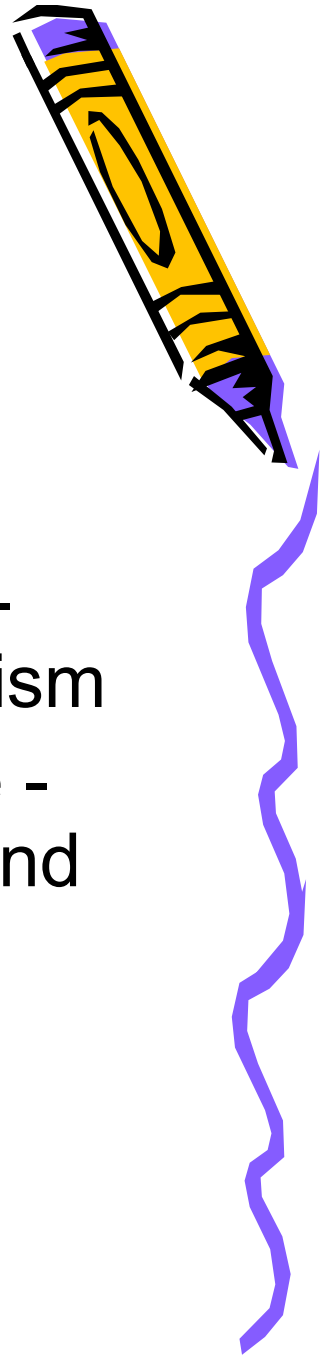


ATP Synthesis: Molecules in Motion

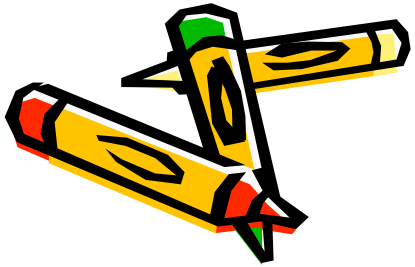
- Ions such as H^+, Na^+, K^+, Ca^{2+} often actively transported across membranes by integral proteins - Ion Pumps.
- Ion Pumps - molecular machines which work by adopting conformations that are permeable to one ion but not others dependent on the state of phosphorylation of the protein.



ATP Synthesis: Molecules in Motion



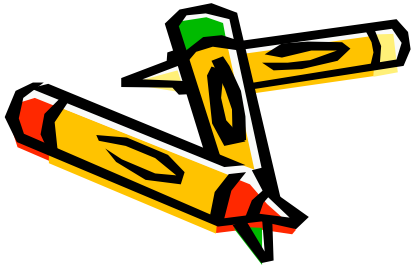
- Protein phosphorylation requires dephosphorylation of ATP, conformational change opens or closes pump is endergonic - requires use of energy stored during metabolism
- Important example of ion pump is H^+-ATPase - present in inner membranes of chloroplasts and mitochondrion.
- $ADP + P + H^+ <=> ATP \quad \Delta G = +31 kJ\ mol^{-1}$



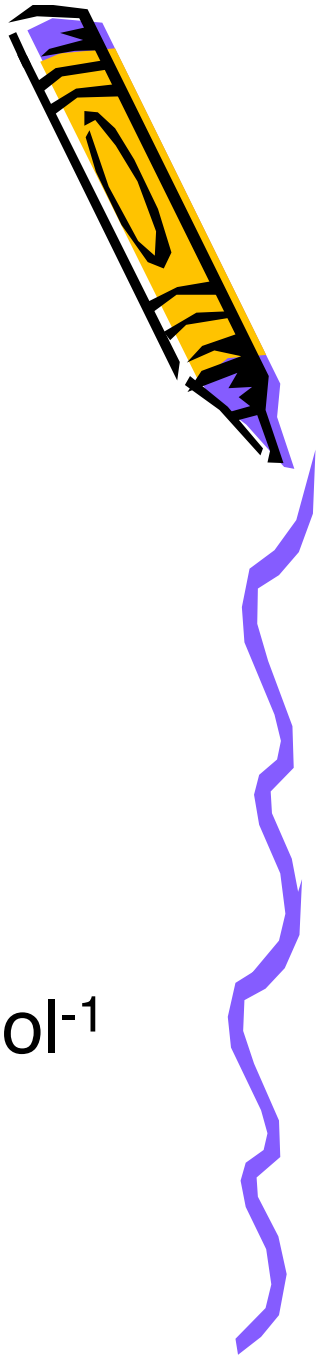
ATP Synthesis: Molecules in Motion

- Chemiosmotic Theory - Peter Mitchell explained how H^+ATPases use flux of protons through membrane to power phosphorylation of ADP to ATP
- Estimate Gibbs energy available for phosphorylation

$$\Delta G_m = RT \ln \frac{\left[H^+\right]_{in}}{\left[H^+\right]_{out}} + F\Delta\phi$$



ATP Synthesis: Molecules in Motion



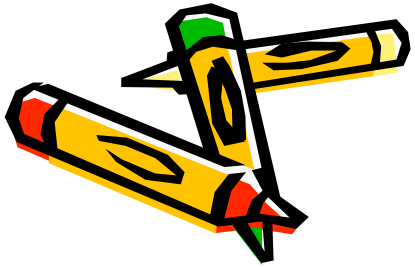
- Proton so Z=1
- Need to substitute for Ph,

$$\Delta pH = pH_{in} - pH_{out} = -\log\left[H^+\right]_{in} + \log\left[H^+\right]_{out}$$

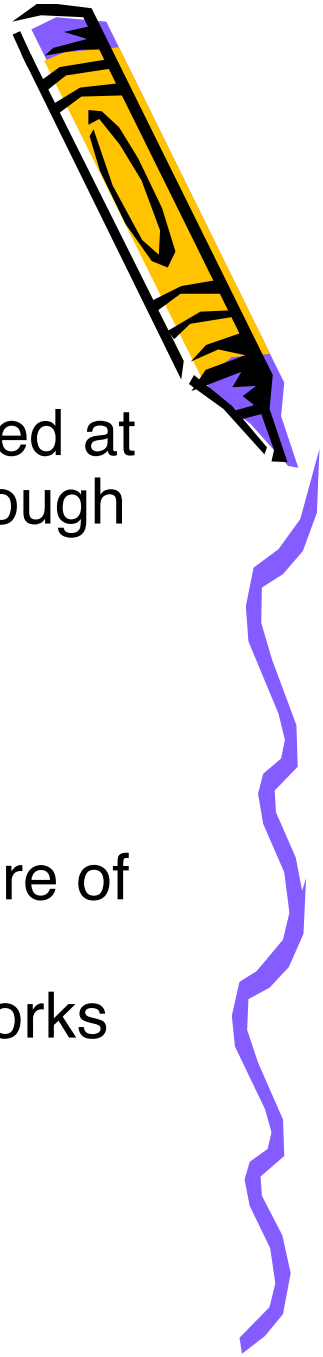
- So

$$\Delta G = F\Delta\phi - 2.303RT\Delta pH$$

ΔpH~ -1.4 and $\Delta\phi$~0.14V, So ΔG_m ~ +21.5 kJ mol^{-1}

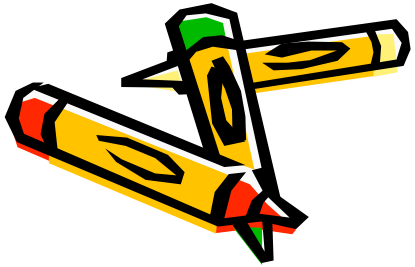


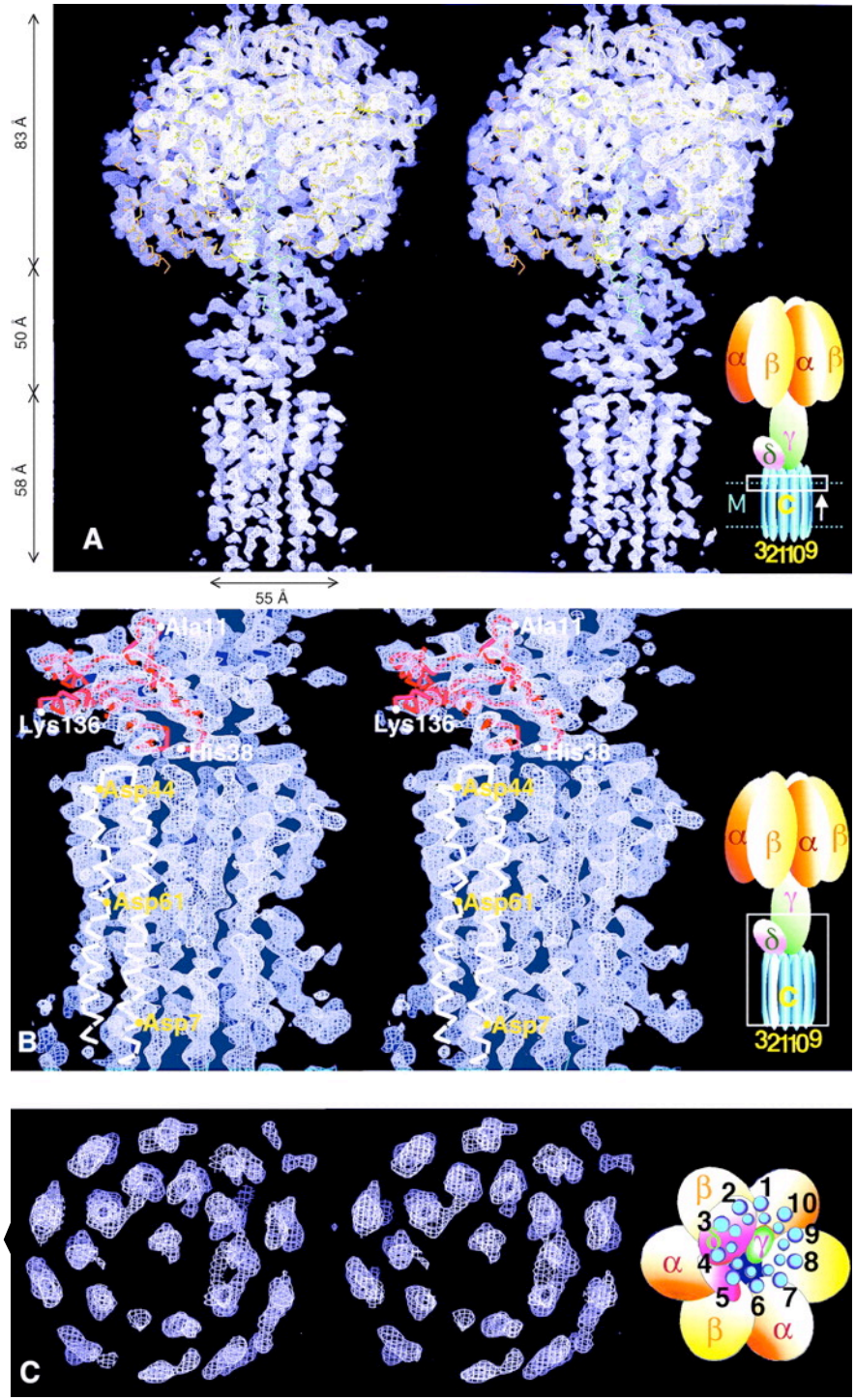
ATP Synthesis: Molecules in Motion



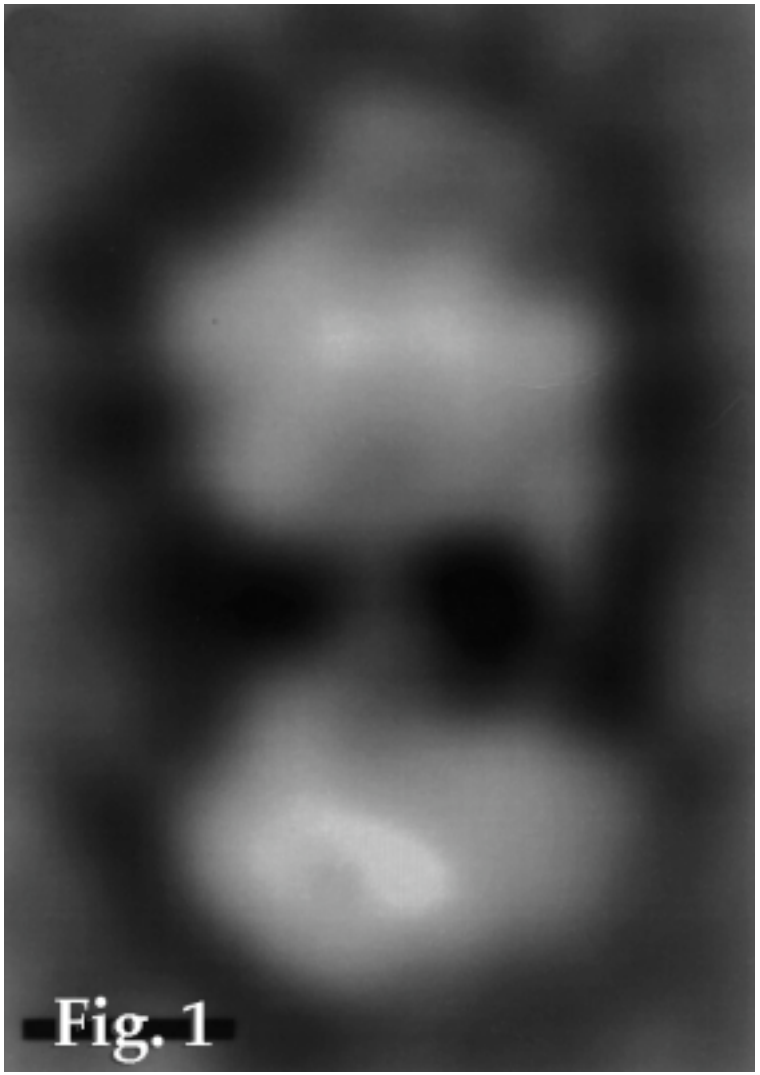
- Need 31kJ mol^{-1} for phosphorylation therefore we need at least 2 mol of protons (probably more) must flow through the membrane for phoshorylation of 1 mol of ADP

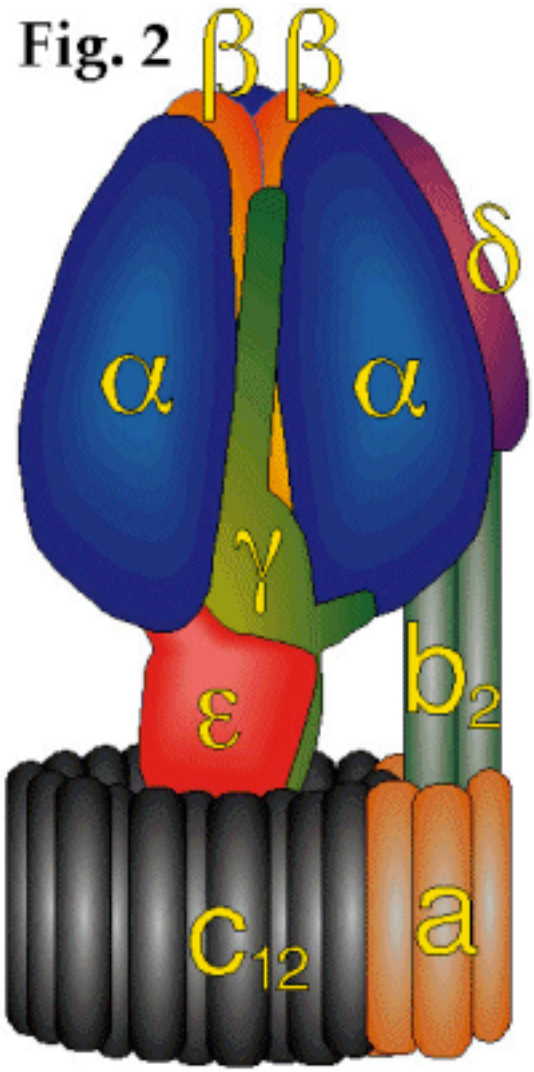
- Coupling of proton flow to phosphorylation is of considerable scientific interest. To understand how proteins flow across membrane need to know structure of ATPase's and model of mechanism. Domain of crystallography, AFM and smFPA. Model of how it works by Paul Boyer



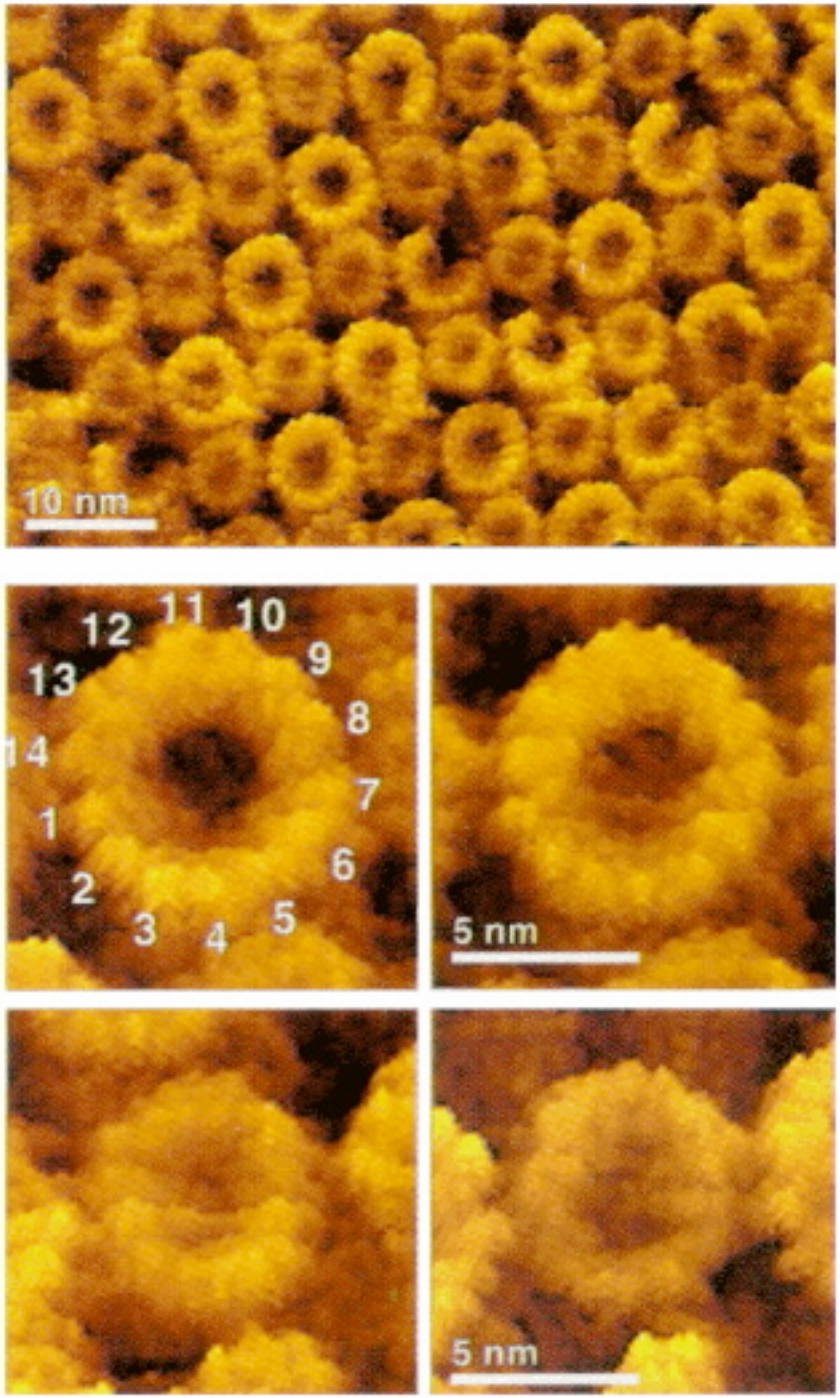


- Walker and colleagues have solved a structure from crystals containing the complete ATP-synthase complex from yeast mitochondria. Its membrane-embedded F0 sector has a rotation generator fueled by the proton-motive force, which provides the energy required for the synthesis of ATP by the F1 domain





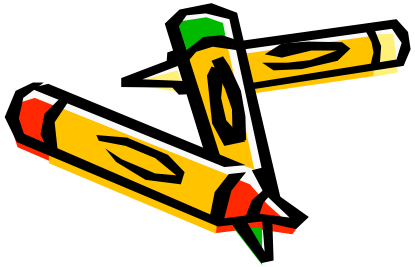
This image of the complete *E. coli* complex, using image averaging and cryo-electron microscopy, and the model derived from it, showing a second stalk

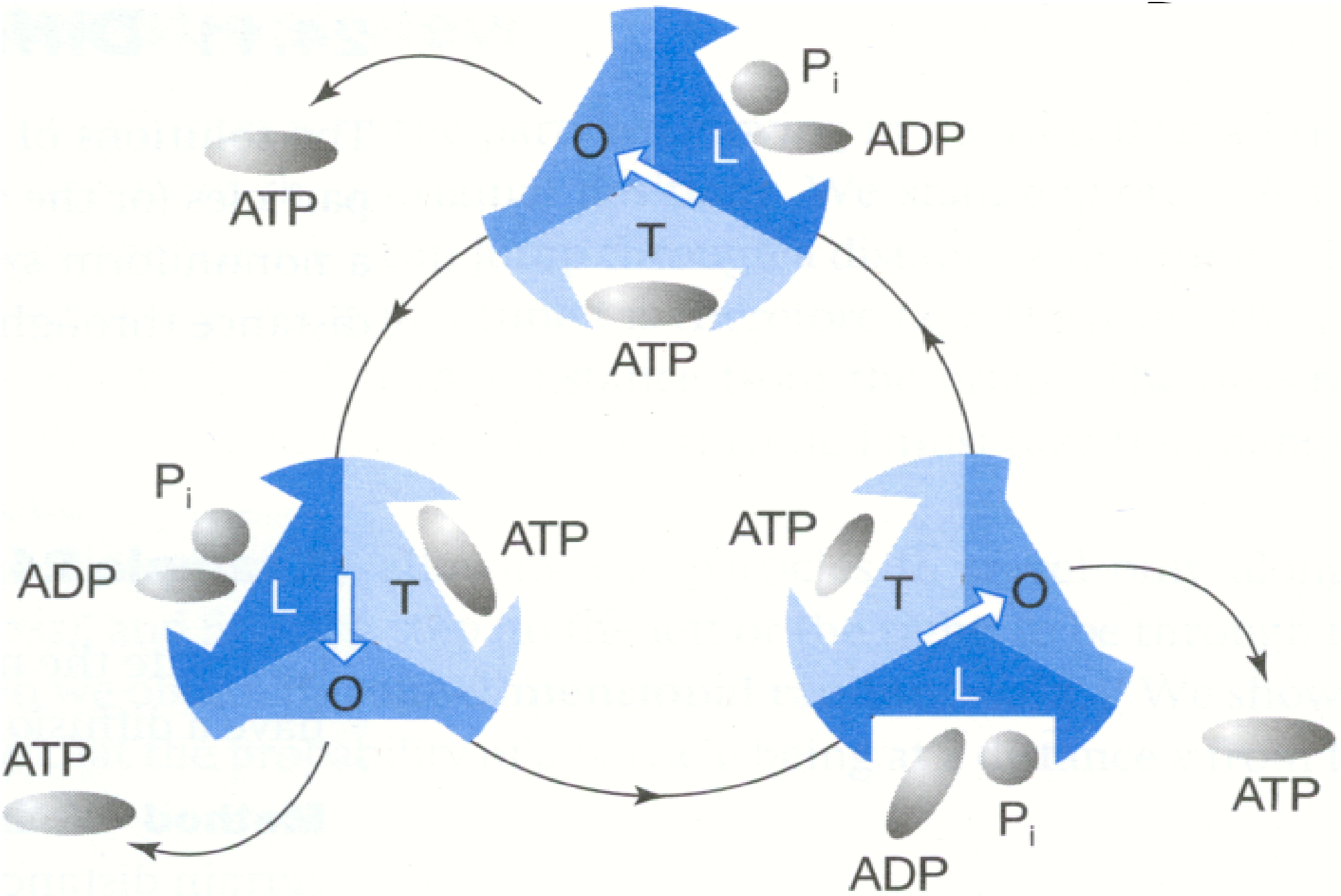


Subunit-III oligomers of chloroplast ATP synthase visualized in 25 mM MgCl2, 10 mM Tris-HCl, pH 7.8, at room temperature using atomic force microscopy (Nanoscope III, Digital Instruments)11. Top, the distinct wide and narrow rings represent the two surfaces of the subunit-IIIx oligomer; middle, wide oligomer ends, showing 14 subunits-III; bottom, narrow oligomer ends. The full grey-level range of these topographs was 2 nm

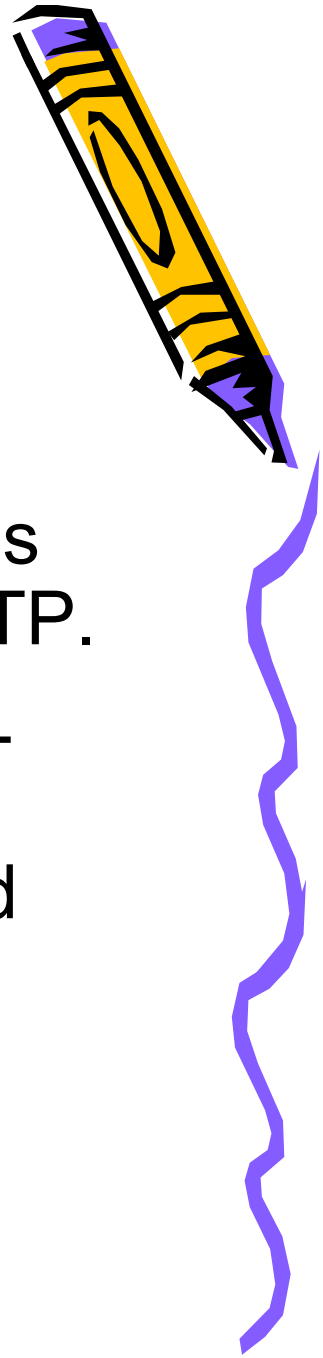
ATP Synthesis: Molecules in Motion

- The conformations of the three pairs of subunits may be loose (L), tight (T) or open (O), one of each type is present at each stage. Protein at centre of interlocked structure, γ subunit (the white arrow) rotates and indicates structural changes that cycle each of the segments between L, T and O

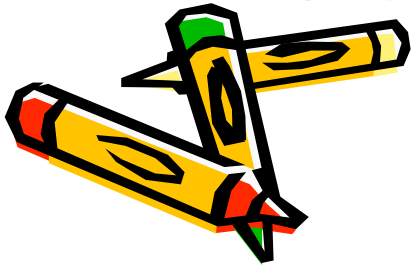



ATP
O
L
P_i
ADP
T
ATP
P_i
ADP
L
T
ATP
O
ATP
ATP
T
O
L
P_i
ADP
ATP

ATP Synthesis: Molecules in Motion

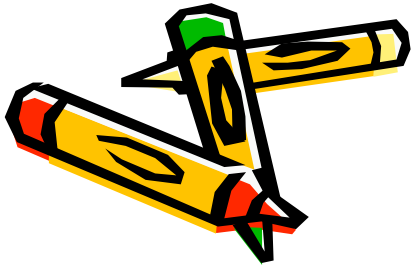


- Start, a T unit holds an ATP
- ADP + P group migrate into an L site -> closes into a T, earlier T opens -> O and releases ATP.
- ADP +P in T site condense to ATP and new L site is ready for cycle to begin again.
- Proton flux drives rotation of the γ subunit and hence conformational changes of the α/β segments, as well as providing energy for condensation.

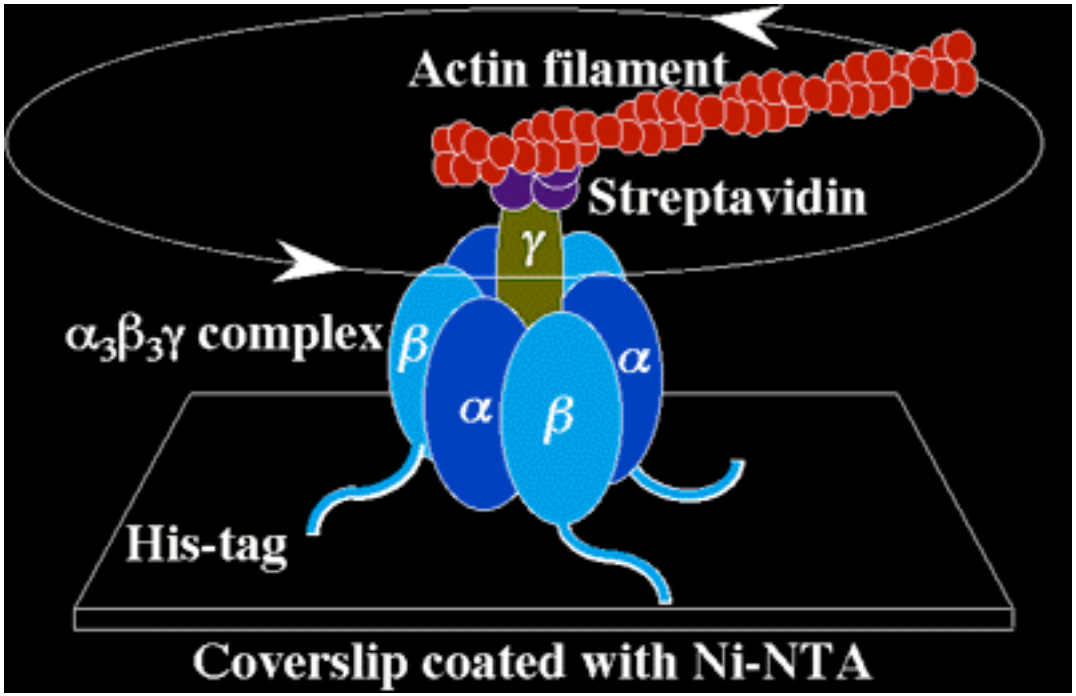


ATP Synthesis: Molecules in Motion

- Technique for monitoring real time events domain of single molecule Fluorescence Polarisation Anisotropy smFPA. Temporal variation in the dipole orientation of a rigidly attached or rotationally diffusing tethered probe.
- Yields information on the angular motion of macromolecules

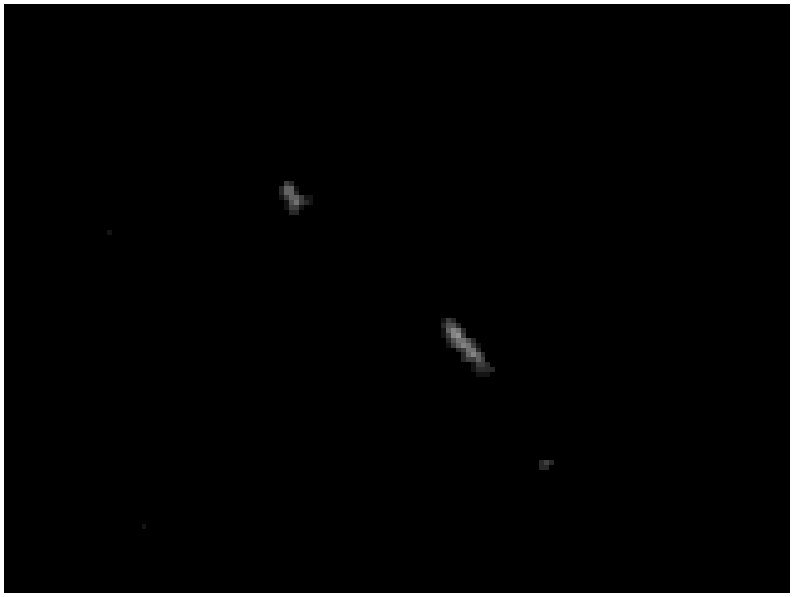


ATP Synthesis: Molecules in Motion



Rotation of the gamma subunit of thermophilic F1-ATPase was observed directly with an epifluorescent microscope. Fluorescently labeled actin filament was attached to the gamma subunit for the observation.

ATP Synthesis: Molecules in Motion



Images of the rotating particles were taken with a CCD camera attached to an image intensifier, recorded on an 8-mm video tape. (Noji et al. *Nature* **386** 299-302 1997