Photochemistry basics

The interaction of molecules in air with light is an important part of atmospheric chemistry. Some of these interactions are purely physical and others involve both physical changes and chemical changes. This is a very brief discussion of the types of changes that may occur and how they are treated in atmospheric chemistry. All photochemical interactions are initiated by the absorption of a light quantum by an atom or molecule.

The interactions of atmospheric molecules and light are important because of:

- The resulting chemical reactions (photolysis)
- The transformation of energy between light and heat that influences atmospheric circulation and climate
- The usefulness of light and other electromagnetic radiation in probing the composition of the atmosphere, for example from satellite observations.

The electromagnetic spectrum looks like this:
microwaves – cause gas phase molecules to rotate
infrared – cause stretching and vibrating of molecular bonds
visible – causes low energy electronic transitions in atoms and molecules
ultraviolet radiation – causes higher energy electronic transitions
x-rays – inner electron excitation and ionization.
y-rays – highly penetrating ionizing radiation associated with radioactivity

In atmospheric chemistry, we deal mainly with incoming solar radiation, which has a spectrum like this:

In terms of chemical reactions in the atmosphere, we are concerned primarily with near UV and visible radiation which excites electronic transitions and can cause chemical reactions. We are also interested in the interaction of chemicals with infrared radiation which causes heating of the atmosphere (i.e. greenhouse gases). In addition to the gases, aerosols and cloud droplets can also scatter and absorb incoming UV and visible radiation.
Absorption

Light absorption occurs only when the energy of an incident photon corresponds exactly to the difference in two energy states of the molecule. Depending on the energy of the photon, that may be a change in rotation, vibration, or electronic state. As explained earlier, light absorption need not result in chemical changes.

A molecule excited by the absorption of a photon can lose the extra energy via several mechanisms:

- dissociation – the molecule breaks apart.
- direct reaction – the excited molecule reacts with another molecule
- isomerization (rearrangement) – internal rearrangement of bonds to make a more stable compound
- collision – losing energy to surrounding molecules without chemical reaction
- internal energy transfer
- luminescence (fluorescence or phosphorescence) – emission of a photon
- photoionization – ejection of an electron to form an ion

Photolysis is a general word describing chemical changes occurring from reactions initiated by light, regardless of the detailed mechanism.
The absorption of light by a gas is described macroscopically by the Beer-Lambert law:

\[ I = I_0 e^{-\sigma N l} \]

where \( I_0 \) is the intensity of incident radiation, \( I \) is the intensity of the exiting beam, \( N \) is the number density of the absorbing molecule, and \( l \) is the path length and \( \sigma \) is the absorption cross section. The product \( \sigma N l \) is called the optical depth. Absorption cross sections are measured in the laboratory as a function of wavelength and temperature.

Quantum yield

As described above, the absorption of a photon by a molecule does not necessarily lead to a chemical reaction. The quantum yield describes the probability of a particular outcome resulting from an absorption event. For example, let’s say that 70\% of the time, absorption of a particular wavelength photon (\( \lambda \)) by a molecule results in dissociation:

\[ AB \xrightarrow{hv} A + B \]

The quantum yield for dissociation at this wavelength, \( \Phi_\lambda \), would be 0.7. If the other 30\% of the time, absorption resulted in fluorescence,

\[ AB \xrightarrow{hv} AB + h\nu' \]

the quantum yield for fluorescence would be 0.3.

As you might expect, photodissociation quantum yields are very wavelength-dependent. The absorbed photon must have sufficient energy to break a chemical bond in the molecule in order to result in dissociation. At longer wavelengths, the quantum yield for dissociation is likely to be zero. Quantum yields used in atmospheric chemistry are determined experimentally in the laboratory.
Atmospheric photolysis rates

Calculating an atmospheric photolysis rate for a given chemical reaction requires three quantities:

- the atmospheric radiation field
- the absorption cross section
- the quantum yield

Kinetically, photolysis is described as a first-order loss, as follows:

\[ A \xrightarrow{hv} B + C \]

\[ \frac{d[A]}{dt} = -k[A] = -j[A] \]

for photolysis reactions, the rate constant is often called \( j \) instead of the usual \( k \) used for thermal reactions but they have the same meaning. The units of \( j \) are \( 1/\text{time} \), usually \( \text{s}^{-1} \).

We can calculate \( j \) for a given reaction as follows:

\[ j = \int \Phi_\lambda \sigma_\lambda F_\lambda d\lambda \]

where \( \Phi_\lambda \) and \( \sigma_\lambda \) are the quantum yield and absorption coefficient as functions of wavelength and \( F_\lambda \) is the spherically integrated photon flux (see discussion below). So, what’s being done here is just to take the product of the quantum yield, absorption coefficient, and photon flux at each wavelength and sum them all up.

Doing this calculation by hand is a lot of work, particularly because of the need to do break everything down by wavelength. Fortunately, there exist a number of computer models which calculate \( j \)-values for various molecules of importance to atmospheric chemistry. “TUV” is an example of one such model. It can be downloaded or run on-line at http://www.acd.ucar.edu/TUV.
Some comments about the atmospheric radiation field:

As shown above, in order to calculate photolysis rates, one needs to know the rate at which photons of various wavelengths are passing through a given volume of air. This is called the “actinic flux” and it is really a spherical integral of the photon flux at a point in the atmosphere.

The photon flux at any given location is a function of:

a) the flux of photons from the sun reaching the top of the atmosphere, and the solar zenith angle (angle between the incident sun’s rays and the earth’s surface).

b) all the light absorption and scattering above and below the location of interest. This includes reflection from the Earth’s surface, and the optical effects of clouds and aerosols in the atmosphere.

The radiation field consists of two components: the direct and diffuse beams. The direct beam is just incoming sunlight as it moves downward through the atmosphere. The direct beam is attenuated by scattering and absorption in the atmosphere until it hits the ground, where it is finally absorbed and/or converted to scattered light. The scattered light is called “diffuse” because it is moving in many directions with a broad angular distribution.

The radiation field can be measured and modeled. Both are rather complex tasks, because of the complexity of absorption and scattering and the need to determine the light flux as a function of wavelength.
We can look up the absorption cross-sections and quantum yields for many atmospheric gases in one of these data compilations:

http://jpldataeval.jpl.nasa.gov/download.html

Summary of evaluated kinetic and photochemical data for atmospheric chemistry, Atkinson et al., 2004
http://www.iupac-kinetic.ch.cam.ac.uk