CHAPTER 2

SPECTROSCOPY AND PHOTOCHEMISTRY

Photochemical processes play a key role in the chemistry of the Earth's atmosphere. Most important atmospheric reactions begin with molecular photodissiciation, followed by reactions of the photodissociation products. Thus an understanding of the basics of photochemistry is essential in discussions of atmospheric chemistry.

Understanding photochemistry requires an understanding of the quantum mechanical properties of atoms and molecules. Spectroscopic knowledge is also useful in many laboratory studies of atmospheric reactions, and in a variety of methods used to detect and quantify concentrations of important atmospheric species.

In this chapter we discuss some important concepts in the spectroscopy and photochemistry of atoms and molecules. A basic understanding of quantum mechanics is assumed.

2.1 PROPERTIES OF LIGHT, ATOMS, AND MOLECULES

The most important advance in the physical sciences over the past 100 years was the gradual realization that the laws of classical physics, developed to describe the macroscopic behavior of matter, required modification when describing systems at an atomic and molecular level. The theory describing the behavior of matter on a microscopic scale is quantum mechanics. In this section we review the most important results from quantum mechanics as applied to atoms and molecules.

In quantum mechanics light possesses both wave-like and particle-like properties. In particular, light can be described in terms of particles, or photons, whose energy is given by the relationship

$$E = h\nu = hc/\lambda \qquad (2.1)$$

where the usual relationship between wavelength and frequency applies

$$c = \nu\lambda \qquad (2.2)$$

In the above equations ν and λ represent the frequency and wavelength of light, respectively, c is the speed of light (equal to 2.998×10^8 m/s), and h is Planck's constant (equal to 6.626×10^{-34} J·s). These equations exhibit the dual nature of light. Eq 2.1, for example, gives the energy of a photon of light in terms of frequency or wavelength, characteristics of waves.

Because the enegy of a photon is proportional to $1/\lambda$, spectroscopists often uses inverse wavelength as a unit of energy. This energy unit, when wavelength is given in cm, is called wavenumbers (cm^{-1}). Energy in wavenumbers is related to the MKS energy unit (Joules) by the expression

$$\tilde{E} = E/hc \qquad (2.3)$$

We will use the standard convention of indicating energy in wavenumbers with the symbol $\tilde{E}$ (and, in general, will use the symbol ~ to indicate any quantity expressed in units of wavenumbers), and energy in conventional units with the symbol E. The conversion factor between Joules and wavenumbers is

$$1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J} \qquad (2.4)$$

It is convenient to express energies for atoms and molecules in wavenumbers because it avoids the problems with such energies being extremely small numbers when expressed in the MKS unit Joules.

When quantum mechanics is applied to atoms it is found that atoms can take on only certain values of energy. These electronic energy levels can by found by solving the appropriate Schrodinger equation for the atom. For a particular electron configuration an atom (or atomic ion) will have one or more possible electronic states. These states can be given labels, called term symbols. The term symbol for an atom has the general form ^{2S+1}L, where S is the total spin angular momentum quantum number and L is the total orbital angular momentum quantum number. The superscript 2S+1 represents the spin degeneracy of the electronic state, that is, the number of distinct states of the atom having the same value for energy. The orbital angular momentum is represented by a symbol based on the value of quantum number for the total orbital angular momentum, L.

L	state
0	S
1	P
2	D
3	F

The term symbols corresponding to a particular electron configuration can be found using standard techniques. For example, for the ground state electron configuration of oxygen, $1s^2 2s^2 2p^4$, there are three electronic states – ^1S, ^3P, and ^1D. These can be placed in order of energy using Hund's rules (which are obtained from an approximate quantum mechanical description of an atom), which apply to different electronic states arising from the same electron configuration

Hund's first rule - The higher the value of S the lower the energy

Hund's second rule – For two states with the same value of S, the higher the value of L the lower the energy

In the present example the three electronic states obtained for the lowest energy electron configuration of oxygen are, in order of energy, $^3P < {}^1D < {}^1S$ (see Fig 2.1). Note that because of interactions between the spin and orbital angular momentum the electronic states with $L \neq 0$ and $S \neq 0$ are actually several different states with slightly different values for energy. For atoms with low atomic number this interaction (called L-S, or Russell-Saunders coupling) is described by an additional quantum number, J, whose value depends on the values for L and S. On those occasions where it is important to distinguish states with different values of J, the value will be given as a subscript in the term symbol, as $^{2S+1}L_J$.
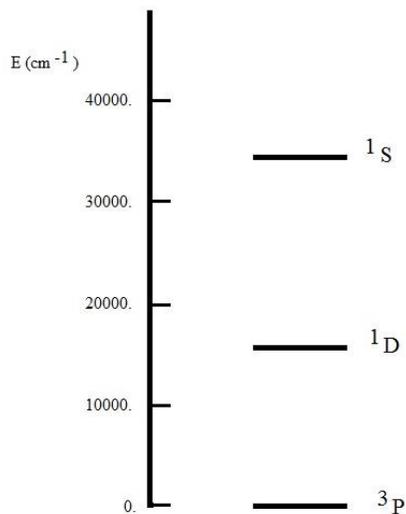

E (cm^{-1})

40000.

30000.

20000.

10000.

0.

^1S

^1D

^3P

Figure 2.1. Electronic states for O atoms. Note that the ^3P state actually consists of three separate states with slightly different energies ($^3P_2 = 0.0$ cm^{-1}, $^3P_1 = 158.$ cm^{-1}, $^3P_0 = 227.$ cm^{-1})

Molecules (or molecular ions) will also have different values for electronic energy depending on the electron configuration of the molecule. For diatomic molecules the different states arising from a particular electron configuration can be found using standard techniques, as was the case with atoms. The different electronic states are represented by a term symbol with the general form $^{2S+1}\Lambda_{g/u}^{+/-}$. S again represents the total spin angular momentum quantum number, while Λ is a symbol representing the quantum number for the projection of the total orbital angular momentum along the internuclear axis. The relationship between Λ and its symbol is similar to that between L and its symbol for atoms

Λ	state
0	Σ
± 1	Π
± 2	Δ

Note that all states except the $\Lambda = 0$ state are doubly degenerate. In addition, for homonuclear diatomic molecules the symbol g or u is used to indicate whether the electronic wavefunction is symmetric (g) or antisymmetric (u) with respect to inverson through the center of mass of the molecule. For all diatomic molecules in Σ electronic states the symbol + or − is used to indicate whether the electronic wavefunction is symmetric (+) or antisymmetric (-) with respect to reflection through a plane containing the internuclear axis. Hund's rules again apply for the energy ordering of states arising from the same electron configuration, with the modification that L is replaced by Λ in Hund's second rule. For example, for the ground state electron configuration for O_2, $(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^2$, there are three electronic states, $^1\Sigma_g^+$, $^3\Sigma_g^-$, and $^1\Delta_g$. Based on Hund's rules the energy ordering of these states is $^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma_g^+$, as shown in Fig. 2.2.
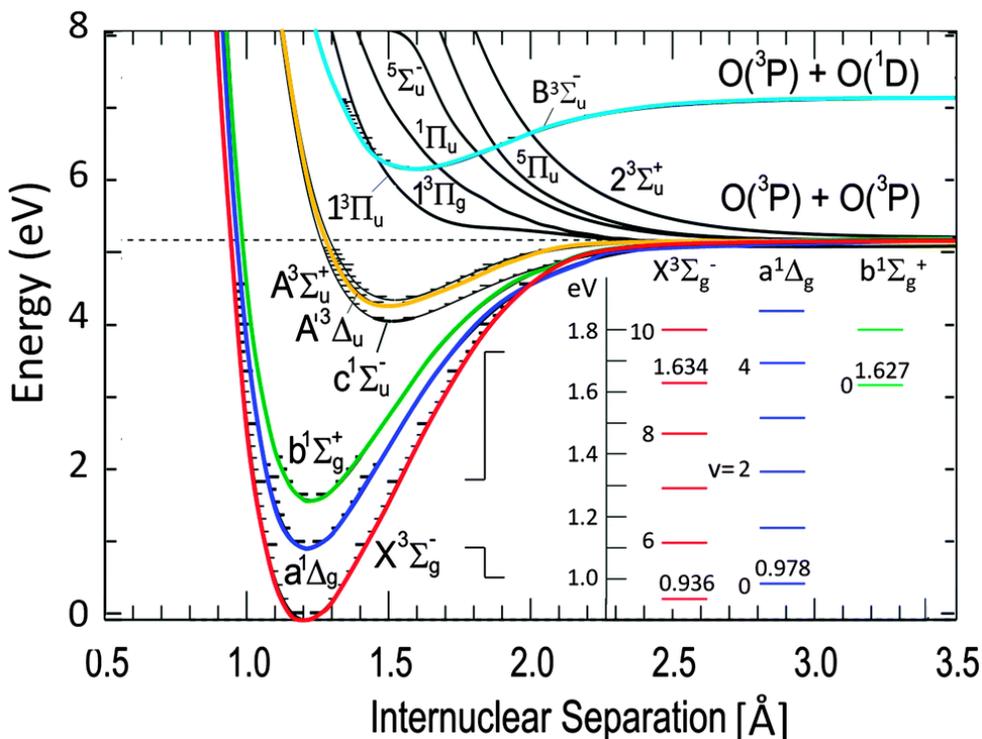

Figure 2.2. Electronic states for O_2. The left side of the figure shows the potential energy curves for the lowest energy electronic states of O_2, while the right side of the figure indicates the location of vibrational energy levels for the $X^1\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states. Note that 1 eV = 8066. cm^{-1}. Figure from T. G. Slanger, P. C. Cosby, **J. Phys. Chem.** 1988, **92**, 267-282.

In general it is more difficult to characterize the electronic states of polyatomic molecules than it is those for diatomic molecules. Exceptions occur for molecules with a high degree of symmetry, such as CH_4 or C_6H_6, where group theory can be used to label the electronic states by their symmetry properties. However, even for molecules with low symmetry the total spin quantum number S still applies. By convention, we often characterize the electronic states for polyatomic molecules based on their spin degeneracy, so that S = 0 states are singlet states, S = 1 states are triplet states, and so forth. Since for systems with an odd number of electrons the quantum number S will take on half integer values (S = ½, $^3/_2$, ...) we can talk about doublet states (S = ½), quartet states (S = $^3/_2$), and so forth for those systems.

Unlike atoms, molecules can also possess vibrational and rotational energy. These energies are quantized, that is, they can only take on particular values, found by solving the appropriate Schrodinger equation. For diatomic molecules, in the RRHO (rigid rotor – harmonic oscillator) model, the rotational and vibrational energy levels are given by the expressions

$$\tilde{E}(rotation) = J\,(J+1)\,B \qquad J = 0,\ 1,\ 2,\ ... \qquad M_J = 0,\ \pm1,\ \pm2,\ ...,\ \pm J \tag{2.5}$$

$$\tilde{E}(vibration) = (v + \tfrac{1}{2})\,\omega \quad v = 0,\ 1,\ 2,\ ... \tag{2.6}$$

where B is the rotational constant, ω is the vibrational constant, J and M_J are quantum numbers for rotation, and v is the quantum number for vibration. The values of B and ω are related to the properties of the molecule, with

$$B = h/8\pi^2 c\mu r_e^2 \tag{2.7}$$

$$\omega = (1/2\pi c)\,(k/\mu)^{1/2} \tag{2.8}$$

In the above expressions r_e is the equilibrium bond distance, k is the force constant for the bond (related to the curvature of the poential energy curve at $r = r_e$), and $\mu = m_A m_B/(m_A + m_B)$ is the reduced mass of the diatomic molecule AB. By an appropriate choice of units the values for B and ω will be in units of wavenumbers. For diatomic molecules, typical values for B are $0.1 - 10\ cm^{-1}$, and typical values for ω are $100 - 3000\ cm^{-1}$.

The above equations are only approximate, as they ignore interactions between vibrational and rotational motion of the molecule and anharmonic effects. These can be accounted for by straightforward extentions of eq 2.5 and 2.6.

Polyatomic molecules will also have both rotational and vibrational energy, which, as for diatomic molecules, will be quantized. The main difference between a diatomic molecule and a polyatomic molecule is the number of unique (normal mode) vibrations that occur. In general, for a molecule containing N atoms, there will be 3N - 5 normal mode vibrations (if the molecule is linear) or 3N - 6 normal mode vibrations (if the molecule is nonlinear). For small molecules these normal mode vibrations are relatively easy to illustrate, as is done for formaldehyde in Figure 2.3. The rotational and vibrational energy levels for a polyatomic molecule can often be obtained to a first approximation by an extention of the RRHO model.

Atoms and molecules can interact with light by absorbing or emitting photons to move between energy levels. Such transitions must satisfy energy conservation, with the energy of the absorbed or emitted photon corresponding to the difference in energy between two states of the atom or molecule (note that we assume all interactions involve a single photon, and so ignore multiphoton processes). Transitions are also subject to selection rules, which classify transitions as allowed and forbidden based on approximate solutions to the appropriate Schrodinger equation and a semiclassical model for the interaction of light with atoms or molecules (the dipole approximation). The selection rules that apply for atoms, diatomic molecules, and polyatomic molecules are as follows:

Atoms	(electronic)	$\Delta L = 0, \pm 1$ (except that $L = 0$ to $L = 0$ is forbidden)
		$\Delta S = 0$
Diatomic molecules	(electronic)	$\Delta\Lambda = 0, \pm 1$
		$\Delta S = 0$
		$+$ to $+$ and $-$ to $-$ are allowed
		g to u and u to g are allowed

(vibration, for energy levels in the same electronic state)
        molecule must be heteronuclear
        $\Delta v = \pm 1$

(rotation, for energy levels in the same electronic state)
        molecule must be heteronuclear
        $\Delta J = \pm 1$

Polyatomic molecules	(electronic)	$\Delta S = 0$

Notice that the selection rule $\Delta S = 0$ applies to allowed electronic transitions for atoms, diatomic molecules, and polyatomic molecules, and so is a general selection rule for such transitions.
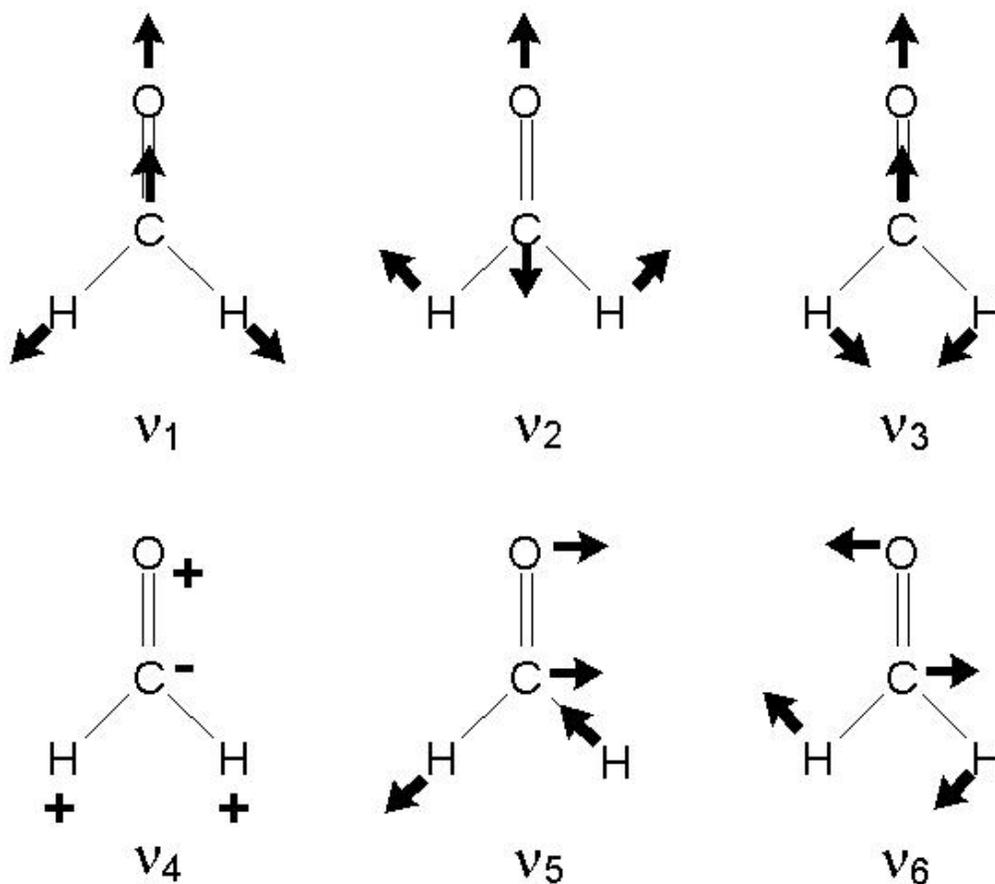

Figure 2.3. Normal mode vibrations for formaldehyde (H_2CO).

Since selection rules are obtained from approximate solutions to the Schrodinger equation, transitions classified as forbidden will often take place due to factors ignored in the approximations. However, forbidden transitions are generally weak. Allowed transitions are often strong, but may also be weak depending on other factors not taken into account in the selection rules (for example, unfavorable Franck-Condon factors for transitions between vibrational states in different electronic states of a molecule).

Finally, one can derive a general expression for the absorption of light by an atom or molecule. This expression, which applies to one photon absorption of monochromatic light by a single light absorbing molecule in the weak intensity limit, is called Beer's law. While Beer's law can be written in a variety of ways, it is most commonly written by atmospheric chemists as follows
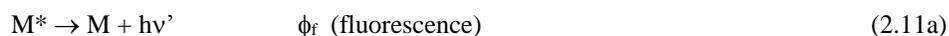
$$I_\ell = I_0 \exp(-\sigma N \ell) \tag{2.9}$$

In the above expression I_0 is the initial intensity of light and I_ℓ is the intensity after traveling a distance ℓ through a sample of absorbing molecules. N is the concentration of absorbing molecules and σ is the absorption cross-section of the absorbing molecule. The usual units for the terms in eq 2.9 are cm^2/molecule for σ, molecules/cm^3 for N, and cm for ℓ, though other units can be used. Absorption cross-sections, when given in the form used in eq 2.9, are often labeled "base e" because of the fact that the common form of Beer's law used by chemists is in terms of A, the absorbance, which is a "base 10" unit ($A = -\log_{10}(I_\ell/I_0)$). There is ample room for confusion, particularly when obtaining cross-section from papers appearing prior to 1980, when alternative forms of Beer's law were often used. Care therefore should be used when taking data from older research papers.

Note that I_0, I_ℓ, and σ all depend on the wavelength of light being used. σ will also depend on temperature (and this temperature dependence will occasionally be important) and may also sometimes depend on concentration (as when the absorbing molecules form dimers or complexes with inert molecules in the system).

2.2 PHOTOPHYSICAL AND PHOTOCHEMICAL PROCESSES

Photophysics is the general term used to refer to physical processes occurring following the absorption of light by a molecule (fluorescence, phosphorescence, and quenching) while photochemistry is the term used for chemical processes occurring following the absorption of light by a molecule (dissociation, isomerization). It is common to use the term photochemistry to include both photophysical and photochemical processes, though strictly speaking this is incorrect. We are most interested in photodissociation, the decomposition of a molecule into smaller fragments following absorption of a photon of light, and so will focus the discussion below on the absorption of UV or visible light, which is in the energy range usually required for photodissociation to occur.

Consider the processes that can take place following the absorption of a photon of light by a molecule (we assume single photon absorption here, though in laboratory experiments using lasers or other intense light sources multiphoton absorption processes may occur.)

$$M + h\nu \rightarrow M^* \tag{2.10}$$

$$M^* \rightarrow M + h\nu' \qquad \phi_f \text{ (fluorescence)} \tag{2.11a}$$

$$M^* \rightarrow M + h\nu'' \qquad \phi_p \text{ (phosphorescence)} \tag{2.11b}$$

$$M^* \rightarrow \text{"fragments"} \qquad \phi_d \text{ (photodissociation)} \tag{2.11c}$$

$$M^* \rightarrow M^+ \qquad \phi_{iso} \text{ (photoisomerization)} \tag{2.11d}$$

$$M^* + Q \rightarrow M + Q \qquad \phi_q \text{ (quenching)} \tag{2.11e}$$

Processes given above include fluorescence (light emission from M* to an electronic state with the same value of S, an allowed process), phosphorescence (light emission from M* to an electronic state with a different value of S, a forbidden process), photodissociation, photoisomerization, and quenching, where the excess energy in M* is given up by collision with another molecule. Note that in many cases several different combinations of products may be formed by photodissociation.
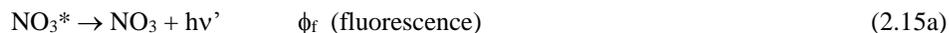
The term primary quantum yield (ϕ) is used to indicate the initial fate of M* following photon absorption (though this is a bit ambiguous, as processes such as vibrational relaxation and intersystem crossing are generally ignored). The primary quantum yield for a particular process is

$$\phi_i = \frac{\text{number of molecules for } i^{th} \text{ initial process}}{\text{number of photons absorbed}} \qquad (2.12)$$

Primary quantum yields can be given for the processes discussed above, such as ϕ_f for fluorescence, ϕ_p for phosphorescence, and so forth, as indiced. For cases where several different combinations of photodissociation products can form, the primary quantum yield for each set of products can be labeled ϕ_{d1}, ϕ_{d2}, and so forth. Because there must be something that initially occurs following the absorption of a photon by a molecule, the primary quantum yields obey the relationship

$$\Sigma_i \, \phi_i = 1 \qquad (2.13)$$

As an example, consider the processes taking place following absorption of a photon in the visible region of the spectrum by nitrogen trioxide, NO_3.

$$NO_3 + h\nu \rightarrow NO_3* \qquad (2.14)$$

$$NO_3* \rightarrow NO_3 + h\nu' \qquad \phi_f \text{ (fluorescence)} \qquad (2.15a)$$

$$NO_3* \rightarrow NO_3 + h\nu'' \qquad \phi_p \text{ (phosphorescence)} \qquad (2.15b)$$

$$NO_3* \rightarrow NO_2 + O \qquad \phi_{d1} \text{ (photodissociation)} \qquad (2.15c)$$

$$NO_3* \rightarrow NO + O_2 \qquad \phi_{d2} \text{ (photoisomerization)} \qquad (2.15d)$$

$$NO_3* + Q \rightarrow NO_3 + Q \qquad \phi_q \text{ (quenching)} \qquad (2.15e)$$

Two dissociation processes occur, and are distinguished as d1 and d2. In both photodissociation processes the products are formed in their ground electronic states.

It is often difficult to measure the primary quantum yield for a process directly, particularly in cases where photodissociation forms highly reactive initial products. Instead, primary quantum yields are often found by measuring the yield of a particular stable final product. This sort of quantum yield, called the overall quantum yield, is defined as

$$\Phi_A = \frac{\text{number of molecules of A formed}}{\text{number of photons absorbed}} \qquad (2.16)$$

Unlike primary quantum yields, there is no requirement for the sum of the overall quantum yields to be equal to 1.

For example, if light absorption by NO_3 was studied in a mixture of NO_3 and synthetic air (80% N_2 and 20% O_2) under conditions where $p_{NO3} \ll p_{air}$, we would expect that oxygen atoms produced by process 2.15c would be quantitatively converted into ozone (O_3) by the reaction

$$O + O_2 + M \rightarrow O_3 + M \qquad (2.17)$$

By measuring the number of molecules of ozone formed and the total number of photons absorbed, the overall quantum yield for ozone production could be used to find the primary quantum yield for process 2.15c

$$\phi_{2.15c} = \Phi_{O_3} \tag{2.18}$$

Note that using overall quantum yields to find primary quantum yields requires a good understanding of the chemical reactions taking place following photodissociation.

2.3 ATMOSPHERIC PHOTOCHEMISTRY

The source of light for photochemical reactions in the atmosphere is the sun. To a first approximation the sun can be modeled as an ideal blackbody emitter of light at a temperature $T = 5770.$ K. The intensity of light emitted by an ideal blackbody ($M(\lambda,T)$) is given by the Planck equation

$$M(\lambda,T) \, d\lambda = (2\pi hc^2/\lambda^5) \, [\, \exp(hc/\lambda kT) -1 \,]^{-1} \, d\lambda \tag{2.19}$$

where k is the Boltzmann constant ($k = 1.381 \times 10^{-23}$ J/K). An ideal blackbody satisfies Wien's law for the wavelength of maximum intensity

$$\lambda_{max} = C_W/T \tag{2.20}$$

where $C_W = 0.290$ cm·K is the Wein's law constant, and the Stefan-Boltzmann law

$$M(T) = \int_0^\infty M(\lambda,T) \, d\lambda = \sigma T^4 \tag{2.21}$$

where $\sigma = 5.67 \times 10^{-8}$ J/m^2·K^4·s is the Stefan-Boltzmann constant. Note that Wein's law predicts that the maximum intensity of light emitted by the sun occurs at $\lambda_{max} = 500.$ nm.

The intensity of sunlight reaching the Earth can be given in terms of the solar constant ($I_{sol,Earth}$), defined as the total intensity of light above the Earth's atmosphere for a 1 m^2 area oriented perpendicular to the direction of the incoming light and at a distance equal to the average Earth-sun distance. The average value for the solar constant is $I_{sol,Earth} = 1367.$ J/m^2·s, with short term fluctuations of a few tenths of a percent around this average value.

Because the Earth's atmosphere contains light absorbing gases, some wavelengths of light are filtered out as light passes through the atmosphere. This filtering occurs at different altitudes for different wavelengths of light, as indicated in Table 2.1. At wavelengths longer than 290 nm at least a portion of the light emitted by the sun can reach the surface of the Earth, though some filtering in the wavelength region 290 - 360 nm occurs due to weak light absorption by ozone. At wavelenths longer that 360 nm the atmosphere is almost transparent (O_3, NO_2, and a few other gases absorb a small fraction of visible light). Clouds will also act to reduce the intensity of sunlight both by light absorption and light scattering, processes that are difficult to model.

The term actinic flux ($F(\lambda)$) is used to refer to the number of photons passing through a small volume element located at an altitude z above sea level per unit time and wavelength interval. Actinic flux can be expressed in units of photons/cm^2·nm·s (while actinic flux is relative to a test volume, it represents the number of photons passing through the surface of the volume, and so has units of cm^{-2} rather than cm^{-3}). Contributions to actinic flux come from direct, scattered, and reflected sunlight, as illustrated in Figure 2.4. The actinic flux also depends on a variety of other factors besides altitude, including surface albedo, latitude, time of day, time of year, and the presence and thickness of clouds. The dependence of actinic flux on latitude, time of day, and time of year is due to the effect of these factors on the zenith angle, θ, the angle between a line perpendicular to sea level and the direction of incident sunlight.

TABLE 2.1 – LIGHT ABSORPTION BY ATMOSPHERIC GASES

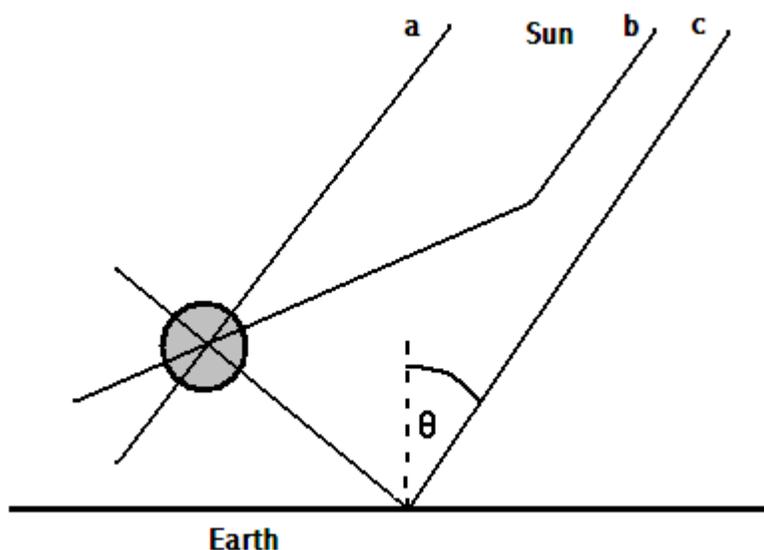| Wavelength region	Altitude where filtering occurs	Absorbing gases
$\lambda < 120$ nm	$z \geq 80$ nm	N_2, O_2, NO
120 nm $\leq \lambda \leq 220$ nm	$z \geq 40$ km	O_2
220 nm $\leq \lambda \leq 300$ nm	$z \geq 15$ km	O_3

Figure 2.4. Flux of solar radiation through a small volume element (gray sphere) at an altitude z above sea level. Contributions to the light flux through this volume include a) direct sunlight, b) scattered sunlight, and c) reflected sunlight. The zenith angle (θ) is also shown.

The photodissociation of a molecule in the atmosphere can be modeled kinetically. The rate law for photodissociation may be written as

$$d[A]/dt = - k_d [A] \tag{2.22}$$

where k_d is the pseudo-first order rate constant for photodissociation. For cases where several different photodissociation processes can occur a rate constant for each process can written, as well as an overall rate constant for photodissociation. If k_{d1}, k_{d2}, ... are the rate constant for the production of particular sets of photodissociation products then k_d, the overall rate constant for photodissociation, is

$$k_d = k_{d1} + k_{d2} + ... = \Sigma_i \, k_{di} \tag{2.23}$$

A method for calculating photodissociation rate constants is given in the next section of the chapter.

2.4 CALCULATION OF THE PHOTODISSOCIATION RATE CONSTANTS

While most atmospheric modeling programs have subroutines that calculate photodissociation rate constants (k_p) for the conditions being modeled, it is a useful exercise to be able to calculate the photodissociation rate constant for a particular molecule and set of conditions "by hand". This demonstrates the factors that go into determining the rate constant, and is also useful in finding rate constants for photodissociation for typical conditions.

The method we will use is as follows. k_{di}, the rate constant for the ith photodissociation process, is given by the expression

$$k_{di} = \int_\lambda \sigma(\lambda)\, \phi_i(\lambda)\, F(\lambda)\, d\lambda \qquad\qquad (2.24)$$

$$\cong \sum_n \sigma_{ave,n}(\lambda)\, \phi_{i,ave,n}(\lambda)\, F_{ave,n}(\lambda) \qquad\qquad (2.25)$$

$$= \sum_n \Delta k_{p,i,n}\ , \text{ where } \Delta k_{p,i,n} = \sigma_{ave,n}(\lambda)\, \phi_{i,ave,n}(\lambda)\, F_{ave,n}(\lambda) \qquad\qquad (2.26)$$

In the above expressions k_{di} is the rate constant for the ith photodissociation process (since in some cases there may be several possible sets of photodissociation products). $\sigma(\lambda)$ is the absorption cross-section, $\phi_i(\lambda)$ is the quantum yield for the ith photodissociation process, and $F(\lambda)$ is the actinic flux. The integral (eq 2.24) is usually approximated by a summation (eq 2.25) where average values for these quantities are used.

The procedure we will use to find k_{di} is as follows:

1) Find the value for zenith angle (θ) for the conditions of the calculation. Use Table 3.9 (Chapter 2 appendix), correctly converting afternoon times to their corresponding morning times, southern latitudes to their corresponding northern latitudes and time of year, and interpolating between values when required.

2) Find the value for the correction factor accounting for variations in the Earth-sun distance with time of year, Table 3.8 (Chapter 2 appendix). We will call this correction factor f_s.

3) Cloud cover. There are corrections that can be applied for cloud cover. We will always assume cloudless conditions in our calculations.

4) Albedo and altitude. We will use table 3.7 (Chapter 2 appendix) for $F_{ave}(\lambda)$. This corresponds to an altitude $z = 0.0$ km, cloudless conditions, and a "best estimate" for albedo. Tables of actinic flux for other altitudes and albedos are also available, as well as corrections to model the effects of clouds on actinic flux.

As an example we will calculate k_d for photodissociation of hydrogen peroxide (H_2O_2). The absorption spectrum for H_2O_2 is given in Figure 2.5. The absorption cross-sections, given in Table 2.2, are from a recent JPL/NASA review of atmospheric photochemistry.

$$H_2O_2 + h\nu\ \rightarrow\ 2\ OH \qquad\qquad (2.27)$$

is $\phi = 1$ across the entire near UV band of the molecule. As an aside we note that the above reaction is a minor source of OH radical in the troposphere. The calculation will be carried out for 1200 hours (noon) on September 15th, for a latitude of 26.°N (roughly the latitude of Miami), at sea level ($z = 0$ km) for "best estimate" surface albedo.
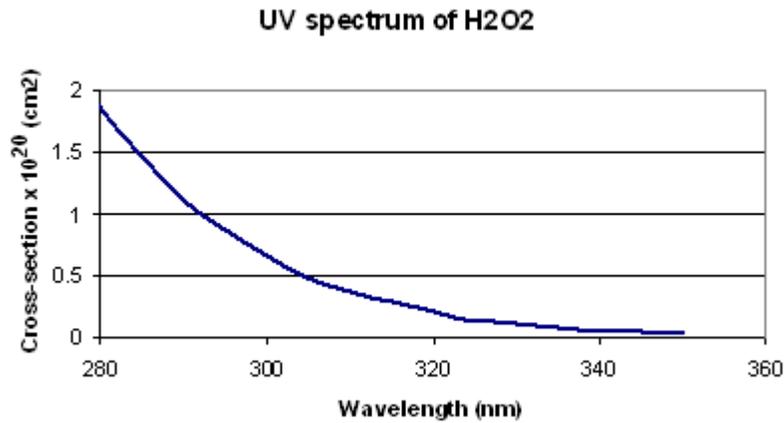
UV spectrum of H2O2

Figure 2.5. Absorption spectrum of H_2O_2.

TABLE 2.2 - ABSORPTION CROSS-SECTIONS FOR H2O2 AT T = 298. K

Wavelength (nm)	$\sigma \times 10^{20}$ (cm²/molecule)	Wavelength (nm)	$\sigma \times 10^{20}$ (cm²/molecule)
280.	2.0	320.	0.22
285.	1.5	325.	0.16
290.	1.2	330.	0.13
295.	0.90	335.	0.10
300.	0.68	340.	0.07
305.	0.51	345.	0.05
310.	0.39	350.	0.04
315.	0.29		

We proceed as follows:

1) Zenith angle. For our conditions we must interpolate both for latitude and date. Interpolated values are given in parentheses.

TABLE 2.3 – CALCULATION OF ZENITH ANGLE

latitude	20°N	26°N	30°N
Sept 1ˢᵗ	11.6	(17.6)	21.6
Sept 15ᵗʰ		(23.0)	
Oct 1ˢᵗ	23.1	(29.1)	33.1

Interpolation between latitudes: $\theta(26°N) = \theta(20°N) + (6/10) [\theta(30°N) - \theta(20°N)]$

Interpolation between dates: $\theta(Sep.15) = \theta(Sep.1) + [(15-1)/30] [\theta(Oct.1) - \theta(Sep.1)]$

2) Correction factor for Earth-sun distance variation: f_s(Sept.15) = 0.989

3) Cloud conditions: no clouds.

4) z = 0 km, "best estimate" albedo, use Table 3.7 (Chapter 2 appendix).

The calculation of the photodissociation rate constant in given in Table 2.4.

TABLE 2.4 – CALCULATION OF THE PHOTODISSOCIATION RATE CONSTANT FOR H_2O_2
_____

λ range (nm)	$\sigma(\lambda)$ x 10^{20} (cm^2/molecule,e)	$F(\lambda)$ x 10^{-14} (photon/cm$^2 \cdot$s)	Δk_d x 10^6 (s^{-1})
290-292		0.00	0.00
292-294		0.00	0.00
294-296		0.00	0.00
296-298	0.81	0.01	0.0081
298-300	0.72	0.02	0.0144
300-302	0.65	0.05	0.0325
302-304	0.58	0.14	0.0812
304-306	0.51	0.27	0.1377
306-308	0.46	0.42	0.1932
308-310	0.41	0.57	0.2337
310-312	0.37	0.84	0.3108
312-314	0.33	1.08	0.3564
314-316	0.29	1.23	0.3568
316-318	0.26	1.52	0.3952
318-320	0.23	1.56	0.3588
320-325	0.19	4.92	0.9348
325-330	0.145	7.22	1.0469
330-335	0.115	7.77	0.8936
335-340	0.085	7.54	0.6409
340-345	0.06	8.19	0.4914
345-350	0.045	8.29	0.3730
350-355	0.02	9.53	0.1906

k_d(uncorrected) = Σ_n $\Delta k_{d,n}$ = 7.0499 x 10^{-6} s^{-1}

k_d(corrected) = f_s k_d(uncorrected) = (0.989) x 7.0499 x 10^{-6} s^{-1}= 6.972 x 10^{-6} s^{-1} $\cong$ 7.0 x 10^{-6} s^{-1}.

Note that in the above table values for $\sigma_{ave,n}(\lambda)$ were interpolated between the values given in the JPL/NASA review.
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Based on the above, we may estimate the half-life for H_2O_2 for the above conditions and assuming photodissociation is the main removal mechanism.

$$t_{1/2} = \ln(2)/k_d = 27.6 \text{ hours (about 1 day)} \tag{2.28}$$

In fact, the true half-life for H_2O_2 would have to be found using $k_{total} = k_d + k$(other removal processes), and using a value for k_d averaged over the conditions found in the atmosphere.

2.5 SUMMARY

The interaction of light with molecules plays an important role in atmospheric chemistry. Vibrational-rotational transitions in molecules, which occur in the infrared region of the spectrum, can be used to detect species both in the laboratory and in field studies. Infrared absorption of minor and trace gases in the Earth's atmosphere also plays an important role in establishing the average surface temperature of the Earth, which can change if the concentrations of minor and trace gases change. Electronic transitions in molecules, which occur in the UV and visible regions of the spectrum, can lead to photodissociation, the major process in initiating chemical reactions in both the troposphere and stratosphere. UV-visible spectroscopy (including fluorescence spectroscopy) can also be used to detect molecules. Finally, by knowing the absorption cross-section, photodissociation quantum yield, and actinic flux of photons as a function of wavelength, photodissociation rate constants can be calculated for atmospheric species of interest.

APPENDIX – There is an appendix to Chapter 2, taken from B. J. Finlayson-Pitts and J. N. Pitts, Jr. <u>Chemistry of the Upper and Lower Atmosphere</u> (New York, Academic Press, 2000) pp 66-68.