

## CHAPTER 3

### SPECTROSCOPY AND PHOTOCHEMISTRY OF ATMOSPHERICALLY IMPORTANT SPECIES

In the last chapter we reviewed some general results from quantum mechanics as applied to atoms and molecules. In addition, we learned how to calculate  $k_d$ , the rate constant for the photodissociation of a molecule. The value for  $k_d$  depends on a variety of factors, including environmental factors such as light intensity, and properties of the molecules themselves, such as their absorption cross-section and primary quantum yields for various photodissociation processes. Both absorption cross-sections and primary quantum yields can themselves depend to an extent on environmental factors such as temperature and total pressure.

In the present chapter the spectroscopic and photochemical properties of a number of molecules important to atmospheric chemistry are reviewed. Much of the information in this chapter comes from two sources which are themselves excellent secondary sources for atmospheric data. The first is the JPL/NASA review of kinetic and photochemical data for atmospheric modeling. The most recent review (Evaluation Number 15) was carried out in 2006, and is available for download at <http://jpldataeval.jpl.nasa.gov/> (Evaluation Number 16 is expected to be released in late 2010). This is a critical evaluation of available kinetic and photochemical data, with recommendations for “best values” and their uncertainties. The second is the MPI-Mainz UV Spectral Atlas, a compilation of absorption cross-section and primary quantum yield measurements for a variety of gas phase molecules. Unlike the JPL/NASA review, no systematic attempt is made to critically evaluate the data.

#### 3.1 GENERAL CONSIDERATIONS

The two properties of a molecule that determine its photochemistry in the atmosphere are the absorption cross section and primary quantum yields for photodissociation. Absorption cross sections depend on the properties of the ground and excited electronic states involved in the electronic transition taking place in the molecule and are usually determined experimentally. Quantum yields are also measured experimentally. Both of these properties are strongly dependent on wavelength, and both may also show a weak dependence on temperature. In addition, primary quantum yields may also show a strong dependence on total pressure, as quenching of electronically excited molecules by collision is pressure dependent and is often an important alternative to photodissociation.

It is generally much easier to determine the absorption cross sections for a molecule than the quantum yields for photodissociation, since the latter measurement requires knowing how many molecules have absorbed light (usually found by actinometry) and measuring the disappearance of the parent molecule and/or the appearance of photodissociation products or stable secondary products formed from the chemical reaction of unstable primary photodissociation products.

One limiting factor in the production of a particular set of photodissociation products is energy. If the absorbed photon lacks the energy required to form a particular set of photodissociation products than photodissociation by that pathway will not occur, even if the molecule absorbs light.

The threshold wavelength,  $\lambda_t$ , can be defined as the longest wavelength of light with sufficient energy to form a particular set of photodissociation products. This wavelength is related to the enthalpy change for photodissociation. For example, for the process



the enthalpy change is

$$\Delta H_{\text{rxn}} = (\Delta H_f(A) + \Delta H_f(B)) - (\Delta H_f(AB)) \quad (3.2)$$

The enthalpy of reaction is usually calculated using room temperature data ( $T = 25. \text{ }^\circ\text{C} = 298. \text{ K}$ ) although it can also be found at absolute zero, in which case it can be assumed that the reactants and products are in their ground vibrational and rotational states.

If we assume that the energy for photodissociation comes entirely from the light photon absorbed by the molecule, then

$$hcN_A/\lambda \geq \Delta H_{\text{rxn}} \quad (3.3)$$

or

$$\lambda \leq hcN_A/\Delta H \quad (3.4)$$

Since the threshold wavelength is the longest wavelength of light capable of photodissociation, it follows that

$$\lambda_t = hcN_A/\Delta H_{\text{rxn}} \quad (3.5)$$

An appendix to this chapter provides the formation enthalpy data needed to calculate  $\lambda_t$  for a particular molecule and seto photodissociation products.

As an example, consider the photodissociation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), the molecule used in the last chapter as an example in the calculation of a photodissociation rate constant. For the process



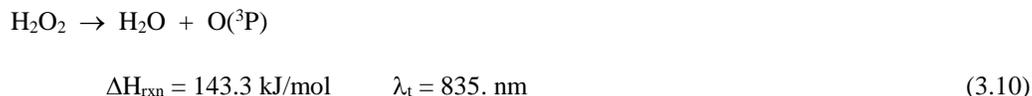
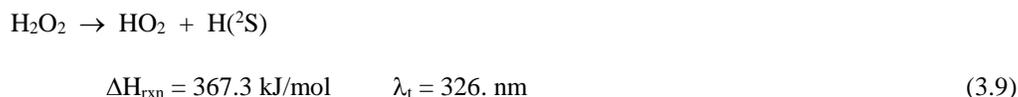
$$\Delta H_{\text{rxn}} = 2 ( 37.28 \text{ kJ/mol} ) - ( - 135.9 \text{ kJ/mol} ) = + 210.5 \text{ kJ/mol} \quad (3.7)$$

and so

$$\begin{aligned} \lambda_t &= (6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (2.998 \times 10^8 \text{ m/s}) (6.022 \times 10^{23} \text{ mol}^{-1}) / (210500. \text{ J/mol}) \\ &= 5.68 \times 10^{-7} \text{ m} = 568. \text{ nm} \end{aligned} \quad (3.8)$$

Note that the threshold wavelength should be considered an approximate cutoff wavelength for the production of a particular set of photodissociation products, since internal energy of the absorbing molecule (vibrational and rotational energy) can contribute to the energy needed for dissociation of the molecule. For wavelengths shorter than  $\lambda_t$  the photodissociation products will possess any additional energy above that required for their formation, either as translational energy or, in the case of molecular products, vibrational and rotational energy. Usually this excess energy dissipates quickly by collisional quenching, but there is evidence that occasionally the reaction of molecules with larger than equilibrium amounts of internal energy can play a role in atmospheric chemistry.

When there are several sets of possible photodissociation products a calculation for the threshold wavelength for each set of products can be made. For example, consider the following processes involving hydrogen peroxide.



Notice that process 3.10 can in principle occur by absorption of light throughout the visible region of the spectrum (and even in a small region in the near infrared). However, this process would require rearrangement of the atoms in hydrogen peroxide during photodissociation, unlike the other two processes, which only require bond breaking, either the O-O bond (3.6) or an O-H bond (3.9). This illustrates another important point. There are other considerations besides energy that determine whether a particular photodissociation process will occur. In general, processes requiring breaking of a single chemical bond are more likely to take place than those requiring extensive rearrangement of the molecular bonds.

Despite these restrictions, equn 3.5 represents an important factor to take into account in looking into molecular photodissociation. This equation will be used extensively in the following discussion.

### 3.2 N<sub>2</sub> AND O<sub>2</sub>

The threshold wavelengths for photodissociation of molecular nitrogen and oxygen lie well within the UV region of the spectrum.



Photodissociation of nitrogen and oxygen will therefore not occur in the troposphere. Photodissociation of molecular oxygen could, however, occur in the stratosphere, where there is light at wavelengths longer than ~ 200 nm.

There are weak diffuse absorption bands for oxygen in the region between 190 nm and 300 nm (the Herzberg continuum), arising from the X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> ground electronic state and a weakly bound A<sup>3</sup>Σ<sub>u</sub><sup>+</sup> electronic state, as shown in Figure 3.1. The transition is forbidden (as it is a – to + transition) and so is weak. However, because of the large amounts of molecular oxygen in the atmosphere, some light absorption in this wavelength region is found. Absorption at wavelengths smaller than 240. nm leads to formation of ground state oxygen atoms. This photodissociation plays a role in stratospheric chemistry, as it is a source for stratospheric ozone.

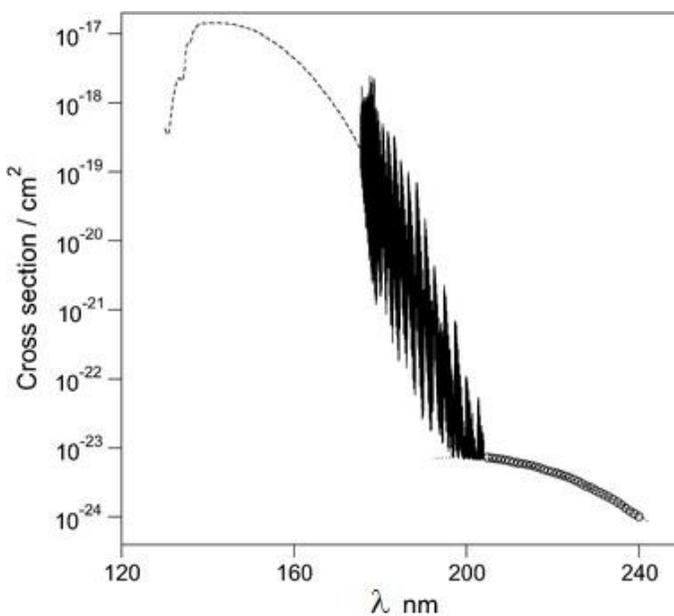


Figure 3.1. UV absorption spectrum of O<sub>2</sub>.

There are additional extremely weak absorption bands for molecular oxygen around 700. nm and 1100. nm resulting from forbidden transitions to the  $b^1\Sigma_g^+$  and  $a^1\Delta_g$  electronic states. In addition, extremely weak continuous absorption by  $(O_2)_2$  dimers has been observed in the laboratory. None of these processes is expected to be important in atmospheric chemistry

### 3.3 OZONE

Ozone ( $O_3$ ) is perhaps the most important molecule in atmospheric photochemistry. In the stratosphere strong light absorption by ozone in the 200 nm – 300 nm region (the Hartley band, Figure 3.2) prevents high energy UV radiation from reaching the surface of the Earth, and is also responsible for heating of the stratosphere. In the troposphere, ozone photodissociation leads to formation of hydroxyl radical (OH), an important oxidizing agent.

Ozone absorbs light throughout the near UV, visible, and near IR regions of the spectrum. In all cases the primary quantum yield for photodissociation is 1, with a variety of potential photodissociation products. Threshold wavelengths for various combinations of products are given in Table 3.1.

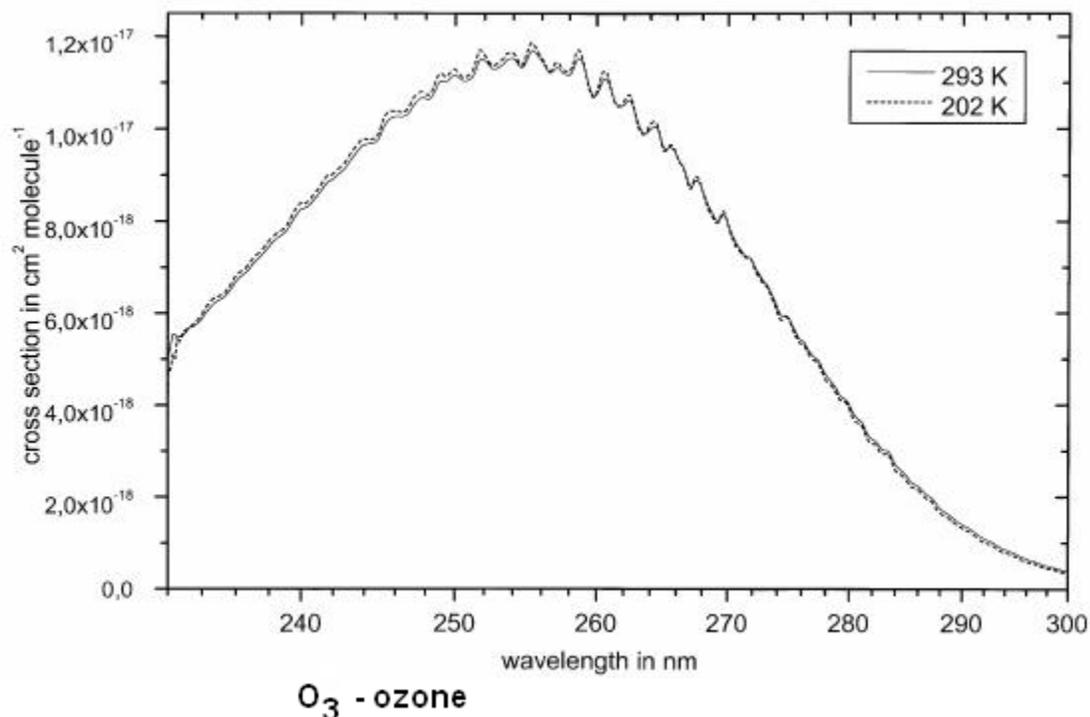


Figure 3.2. The Hartley band of ozone.

The Hartley band extends from 200 nm to 300 nm. The absorption is continuous with weak structure near the peak of the spectrum. The long wavelength side of the Hartley band merges into a much weaker structured system called the Huggins bands.

While several possible sets of photodissociation products can be formed by light absorption in the Hartley band, the largest primary quantum yield occurs for the spin allowed process



The quantum yield for production of O(<sup>1</sup>D) atoms is ~ 0.9 throughout most of the Hartley band, but drops off at wavelengths longer than 310 nm, the threshold wavelength for process 3.13. However, the primary quantum yield for O(<sup>1</sup>D) production does not drop to zero at longer wavelengths due to two processes. The first is photodissociation of vibrationally and/or rotationally excited ozone, where the internal energy can contribute to the photodissociation process. The second is photodissociation by the spin forbidden process



The threshold wavelength for process 3.14 is 411 nm, and so production of O(<sup>1</sup>D) at wavelengths longer than 310 nm is energetically allowed.

**TABLE 3.1 – THRESHOLD WAVELENGTHS (nm) FOR O<sub>3</sub> PHOTODISSOCIATION PRODUCTS**

O <sub>2</sub> molecule	X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	a <sup>1</sup> Δ <sub>g</sub>	b <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>
O atom			
<sup>3</sup> P	1180.	612.	463.
<sup>1</sup> D	411.	310.	267.

Because of the importance of O(<sup>1</sup>D) production in the troposphere at wavelengths longer than 290 nm there have been several measurements of the primary quantum yield for O(<sup>1</sup>D) production in this region. Figure 3.3 summarizes recent results.

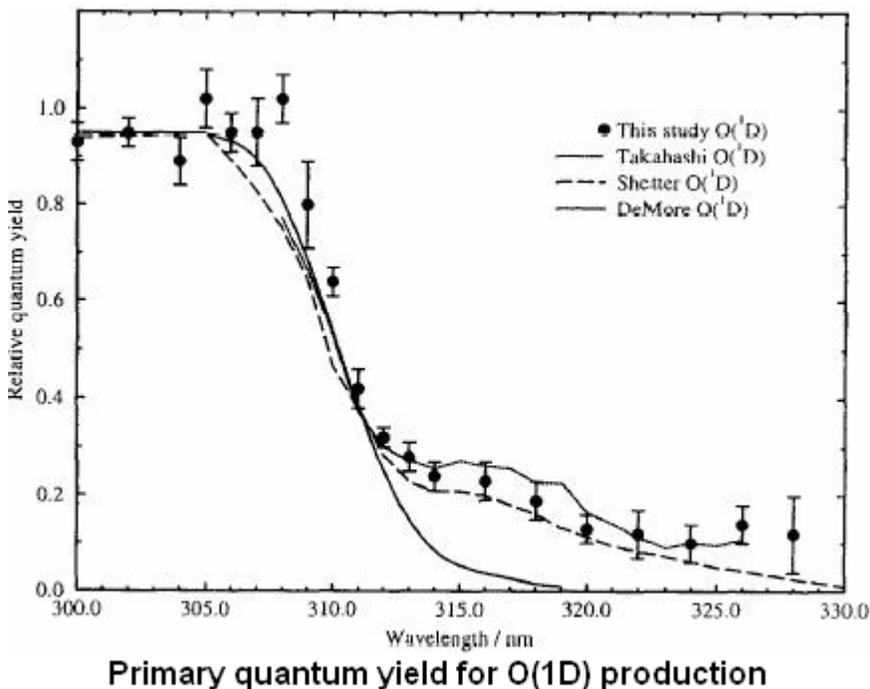
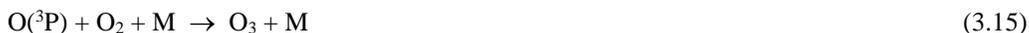


Figure 3.3. Primary quantum yield for O(<sup>1</sup>D) production in ozone photodissociation.

Ozone also absorbs light at wavelengths in the visible and near IR regions of the spectrum, also leading to photodissociation. The strongest of these light absorptions occurs in the Chappuis band between 400nm and 800 nm (Figure 3.4). The Chappuis bands are much weaker than the Hartley band. Ozone photodissociation in the Chappuis is not believed to be important in either the troposphere or the stratosphere, since only ground state (<sup>3</sup>P) oxygen atoms are produced. These atoms will simply reform ozone by the process



### 3.4 NITROGEN OXIDES AND OTHER NITROGEN COMPOUNDS

Several different nitrogen oxides are found in the stratosphere. Some of these species absorb light in the visible or actinic UV region of the spectrum. Their photochemistry therefore plays a role in tropospheric chemistry.

Nitrogen dioxide (NO<sub>2</sub>) has a strong and highly structured absorption system at wavelengths shorter than 600 nm. The threshold wavelength for the production of the lowest energy products



is 400 nm. This is the only photodissociation process that can take place with NO<sub>2</sub> in the troposphere. Experimentally the primary quantum yield for NO(<sup>2</sup>Π) is ~ 1 at wavelengths shorter than 395 nm, but rapidly drops to ~ 0 at longer wavelengths. This indicates that most NO<sub>2</sub> molecules with sufficient energy to dissociate in fact do so.

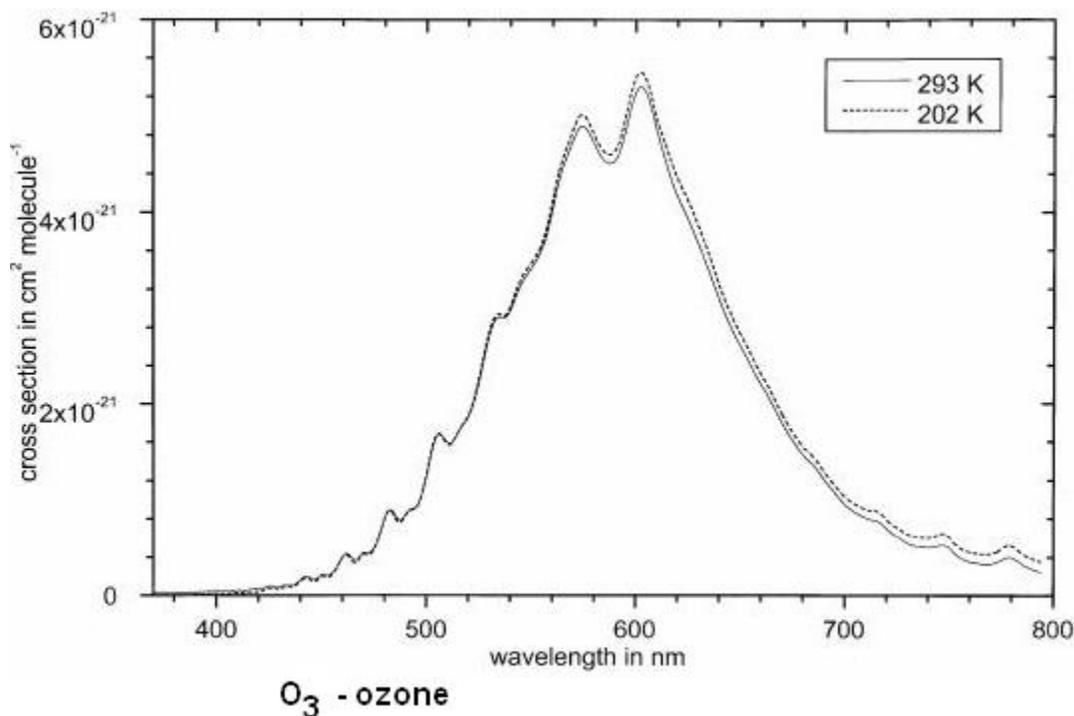


Figure 3.4. The Chappuis absorption band of ozone.

Nitrate radical ( $\text{NO}_3$ ) has a strong absorption band in the region from 550 nm to 700 nm (Figure 3.5). Two possible photodissociation processes can occur



The threshold wavelength for process 3.17 is 585 nm. The reactants and products in process 3.18 have approximately the same energy but are separated by an energy barrier. Both processes are found to occur. The primary quantum yield for  $\text{NO}_2$  production (process 3.16) is  $\sim 1$  at wavelengths shorter than 585 nm, but rapidly decreases to  $\sim 0$  at longer wavelengths. The primary quantum yield for process 3.18 is about zero at wavelengths shorter than 585 nm, rises to a peak of  $\sim 0.35$  at 595 nm, and then gradually drops to zero at longer wavelengths. Since the combined primary quantum yield for photodissociation at long wavelengths is less than one other processes, such as fluorescence and quenching, must occur.

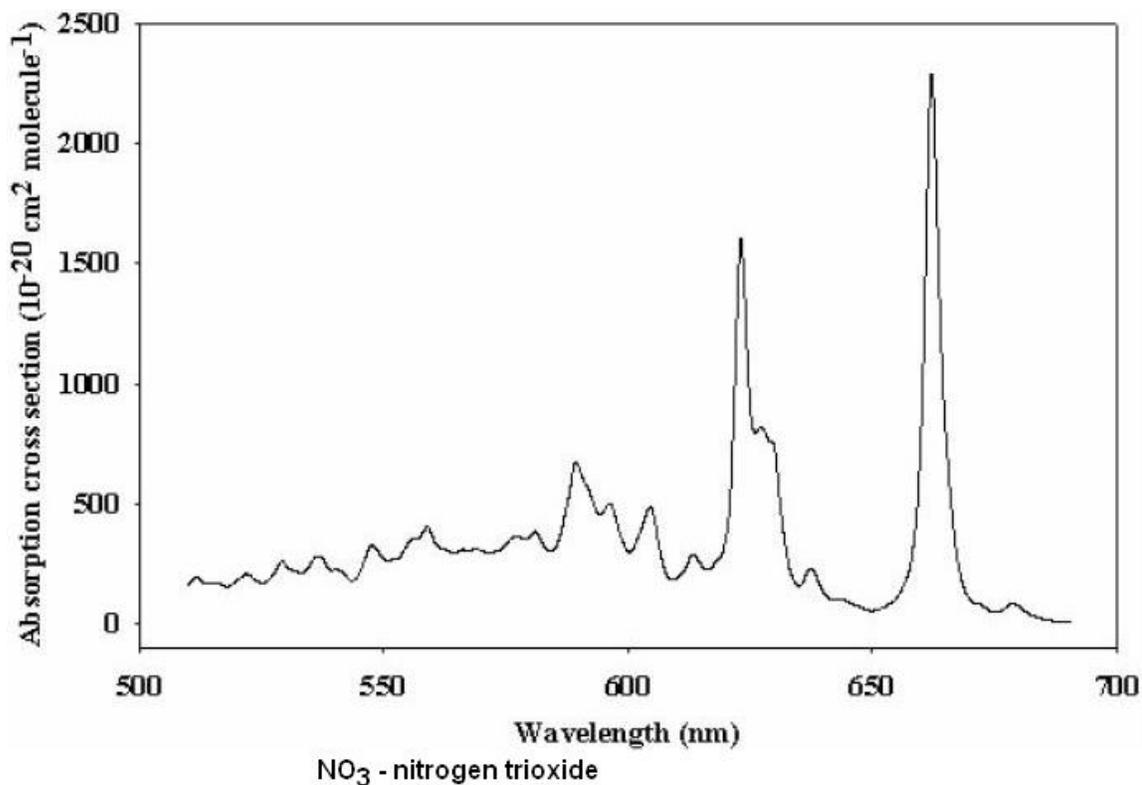


Figure 3.5. Absorption spectrum of nitrate radical ( $\text{NO}_3$ )

Both nitrous acid ( $\text{HONO}$ ) and nitric acid ( $\text{HNO}_3$ ) absorb light in the near UV region of the spectrum. Light absorption by nitrous acid occurs as highly structured bands at wavelengths shorter than 400 nm (Figure 3.6). Nitric acid has a continuous absorption at wavelengths shorter than 340 nm. The quantum yield for the process



is approximately 1 at wavelengths shorter than 400 nm. The quantum yield for the corresponding process in nitric acid



is also approximately 1 at wavelengths shorter than 315 nm. Both molecules are therefore potential sources of hydroxyl radical in the troposphere.

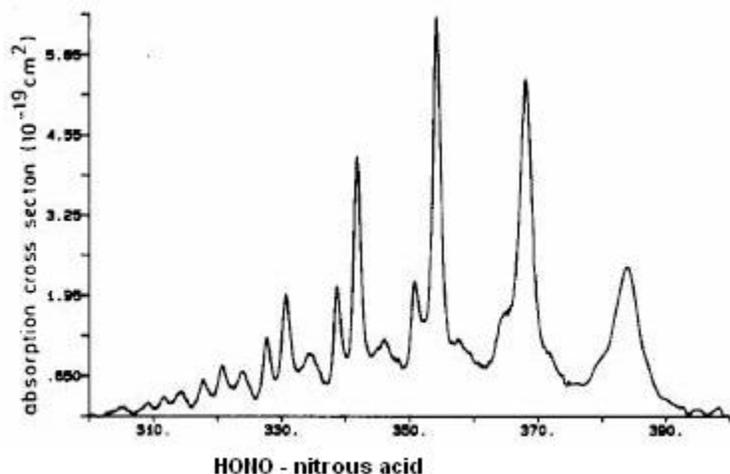


Figure 3.6. Absorption spectrum of nitrous acid (HONO).

Nitrous oxide ( $N_2O$ ) does not absorb light in the visible or actinic UV and so does not photodissociate in the troposphere. Since there are no other processes that remove  $N_2O$  in the troposphere, its main fate is migration into the stratosphere. The molecule does absorb light at wavelengths shorter than 240 nm (Figure 3.7), and so photodissociation in the stratosphere is a possible removal process. At these wavelengths two sets of photodissociation products can form



experimentally, the quantum yield for process 3.21 is  $\sim 0$ , and that for process 3.22 is  $\sim 1$ , indicating that photodissociation of  $N_2O$  in the stratosphere usually forms electronically excited oxygen atoms.

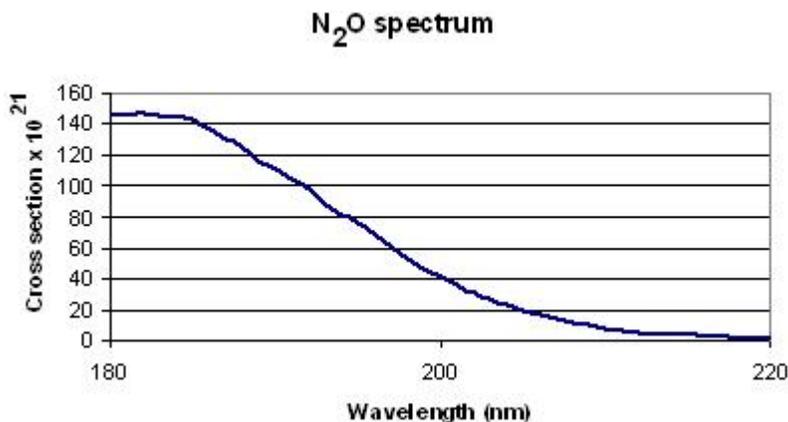


Figure 3.7. Absorption spectrum of nitrous oxide ( $N_2O$ ).

Other nitrogen compounds, including organic nitrates and peroxyacetyl nitrate (PAN) also absorb light in the visible or near UV region of the spectrum. We will not, however, discuss these classes of molecules.

### 3.5 OTHER MOLECULES

The spectroscopy and photochemical properties of several other molecules or classes of molecules is of somewhat lesser importance than the molecules already discussed. A few comments concerning other molecules are made in this section.

Sulfur dioxide ( $\text{SO}_2$ ) has three absorption bands in the near UV region. There is a weak absorption band between 340 nm and 420 nm (Figure 3.8) due to a forbidden transition between the singlet ground electronic state and the lowest energy triplet electronic state. Between 240 nm and 340 nm there is a stronger absorption band due to an allowed singlet to singlet transition, while at wavelengths shorter than 240 nm a second allowed singlet to singlet transition occurs. Since the threshold wavelength for the process



is 217 nm, this second singlet to singlet band system is the lowest energy transition resulting in photodissociation of sulfur dioxide. Due to the small value for the threshold wavelength photodissociation of sulfur dioxide will not takeplace in the troposphere. Photodissociation could occur in the stratosphere, but there are efficient removal processes for sulfur dioxide in the troposphere that usually prevent it from moving into the stratosphere.

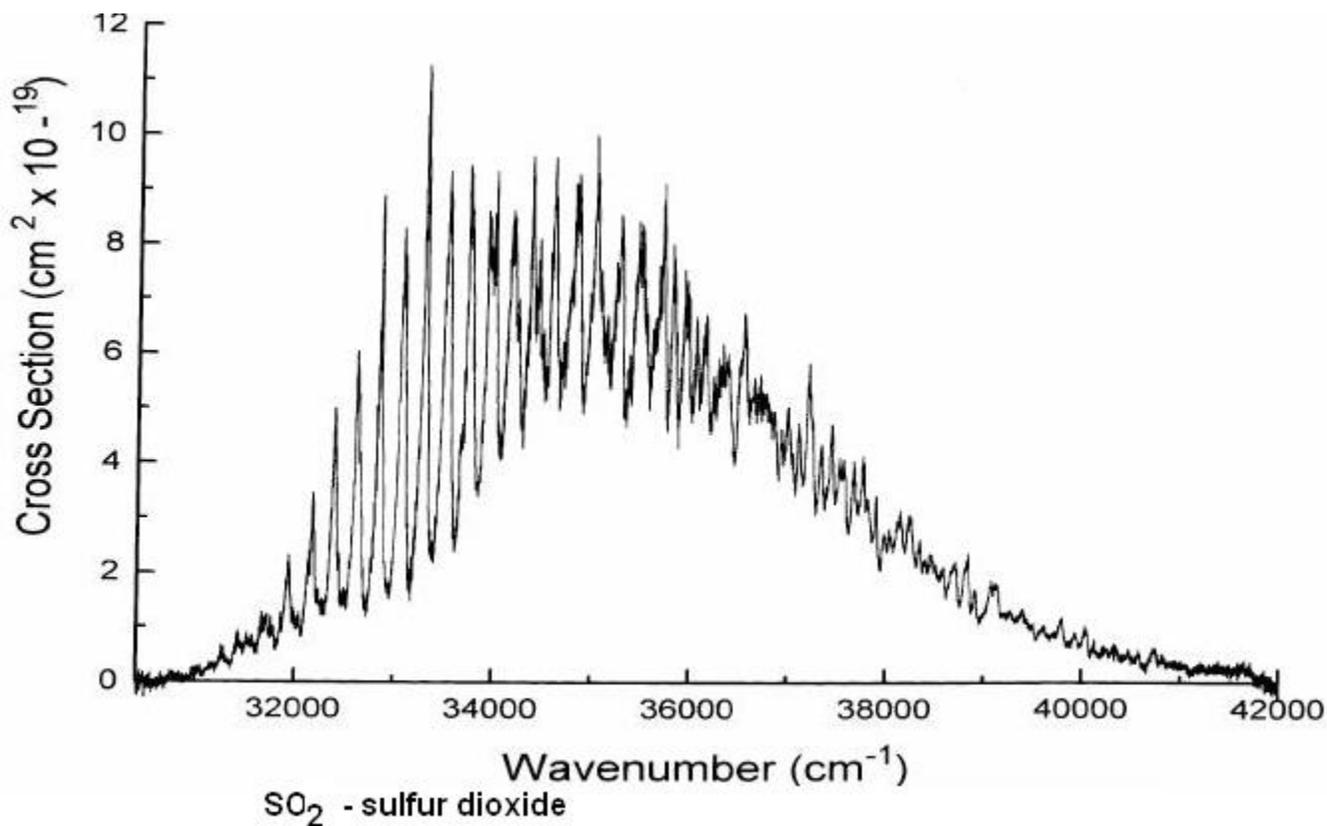


Figure 3.8. Near UV absorption spectrum of sulfur dioxide.

Other small sulfur containing molecules such as hydrogen sulfide (H<sub>2</sub>S), carbon disulfide (CS<sub>2</sub>), and carbonyl sulfide (COS) do not absorb light in the actinic UV region. Photodissociation of these molecules in the troposphere therefore does not occur.

Peroxide molecules such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and organic peroxides have a continuous absorption spectrum in the near UV region due to the breaking of the weak O-O single bond. Light absorption for hydrogen peroxide occurs at wavelengths below 350 nm, as shown in Figure 2.3 in the last chapter. Larger organic peroxides absorb light at slightly longer wavelengths, such as methyl peroxide (CH<sub>3</sub>OOH), which absorbs light at wavelengths longer than 370 nm. Hydroperoxide (HO<sub>2</sub>) also absorbs in this region. Photodissociation therefore represents one removal process for peroxide molecules. Though slow (as seen in the calculation of the photodissociation rate constant in Chapter 2), photodissociation is a minor source of hydroxyl radical in the troposphere.

Aldehydes and ketones absorb light in the near UV region due to the presence of the C=O chromophore. Formaldehyde, the smallest aldehyde, has a highly structured absorption spectrum at wavelengths between 240 nm and 370 nm. Two sets of photodissociation products have been observed in the laboratory, corresponding to the processes



The first process forms radicals capable of further reaction, and can lead to the production of hydroperoxyl radical and, indirectly, hydroxyl radical. It has a threshold wavelength of 325 nm. The second process forms stable products with approximately the same energy as formaldehyde, but there is an energy barrier between the reactant and products. Normally process 3.25 would be expected not to occur since it requires a rearrangement of the chemical bonds during the photodissociation process. However, it is found to be the more dominant photodissociation process at some wavelengths. Primary quantum yields for these two processes as a function of wavelength are given in Table 3.2, and show a relatively complicated dependence on wavelength. Note that the quantum yield for process 3.24 falls to zero at wavelengths above the threshold wavelength. The quantum yields do not add up to 1 at some wavelengths, indicating that fluorescence and quenching are competing processes.

**TABLE 3.2 – PRIMARY QUANTUM YIELDS FOR HCHO PHOTODISSOCIATION<sup>a</sup>**

Wavelength (nm)	H + HCO	CO + H <sub>2</sub>
240.	0.27	0.49
250.	0.29	0.49
260.	0.30	0.49
270.	0.38	0.43
280.	0.57	0.32
290.	0.73	0.24
300.	0.78	0.21
310.	0.74	0.25
320.	0.57	0.41
330.	0.26	0.70
340.	0.03	0.62
350.	0.00	0.38

<sup>a</sup> In 1.00 atm air, at T = 298 K.

Larger aliphatic aldehydes have a continuous absorption spectrum with weak structure peaking at around 290 nm and extending out to about 350 nm. Aliphatic ketones have a similar spectrum but shifted slightly further

into the UV, peaking at around 280 nm, with little evidence for superimposed structure. In general, the larger the aldehyde or ketone the smaller the primary quantum yields for photodissociation, since it takes longer for the energy picked up from the absorbed photon to concentrate into the bonds that need to break for dissociation to occur. This makes competing processes such as fluorescence and quenching more likely to occur. As is the case for formaldehyde, photodissociation of larger aldehydes and of ketones can lead to a variety of photodissociation products.

Finally, chlorofluorocarbons (CFCs), a family of fully halogenated small alkanes such as  $\text{CFCl}_3$  (CFC-11) do not absorb in the actinic UV and therefore will not photodissociate in the troposphere. Since they are stable with respect to other removal processes their main fate is migration into the stratosphere, where photodissociation can occur at shorter wavelengths. This has implications for the chemistry of stratospheric ozone. The discussion of the spectroscopy and photochemistry of CFCs and related molecules will therefore be deferred until our general discussion of stratospheric chemistry.

### **3.6 SUMMARY**

Photodissociation plays an important role in atmospheric chemistry. Simple thermochemical arguments can be used to find the threshold for the production of various products by photodissociation, though other factors will also play a role in the photodissociation process. Photodissociation by molecular oxygen, ozone, nitrogen oxides, peroxides, aldehydes, and ketones all play a role in the chemistry of the troposphere and/or the chemistry of the stratosphere.