Differential Absorption Spectroscopy

Absorption spectroscopy is a well-established tool for the analysis of the chemical composition of gases. As such, it has played a prominent role in the discovery of the physical and chemical properties of the earth’s atmosphere.

6.1 The History of Absorption Spectroscopy

Spectroscopic studies of the earth’s atmosphere date back more than 100 years. Some milestones in the investigation of atmospheric composition through spectroscopy include:

1879 – Marie Alfred Cornu concludes from the change of the edge of the intensity decay in the UV that a trace species in the earth’s atmosphere must be causing the UV-absorption (Cornu, 1879).

1880 – Sir Walter Noel Hartley discovers the absorption of UV-radiation (below 300 nm) by ozone. This led to the name Hartley-bands for ozone absorption below 300 nm (Hartley, 1880, 1881).

1880 – M. J. Chappuis discovers the absorption of visible light by ozone, which is today called the Chappuis-band. Chappuis also speculates that light absorption by ozone is the reason for the blue colour of the sky (Chappuis, 1880).

1890 – Sir William Huggins discovers a new group of lines in the spectrum of Sirius, which are later explained by Fowler and Strutt as absorption of terrestrial ozone. The long wavelength UV-bands of ozone are, therefore, called Huggins-bands today.

1904 – Discovery of the infrared absorption of ozone near 4.8, 5.8, and 9.1–10 μm by Knut Johan Ångström.

1913 – Balloon measurements of the UV absorption of ozone up to 10 km altitude by Albert Wigand showed essentially no change with altitude.

1918 – John William Strutt (better known as Lord Rayleigh) concludes that atmospheric ozone must reside in a layer above 10 km altitude above the surface.
1920 – First ozone column measurements were made by Charles **Fabry** and Henri **Buisson**, who determine a column of about 3 mm (at atmospheric pressure), with large variations.

1925 – First application of a dedicated ozone spectrometer by Gordon Miller Bourne **Dobson** (Dobson and Harrison, 1926).

1926 – Paul **Götz** confirms the theory of an ozone layer by observing the so-called ‘Umkehr’ effect, and determines its altitude to be about 25 km.

1934 – Direct observation of the ozone layer by UV-spectroscopy by Erich **Regener** (TH Stuttgart).

1948 – Marcel **Migeotte** (Ohio State University) discovers methane and carbon monoxide in the earth atmosphere by near-infrared absorption spectroscopy (Migeotte, 1948, 1949).

1950 – Discovery of the emission bands of the hydroxyl radical (OH) in the nightglow (the Meinel bands of the OH-radical). As a consequence, HO$_2$-chemistry is viewed in connection with ozone chemistry by David R. **Bates** and Marcel **Nicolet** (1950), and Bates and Witherspoon (1952).

1975 – First detection of OH in the atmosphere by Dieter **Perner** and colleagues using differential optical absorption spectroscopy (Perner et al., 1976).

This list illustrates the role that spectroscopy has played in the measurement of reactive trace gases in the atmosphere, most notably ozone. The reader may notice that the identification and quantification of gases was primarily accomplished by the analysis of atmospheric absorptions. This is still the case in most current applications of atmospheric spectroscopy. The use of emission bands is restricted to the thermal infrared wavelength region (see Chap. 5) or to the excited gas molecules in the upper atmosphere, which emit light at higher energies, i.e. shorter wavelength. Both applications are in use today, but are not the topic of discussion in this book.

The initial use of spectroscopy in the atmosphere concentrated on the identification of various gases. Soon, however, this method was put in use to quantify the concentrations (or column densities) of these species. In particular, the contributions of Dobson, who constructed the first instrument for the regular measurement of atmospheric ozone, should be singled out (Dobson and Harrison, 1926).

This chapter focuses on a modern method to quantitatively measure a large variety of trace gases in the atmosphere. DOAS is now one of the most commonly used spectroscopic methods to measure trace gases in the open atmosphere. At the beginning, we give a general introduction to absorption spectroscopy and DOAS. This is followed by an overview of different experimental approaches of DOAS and a discussion of the precision and accuracy of this method. The last section of this chapter is dedicated to a rigorous mathematical description of the various DOAS applications.