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, \( \text{HO}_x \)-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.
6.2 Classical Absorption Spectroscopy

The basis of the early spectroscopic measurements, and many present quantitative trace gas analytical methods in the atmosphere and the laboratory, is Lambert–Beer’s law, often also referred to as Bouguer–Lambert law. The law was presented in various forms by Pierre Bouguer in 1729, Johann Heinrich Lambert in 1760, and August Beer in 1852. Bouguer first described that, ‘In a medium of uniform transparency the light remaining in a collimated beam is an exponential function of the length of the path in the medium’. However, there was some confusion in the naming of this law, which may be either the name of individual discoverer or combinations of their names. In this book, we have referred to it as Lambert–Beer’s law.

A variety of spectroscopic techniques make use of the absorption of electromagnetic radiation by matter (Fig. 6.1). In a formulation suitable for the analysis of gaseous (or liquid) absorbers, Lambert–Beer’s law can be written as:

\[
I(\lambda) = I_0(\lambda) \cdot \exp (-\sigma(\lambda) \cdot c \cdot L) .
\] (6.1)

Here, \( I_0(\lambda) \) denotes the initial intensity of a light beam emitted by a suitable source of radiation, while \( I(\lambda) \) is the radiation intensity of the beam after passing through a layer of thickness \( L \), where the absorber is present at a uniform concentration of \( c \). The quantity \( \sigma(\lambda) \) denotes the absorption cross-section at wavelength \( \lambda \). The absorption cross-section as a function of wavelength is a characteristic property of any species. The determination of the light path length, \( L \), is usually trivial for active DOAS applications (see Chap. 4). Once those quantities are known, the average trace gas concentration, \( c \), can be calculated from the measured ratio \( I_0(\lambda)/I(\lambda) \):

\[
c = \ln \left( \frac{I_0(\lambda)}{I(\lambda)} \right) = \frac{D}{\sigma(\lambda) \cdot L} .
\] (6.2)

**Fig. 6.1.** The basic principle of absorption spectroscopic trace gas detection. A beam of light passes through a volume of length \( L \) containing the absorber with concentration \( c \). At the end of the light path the intensity is measured by a suitable detector.
The expression
\[ D = \ln \left( \frac{I_0(\lambda)}{I(\lambda)} \right), \tag{6.3} \]
is called the optical density of a layer of a given absorber. Note that, in the literature, the decadal as well as the natural logarithm is used in the definition of optical density. In this book, we will exclusively use the natural logarithm.

Equation (6.2) is the basis of most absorption spectroscopic applications in the laboratory, where the intensities \( I(\lambda) \) and \( I_0(\lambda) \) are determined by measurements with and without the absorber in the light beam.

However, the application of Lambert–Beer’s law is more challenging in the open atmosphere. Here, the true intensity \( I_0(\lambda) \), as it would be received from the light source in the absence of any atmospheric absorber, is difficult to determine. It would involve removing the air, or more precisely the absorbing gas, from the atmosphere. While this may seem to present a dilemma rendering atmospheric absorption spectroscopy useless in this case, the solution lies in measuring the so-called ‘differential’ absorption, i.e. the difference between the absorptions at two different wavelengths. This principle was used by Dobson in the 1930s to determine the total column of atmospheric ozone. In an ingenious experimental setup, the Dobson spectrometer compares the intensity of direct solar light of two wavelengths – \( \lambda_1, \lambda_2 \) – with different ozone absorption cross-section, \( \sigma_1 = \sigma(\lambda_1), \sigma_2 = \sigma(\lambda_2) \) (Dobson and Harrison, 1926).

### 6.3 The DOAS Principle

A schematic setup of an experiment to measure trace gas absorptions in the open atmosphere is shown in Fig. 6.2. Similar to Fig. 6.1, light emitted by a suitable spectral broadband source with an intensity \( I_0(\lambda) \) passes through a volume with absorbers (here the open atmosphere), and is collected at the end of the light path. As the light travels through the atmosphere, its intensity is reduced through the absorption of a specific trace gas. However, it also undergoes extinction due to absorption by other trace gases, and scattering by air molecules and aerosol particles. The transmissivity of the instrument (mirrors, grating, retro-reflectors, etc.) will also decrease the light intensity, as will the light beam widening by turbulence. By expanding Lambert–Beer’s law, one can consider the various factors that influence the light intensity by an equation that includes the absorption of various trace gases with concentration \( c_j \) and absorption cross-sections \( \sigma_j(\lambda) \), Rayleigh and Mie extinction, \( \varepsilon_R(\lambda) \) and \( \varepsilon_M(\lambda) \) (described by \( \varepsilon_R(\lambda) \approx \sigma_{R0}(\lambda) \cdot \lambda^{-4} \cdot c_{\text{AIR}} \) and \( \varepsilon_M(\lambda) = \sigma_{M0} \cdot \lambda^{-n} \cdot N_A \), respectively; see Chap. 4), and instrumental effects and turbulence, summarised in \( A(\lambda) \):

\[ I(\lambda) = I_0(\lambda) \cdot \exp \left[ -L \cdot \left( \sum (\sigma_j(\lambda) \cdot c_j) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda) \right) \right] \cdot A(\lambda). \tag{6.4} \]
To determine the concentration of a particular trace gas, it would, in principle, be necessary to quantify all other factors influencing the intensity. In the laboratory, this can be achieved by removing the absorber from the light path. In the atmosphere, however, where this is impossible, the multiple factors influencing the intensity pose a dilemma.

Differential optical absorption spectroscopy overcomes this challenge by using the fact that aerosol extinction processes, the effect of turbulence, and many trace gas absorptions show very broad or even smooth spectral characteristics. Certain trace gases, however, exhibit narrowband absorption structures. The foundation of DOAS is thus to separate broad- and narrowband spectral structures in an absorption spectrum in order to isolate these narrow trace gas absorptions (Fig. 6.3). The broad spectrum is then used as a new intensity spectrum $I_0'(\lambda)$, and Lambert–Beer’s law can again be applied to the narrowband trace gas absorptions.

Figure 6.3 illustrates the separation of the narrow- and broadband structures for one absorption band, both for the absorption cross-section and the intensity:

$$\sigma_j(\lambda) = \sigma_{j0}(\lambda) + \sigma'_j(\lambda)$$  \hspace{1cm} (6.5)

$\sigma_{j0}$ in (6.5) varies ‘slowly’ with the wavelength $\lambda$, for instance describing a general ‘slope’, such as that caused by Rayleigh and Mie scattering, while $\sigma'_j(\lambda)$ shows rapid variations with $\lambda$, for instance due to an absorption band (see Fig. 6.3). The meaning of ‘rapid’ and ‘slow’ variation of the absorption cross-section as a function of wavelength is, of course, a question of the observed wavelength interval and the width of the absorption bands to be detected. Inserting (6.5) into (6.4), we obtain:

$$I(\lambda) = I_0(\lambda) \cdot \exp \left[ -L \cdot \left( \sum_j (\sigma'_j(\lambda) \cdot c_j) \right) \right] \cdot \exp \left[ -L \cdot \left( \sum_j (\sigma_{j0}(\lambda) \cdot c_j) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda) \right) \right] \cdot A(\lambda), \hspace{1cm} (6.6)$$
Fig. 6.3. Principle of DOAS: $I_0$ and $\sigma$ are separated by an adequate filtering procedure into a narrow ($D'$, and $\sigma'$) and broad band part ($I'_0$ and $\sigma_b$)

where the first exponential function describes the effect of the structured ‘differential’ absorption of a trace species, while the second exponential constitutes the slowly varying absorptions as well as the influence of Rayleigh and Mie scattering. The attenuation factor $A(\lambda)$ describes the broad wavelength-dependent transmission of the optical system used and turbulence. Thus, we can define a quantity $I'_0$ as the intensity in the absence of differential absorption:

$$I'_0(\lambda) = I_0(\lambda) \cdot \exp \left[ -L \cdot \left( \sum_j \left( \sigma'_j(\lambda) \cdot c_j \right) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda) \right) \right] \cdot A(\lambda) \cdot (6.7)$$

The corresponding differential absorption cross-section $\sigma'_j(\lambda)$ is then substituted for $\sigma_j(\lambda)$ in (6.1) and (6.2). $\sigma'_j(\lambda)$ is determined in the laboratory (i.e. taken from literature data), just like $\sigma_j(\lambda)$. Likewise, a differential optical density, $D'$, can be defined in analogy to (6.3) as the logarithm of the quotient of the intensities $I'_0$ and $I_0$ (as defined in (6.7) and (6.6), respectively):

$$D' = \ln \frac{I'_0(\lambda)}{I(\lambda)} = L \cdot \sum_j \sigma'_j(\lambda) \cdot c_j \cdot (6.8)$$

Atmospheric trace gas concentrations can then be calculated according to (6.2), with differential quantities $D'$ and $\sigma'(\lambda)$ substituted for $D$ and $\sigma(\lambda)$, respectively. A separation of the different absorptions in the sum of (6.8) is
possible because the structures of the trace gases are unique, like a fingerprint (see Sect. 6.5).

Both the separation of broad and narrow spectral structures and the separation of the various absorbers in (6.8) require the measurement of the radiation intensity at multiple wavelengths. In fact, DOAS measurements usually observe the intensity at 500–2000 individual wavelengths to accurately determine the concentrations of the various absorbing trace gases. The use of multiple wavelengths is an expansion of the principles used, for example, by Dobson, which were based on two or four wavelengths.

The use of differential absorptions over an extended wavelength range has a number of major advantages. Because the transmission of optical instruments typically shows broad spectral characteristics, no calibration of the optical properties or their change with time is necessary. This often makes the instrumentation much simpler and less expensive. The use of a multitude of wavelengths allows the unique identification of trace gas absorptions. A further major advantage of this approach is the opportunity to observe and quantify extremely weak absorptions corresponding to optical densities around $D' = 10^{-4}$. In particular, the ability to use very long light paths in the atmosphere, in active DOAS applications sometimes up to 10–20 km long (passive DOAS applications can reach 1000 km), increases the sensitivity of DOAS and, at the same time, provides spatially averaged values.

Before giving a more rigorous mathematical description of the DOAS method, the basic experimental setups, the trace gases that are commonly measured, and the typical detection limits of DOAS will be reviewed in the following sections.

6.4 Experimental Setups of DOAS Measurements

The DOAS principle as outlined earlier can be applied in a wide variety of light path arrangements and observation modes (Fig. 6.4). To provide a general overview of different setups, we introduce a classification system that will later be used in the description of the different analysis methods (see Sect. 6.7 and Chap. 8) and the technical details (Chap. 7).

According to their light sources, we distinguish between active and passive DOAS. In short, active DOAS uses artificial light, while passive DOAS relies on natural light sources, i.e. solar, lunar, or stars. An overview of the most common experimental setups illustrates the breadth of DOAS applications that are in use today (Fig. 6.4).

6.4.1 Active DOAS

Active DOAS applications have one thing in common – they rely on an artificial light source coupled to an optical setup that is used to send and receive
1. Long-Path DOAS (LP-DOAS)

\[ I_0 \rightarrow I \rightarrow \text{Det.} \]

2. Vertical Profiling LP-DOAS

\[ \text{Lamp + Det.} \]

3. Tomographic DOAS

4. Folded-Path DOAS

5. Direct Sunlight DOAS

6. Balloon-borne (direct sunlight) DOAS

7. Satellite-borne DOAS - Occultation

8. Zenith Scattered Light (ZSL-DOAS)

9. Multi-Axis DOAS (MAX-DOAS)

10. Airborne Multi-Axis DOAS (AMAX-DOAS)

**Fig. 6.4.** The DOAS principle can be applied in a wide variety of light path arrangements and observation modes using artificial (1–4) as well as natural direct (5–7) or scattered (8–14) light sources. Measurements can be done from the ground, balloons, aircrafts, and from space.
light in the atmosphere. Spectroscopic detection is achieved by a spectrometer at the end of the light path. In general, active DOAS is very similar to classical absorption spectroscopy, as employed in laboratory spectral photometers. However, the low trace gas concentrations in the atmosphere require very long light paths (up to tens of kilometres in length, see above), making the implementation of these instruments challenging (see Chap. 7 for details). Active DOAS applications are typically employed to study tropospheric composition and chemistry, with light paths that are often parallel to the ground. In addition, active DOAS systems are also used in smog and aerosol chamber experiments.

The earliest applications of active DOAS, i.e. the measurement of OH radicals (Perner et al., 1976), used a laser as the light source along one single path (Fig. 6.4, Plate 1). This long-path DOAS setup is today most commonly used with broadband light sources, such as xenon-arc lamps, to measure trace gases such as O$_3$, NO$_2$, SO$_2$, etc. (e.g. Stutz and Platt, 1997a,b). Expansion of this method involves folding the light beam once by using retro-reflectors on one end of the light path (Axelsson et al., 1990). This setup simplifies the field deployment of long-path DOAS instruments. In addition, applications that use multiple retro-reflector setups to probe on different air masses are possible. Figure 6.4, Plate 2, shows the setup that is used to perform vertical profiling in the boundary layer with one DOAS system. An expansion that is currently under development is the use of multiple crossing light paths to perform tomographic measurements (Fig. 6.4, Plate 3).
In applications where detection in smaller air volumes with high sensitivity is required, folded-path DOAS is often used (Fig. 6.4, Plate 4) (e.g. Ritz et al., 1992). Because the light can pass the multiple reflection cells in these systems up to 144 times, long light paths can be achieved in small air volumes. These systems are the most common DOAS setups in laboratory applications, where interference by aerosols makes the use of classical absorption spectroscopy impossible (e.g. smog and aerosol chambers). Folded-path DOAS has also been used for the same applications as long-path DOAS (e.g. Alicke et al., 2003; Kurtenbach et al., 2002). In particular, the use of laser to measure OH has been successful (see Chap. 10).

Active DOAS measurements have contributed to the discovery and quantification of a number of important atmospheric trace species, most notably the radicals OH and NO$_3$ (Perner et al., 1976; Platt et al., 1979). The elegance of active DOAS is that the expanded Lambert–Beer’s law (6.4) can be directly applied to the calculation of trace gas concentrations based only on the absorption cross-section, without the need for calibration of the instrument in the field. This gives active DOAS high accuracy and, with the long light paths, excellent sensitivity.

6.4.2 Passive DOAS

Passive DOAS utilises light from natural sources. The two most important sources are the sun and the moon. However, the use of light from other stars has also been reported. While the measurement of light directly from moon and stars is possible, sunlight offers two alternatives: direct sunlight and sunlight scattered in the atmosphere by air molecules and particles. We will further subdivide passive DOAS applications into direct and scattered light measurements (see also Chap. 11).

Direct measurements use the sun, moon, or stars as light sources, and thus share the advantage of active DOAS of directly applying Lambert–Beer’s law. However, since the light crosses the entire vertical extent of the atmosphere, a direct conversion of absorptions to concentrations is not possible. Instead, the column density, i.e. the concentration integrated along the path, is the direct result of these measurements. Only by using geometric and radiative transfer calculations can these measurements be converted into vertically integrated column densities (VCD) or vertical concentration profiles. The most common example for VCDs is the total ozone column, which is measured in Dobson units. Figure 6.4 gives several examples for direct passive DOAS setups. Besides direct measurements of sun, moon, and star light from the ground (Fig. 6.4, Plate 5), balloon-borne solar measurements have been very successful (Fig. 6.4, Plate 6). The measurements during the ascent provide vertical profiles of various trace gases. With the recent deployment of space-borne DOAS instruments, i.e. SCIAMACHY, occultation measurements (Fig. 6.4, Plate 7) have also become possible.
6.4 Experimental Setups of DOAS Measurements

Scattered sunlight measurements are more universally used in passive DOAS since they offer the largest variety of applications. The measurement of scattered light from the zenith (Fig. 6.4, Plate 8) was one of the earliest applications of passive DOAS (see Sect. 11.2), and has contributed considerably to our understanding of stratospheric chemistry (e.g. Mount et al., 1987; Solomon et al., 1987, 1988, 1989). In addition, zenith scattered light has also been used to study the radiative transport in clouds (Fig. 6.4, Plate 14), which is an important topic in climate research (Pfeilsticker et al., 1998b, 1999). A more recent development of passive scattered DOAS is the use of multiple viewing geometries (Fig. 6.4, Plate 9). This multi-axis DOAS (MAX-DOAS) uses the fact that, at low viewing elevations, the length of the light path in the lower troposphere is considerably elongated (e.g. Höninger et al., 2004). It is thus possible to probe the lower troposphere sensitively. In addition, vertical profiles can be derived if enough elevation angles are measured. MAX-DOAS can also be employed from airborne platforms, allowing the measurements below and above the flight altitude (Fig. 6.4, Plate 10), as well as determination of vertical concentration profiles. An expansion of MAX-DOAS, which is currently under development, is Imaging DOAS (Fig. 6.4, Plate 11), where a large number of viewing elevations are measured simultaneously to visualise pollution plumes.

Over the past decade, DOAS has also been used for satellite-borne measurements (Fig. 6.4, Plates 12, 13), which use sunlight scattered either by the atmosphere, the ground, or both (see Sect. 11.5). Two viewing geometries of these measurements are possible (for details and examples, see Chap. 11). In the nadir geometry, the DOAS system looks down towards the earth’s surface. Instruments such as GOME provide global concentration fields of trace gases, such as O$_3$, NO$_2$, and HCHO. The SCIAMACHY instrument also employs measurements in limb geometry, which allow the determination of vertical trace gas profiles with high resolution (Fig. 6.4, Plate 13).

The advantage of passive DOAS applications is the relatively simple experimental setup. For example, scattered light measurements require only small telescopes. In addition, no artificial light source is needed. However, a number of additional challenges have to be addressed in passive DOAS applications. Because solar and lunar light is spectrally highly structured, special care needs to be taken. To detect very small trace gas absorptions, the strong Fraunhofer bands must be accurately measured. In addition, the fact that the light source structure contains narrow and deep absorptions also makes the application of the DOAS technique, which was outlined in Sect. 6.3, more difficult. This will be discussed in more detail below. The largest challenge in using passive DOAS is the conversion of the observed column densities to vertical column densities, concentrations, and vertical profiles. This is, in particular, the case for scattered light setups, where the length of the light path is difficult to determine. The interpretation of these measurements, therefore, must be based on detailed radiative transfer calculations (see Chap. 9).
6.5 Trace Gases Measured by DOAS

The separation of broad and narrow spectral structures (Sect. 6.3), while making absorption spectroscopy usable in the atmosphere, restricts DOAS measurements to trace gases that have narrow band absorption structures with widths narrower than ≈10 nm. In theory, all gases that have these narrow absorption bands in the UV, visible, or near IR can be measured. However, the concentrations of these compounds in the atmosphere, and the detection limits of today’s DOAS instruments, restrict the number of trace gases that can be detected. As DOAS instruments improve in the future, this list will most likely grow.

Figures 6.5 and 6.6 show the absorption cross-sections of a number of trace gases that are regularly measured by DOAS. A number of features about these cross-sections should be pointed out here. First and most importantly, each trace gas spectrum has a unique shape. Most of the trace gases only absorb in certain wavelength intervals. However, many spectral regions can contain a large number of simultaneous absorbers. For example, between 300 and 400 nm, the following trace gases will show absorption features if they are present at high enough concentrations: O$_3$, SO$_2$, NO$_2$, HONO, HCHO, and BrO. Because of their unique spectral structure, a separation of the absorptions is possible. From (6.8), it is clear that spectral regions with higher $\sigma$ will show the largest optical densities. These spectral intervals are thus preferred for DOAS measurements since the sensitivity improves in these wavelength regions. In principle, each trace gas has an optimal wavelength interval. In practice, however, one has to often compromise in the choice of the wavelength interval to measure more than one trace gas simultaneously. Because expanding the wavelength window reduces the spectral resolution of typical grating spectrometers, the sensitivity is also reduced.

The choice of trace gases thus depends on the specific application. In Fig. 6.7, we have attempted to aid in the choice of the best wavelength region by visualising the detection limits of an extended set of trace gases for long-path applications in the troposphere.

It should be added that a number of other trace gases, besides those shown in Figs. 6.5 and 6.6, can be measured. Table 6.1 gives an overview of the various trace gases measured by DOAS, including stratospheric trace gases. At shorter wavelengths, the usable spectral range of DOAS is limited by rapidly increasing Rayleigh scattering and O$_2$ absorption (Volkamer et al., 1998). Those effects limit the maximum light path length to ≈200 m in the wavelength range from 200–230 nm, where, for instance, the sole usable absorption features of species such as NO (Tajime et al., 1978) and NH$_3$ are located (see Fig. 6.7 and Table 6.1).
Fig. 6.5. Details of the absorption cross-section features of a number of species of atmospheric interest as a function of wavelength (in nm). Note the ‘fingerprint’ nature of the different spectra.
Fig. 6.6. Details of the differential absorption cross-section features of a number of monocyclic aromatic species, O$_2$, and O$_3$ as a function of wavelength (in nm). Note the ‘fingerprint’ nature of the different spectra.
Fig. 6.7. Overview of UV-visible spectral ranges usable for the detection of atmospheric trace gases. Vertical scale: Log of absorption cross-section of the molecule ($10^{-20}$ to $10^{-17}$ cm$^2$/molec.), as well as an approximate detection limit at 10 km light path length (1 ppt to 1 ppb, see insert). Molecules exhibiting strong rotational structure at atmospheric pressure are noted by an asterisk ($^*$)
Table 6.1. Substances detectable by active UV/visible absorption spectroscopy. Detection limits were calculated for a minimum detectable optical density of $5 \times 10^{-4}$

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength interval (nm)</th>
<th>Approximate absorption $10^{-19} \text{cm}^2/\text{molec.}$</th>
<th>differential cross-section $10^{-19} \text{cm}^2/\text{molec.}$</th>
<th>Column density detection limit $10^{15} \text{molec./cm}$</th>
<th>Detection limit (5 km light path) ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>200–230</td>
<td>65</td>
<td>0.077</td>
<td>62$^{a}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>290–310</td>
<td>5.7</td>
<td>0.88</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>CS$_2$</td>
<td>320–340</td>
<td>0.4</td>
<td>13</td>
<td>1000</td>
<td></td>
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<tr>
<td>NO</td>
<td>200–230</td>
<td>24</td>
<td>0.21</td>
<td>167$^{a}$</td>
<td></td>
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<td>NO$_2$</td>
<td>330–500</td>
<td>2.5</td>
<td>2.0</td>
<td>160</td>
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<td>NO$_3$</td>
<td>600–670</td>
<td>200</td>
<td>0.025</td>
<td>2</td>
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<td>200–230</td>
<td>180</td>
<td>0.028</td>
<td>22$^{a}$</td>
<td></td>
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<td>330–380</td>
<td>5.1</td>
<td>0.98</td>
<td>78</td>
<td></td>
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<tr>
<td>O$_3$</td>
<td>300–330</td>
<td>0.1</td>
<td>50</td>
<td>4000</td>
<td></td>
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<tr>
<td>H$_2$O</td>
<td>above 430</td>
<td>$3 \cdot 10^{-4}$</td>
<td>$1.67 \cdot 10^4$</td>
<td>$1.33 \cdot 10^4$</td>
<td></td>
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<tr>
<td>CH$_2$O</td>
<td>300–360</td>
<td>0.48</td>
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<td>0.14</td>
<td>11</td>
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<tr>
<td>Molecule</td>
<td>Range</td>
<td>Mixing Ratio</td>
<td>Peak Height</td>
<td>Seasonal Variation</td>
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<td>--------------</td>
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<td>OCIO</td>
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<td>0.047</td>
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<tr>
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<tr>
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<td>3.5</td>
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<td>0.28</td>
<td>22</td>
<td></td>
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<tr>
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<td>0.029</td>
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<td></td>
</tr>
<tr>
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<td>480–600</td>
<td>110</td>
<td>0.045</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>240–270</td>
<td>21.9</td>
<td>0.23</td>
<td>180&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>250–280</td>
<td>12.8</td>
<td>0.39</td>
<td>310&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Xylene (o/m/p)</td>
<td>250–280</td>
<td>2.1/6.6/20.3</td>
<td>2.4/0.76/0.25</td>
<td>2000/650/210&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>260–290</td>
<td>198</td>
<td>0.0025</td>
<td>20&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Cresol (o/m/p)</td>
<td>250–280</td>
<td>20.1/31.8/87.2</td>
<td>0.25/0.16/0.06</td>
<td>200/135/50&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>280–290</td>
<td>44</td>
<td>0.11</td>
<td>90&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Glyoxal</td>
<td>400–480</td>
<td>10</td>
<td>0.5</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>500-m light path
Selectivity, precision, and accuracy are important aspects of an analytical method. We thus give a brief overview of the different sources of random and systematic errors that must be considered in DOAS. A detailed mathematical treatment of these errors will be given in Chap. 8.

Selectivity describes the ability of an analytical method to clearly distinguish different trace gases in a measurement. In wet-chemical methods, for example, it is often challenging to identify species with similar chemical properties. Spectroscopic methods, on the other hand, provide excellent selectivity, since the absorption structures of different trace gases are a unique property of each compound. This property has been the basis of spectroscopic studies in the laboratory for many years and transfers directly to DOAS. As illustrated in Fig. 6.5, each differential absorption cross-section is unique. The numerical separation procedures described in Chap. 8 are able to separate 10 or more overlaying absorptions without creating cross-sensitivities. A condition for the successful differentiation of the trace gases is, however, that the absorption cross-section of a certain gas does not accidentally contain absorption structures of other trace gases due to, say, impurities in the sample when recording it. Such absorptions could cause interferences in the numerical analysis procedure. Careful analysis of the cross-sections can prevent this problem, and with today’s high-quality laboratory techniques, cross-sections are typically pure. It should be noted here that DOAS is also able to distinguish different isomers of a species, for example, of aromatic hydrocarbons, such as the various xylenes.

The precision of DOAS measurements is mostly determined by the quality of the instrument and atmospheric conditions. Different sources of errors that influence the precision must be considered for the various DOAS applications (see Table 6.2). A common and often the dominating source of error in all applications is random noise in the spectra. The most important noise source originates from photon statistics, and is thus unavoidable. In general, the precision increases as more photons are collected. In addition, the noise of the detector can play a role when light levels are low. With today’s technology, however, detector noise is often a minor problem. In many DOAS applications, unexplained random spectral structures are encountered. These structures have a different origin than pure photon or detector noise. In most cases, their spectra show variations that act simultaneously on a number of neighbouring detector channels. For active DOAS applications, the random spectral interferences (also known as ‘optical noise’) are often the primary limitation of the precision. The influence in passive DOAS measurements is less severe. A detailed discussion of the treatment of these structures is given in Chap. 8. Finally, it should be noted here that both noise and unexplained spectral structures can be determined for each individual absorption spectrum during the analysis routine. Variations in the environmental conditions, such as changes in atmospheric transmission, will automatically be reflected in these uncertainties.
Table 6.2. Errors that influence the precision and accuracy of DOAS

<table>
<thead>
<tr>
<th>Type of instrument</th>
<th>Precision</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active DOAS</td>
<td>• Noise</td>
<td>• Noise</td>
</tr>
<tr>
<td></td>
<td>• Unexplained spectral structures</td>
<td>• Unexplained spectral structures</td>
</tr>
<tr>
<td></td>
<td>• Insignificant: path length</td>
<td>• Insignificant: path length</td>
</tr>
<tr>
<td></td>
<td>• Accuracy of absorption cross-section</td>
<td>• Accuracy of absorption cross-section</td>
</tr>
<tr>
<td>Passive direct</td>
<td>• Noise</td>
<td>• Noise</td>
</tr>
<tr>
<td>light DOAS</td>
<td>• Removal of Fraunhofer bands</td>
<td>• Removal of Fraunhofer bands</td>
</tr>
<tr>
<td></td>
<td>• Temperature-dependent absorption cross-section</td>
<td>• Temperature-dependent absorption cross-section</td>
</tr>
<tr>
<td></td>
<td>• Unexplained spectral structures</td>
<td>• Unexplained spectral structures</td>
</tr>
<tr>
<td>Passive scattered</td>
<td>• Noise</td>
<td>• Noise</td>
</tr>
<tr>
<td>light DOAS</td>
<td>• Removal of Fraunhofer bands</td>
<td>• Removal of Fraunhofer bands</td>
</tr>
<tr>
<td></td>
<td>• Temperature-dependent absorption cross-section</td>
<td>• Temperature-dependent absorption cross-section</td>
</tr>
<tr>
<td></td>
<td>• Unexplained spectral structures</td>
<td>• Unexplained spectral structures</td>
</tr>
<tr>
<td></td>
<td>• Path length/radiative transfer</td>
<td>• Path length/radiative transfer</td>
</tr>
<tr>
<td></td>
<td>• Accuracy of absorption cross-section</td>
<td>• Accuracy of absorption cross-section</td>
</tr>
</tbody>
</table>

The precision of DOAS can also be influenced by uncertainties in the determination of the absorption path length. In the case of active and passive direct DOAS, path lengths can be determined with high accuracy and thus contribute little to the errors in these applications. In contrast, absorption path length determination in passive scattered light DOAS applications is a major challenge. Only through detailed radiative transfer calculations is it possible to convert observed column densities to vertical column densities or concentrations. While the radiative transfer models used in this conversion are well tested, they rely on correct initialisation. Information on the vertical distribution of the trace gases and aerosol, as well as the optical properties of aerosol particles, is required. Since this information is often not available with sufficient detail, the results of the radiative transfer calculations are inherently uncertain. While we treat this uncertainty as a random effect due to its dependence on random temporal changes in the atmosphere, one can argue that this uncertainty may contribute more to systematic uncertainties that influence the accuracy. DOAS offers the opportunity to validate the radiative transfer and determine the uncertainty of this calculation by analysing trace gas absorptions from gases with known concentrations, such as O\textsubscript{2} and O\textsubscript{4}. More information on the radiative transfer calculations, input parameters, and results is given in Chap. 9.
Two other uncertainties are specific for passive DOAS applications. In all passive DOAS applications, the spectral structure of sunlight, the Fraunhofer bands, needs to be accurately removed. Because the optical densities of these bands are, in most cases, much larger than those of the trace gas absorptions, the uncertainty in the removal or modelling of the Fraunhofer structure directly influences the uncertainty of the trace gas measurements. Moreover, due to Raman scattering (see Sect. 4.2.3) in the atmosphere, the Fraunhofer lines are distorted to varying degrees (the ‘Ring Effect’, see Sect. 9.1.6). This also needs to be compensated for. Another error in passive DOAS applications stems from the temperature dependence of the various absorption cross-sections. Even if this dependence is known, the often unknown temperature structure of the atmosphere, the location of the trace gas, and, in case of scattered light applications, the uncertain light path leads to problems in the interpretation of the data.

The determination of the accuracy of any atmospheric measurement is challenging since, in principle, it would require the knowledge of true concentration of the respective trace gas. However, in many cases, it is possible to estimate the various sources of errors, such as sampling artifacts in in-situ methods, from controlled experiments. Fortunately, this is not necessary for DOAS. Sampling artifacts and losses, as well as chemical transformations occurring after sampling that are often encountered by other methods, do not have to be considered in DOAS, since the measurements are made in the open atmosphere without disturbing or influencing the trace gases. Noise, unexplained spectral structures, Fraunhofer band removal, and temperature dependent cross-section influence accuracy in the same way they influence precision. However, the radiative transfer methods used to interpret passive scattered measurements may introduce additional non-random errors that can influence the accuracy, but not the precision, of a measurement. The accuracy of the cross-sections, which is often the largest factor influencing the accuracy of DOAS, is typically in the range of 1–10% (see Appendix B). These numbers will most likely improve in the future, as more laboratory measurements become available.

One of the most important properties of analytical techniques is the detection limit, which gives the smallest possible trace gas amount that can be detected. It is difficult to give this number for all possible DOAS applications, in particular with different path lengths between the setups shown in Fig. 6.4. To provide an overview of the detection limits of DOAS, we have thus listed two different values in Table 6.1. The first is the lowest column density in units of molecules/cm$^2$ that can be measured, assuming a minimum detectable optical density of $5 \times 10^{-4}$. To determine the detection limit for a specific application, this number must be divided by the path length in units of centimetres. The last column in Table 6.1 shows the mixing ratios that can be reached for an active DOAS system with a path length of $L = 5$ km for trace gases absorbing above 300 nm, or $L = 500$ m for trace gases absorbing below 300 nm. Figure 6.7 offers a more graphical view on the same data, and also facilitates the choice of the wavelength with the lowest detection limits.
In summary, DOAS is a highly versatile, selective, and accurate technique. The accuracy is primarily determined by the known uncertainties of the absorption cross-sections used. One of the main advantages of DOAS is the ability to determine the precision of a single measurement based on the analysis of the absorption spectrum. In principle, a DOAS measurement is a “spectral photograph” of the atmospheric composition that allows the identification of its components and the determination of the uncertainty of this measurement.

6.7 Mathematical Description of the DOAS Approach

The following section provides a mathematical description of DOAS, including the influence of the actual measurement on the shape of the absorption structures. This description is the basis of most other topics discussed in this book. While the basic principles in Sect. 6.3 still apply, their application to the analysis of DOAS measurements is limited due to the omission of some important aspects of the DOAS process. An expanded discussion of the principle of DOAS illustrates the approach that needs to be taken to overcome some of the challenges faced in today’s wide variety of DOAS applications.

6.7.1 Fundamentals of the DOAS Approach

We begin our description by considering an idealised experimental setup of a DOAS instrument shown in Fig. 6.8, which serves as a model to describe the different applications shown in Fig. 6.4.

Light of intensity \( I_0(\lambda) \) emitted by a suitable source passes through the open atmosphere and is collected by a telescope. As it passes through the atmosphere, the light undergoes extinction due to absorption by different trace gases, and scattering by air molecules and aerosol particles (see Chap. 4). The intensity \( I(\lambda, L) \) at the end of the light path is given by (6.9), using Lambert–Beer’s law. The absorption of a trace species \( j \) is characterised by its absorption cross-section \( \sigma_j(\lambda, p, T) \), which depends on the wavelength \( \lambda \), pressure \( p \), and temperature \( T \), and by its number concentration \( c_j(l) \) at the position \( l \) along the light path. The Rayleigh extinction and Mie extinction by aerosols is described by \( \varepsilon_R(\lambda, l) \) and \( \varepsilon_M(\lambda, l) \). \( N(\lambda) \) is the photon noise, which depends on \( I(\lambda, L) \). For simplicity, we have omitted the influence of the instrument spectral characteristics and atmospheric turbulence, \( A(\lambda) \), described in Sect. 6.3. The spectrum at the entrance of the spectrograph (Fig. 6.8a) arises from light that passed the atmosphere with several absorbers over length \( L \).

\[
I(\lambda, L) = I_0(\lambda, L) \cdot \exp \left[ - \left( \int_0^L \sum_j (\sigma_j(\lambda, p, T) \cdot c_j(l)) + \varepsilon_R(\lambda, l) \right) + \varepsilon_M(\lambda, l) \, dl \right] + N(\lambda) .
\]

(6.9)
Fig. 6.8. Schematic view of a DOAS instrument used to measure trace gas concentrations. Collimated light undergoes absorption processes on its way through the atmosphere. In (a), an example of this light entering the spectrograph is given, where HCHO is assumed to be the only absorber and the light source has smooth spectral characteristics. This absorption spectrum shows the vibrational–rotational structure of the absorption bands. (b) The same spectrum convoluted by the spectrograph instrumental function reaches the detector. In the detector, the wavelength is mapped to discrete pixels. This spectrum (c) is then stored in the computer and can be analysed numerically (from Stutz and Platt, 1996)
Special consideration must be given to passive scattered light DOAS. The light observed in these applications follows complicated paths in the atmosphere, which are determined by the solar position in the sky, the viewing direction of the telescope, and most importantly the spatial distribution of air molecules and aerosol particles. The measured intensity is the sum over intensities of different light beams. Each of these beams has travelled on an individual path with a specific length through the atmosphere. One can introduce a simplified mathematical formulation of this phenomenon by describing the measured total intensity as an integral over a light path distribution function and a path length dependent $I_0(\lambda, L)$. It is then possible to show the validity of an approximation for cases with weak absorptions, which describes the measured intensity with (6.9). In this approximation, $I_0(\lambda, L)$ represents the total intensity, and $L$ represents the intensity-weighted average path length. In particular, the average path length will be discussed in the context of radiative transfer calculations in Chap. 9. A number of approaches to solve the DOAS problem for scattered light measurements will be described in Chaps. 9 and 11.

In most DOAS instruments, light of intensity $I(\lambda, L)$ is focused on the entrance of a grating spectrograph, with a detector recording the spectrum. Due to the limited resolution of the spectroscopic instruments, the shape of spectrum $I(\lambda, L)$ changes. The mathematical description of this process is a convolution of $I(\lambda, L)$, with the instrument function $H$ of the spectrograph: $I^*(\lambda, L) = I(\lambda, L) \ast H$. Figure 6.8b shows the spectrum $I$ after convolution with a typical instrument function $H$.

$$I^*(\lambda, L) = I(\lambda, L) \ast H = \int I(\lambda - \lambda', L) \cdot H(\lambda') d\lambda'. \quad (6.10)$$

During the recording by a detector, the wavelength range is mapped to $n$ discrete pixels/channels, numbered by $i$, each integrating the light in a wavelength interval from $\lambda(i)$ to $\lambda(i+1)$. This interval is given by the wavelength-pixel-mapping $\Gamma_I$ of the instrument. In the case of a linear dispersion, $\Gamma_I : \lambda(i) = \gamma_0 + \gamma_1 \cdot i$, the spectral width of a pixel is constant $\Delta\lambda(i) = \lambda(i+1) - \lambda(i) = \gamma_1$. The signal $I'(i)$ seen by a pixel $i$ (omitting the response of individual pixels) is given by:

$$I'(i) = \int_{\lambda(i)}^{\lambda(i+1)} I^*(\lambda') d\lambda'. \quad (6.11)$$

In general, the wavelength-pixel-mapping $\Gamma_I$ of the instrument can be approximated by a polynomial:

$$\Gamma_I : \lambda(i) = \sum_{k=0}^{q} \gamma_k \cdot i^k. \quad (6.12)$$

The parameter vector $(\gamma_k)$ determines the mapping of pixel $i$ to the wavelength $\lambda(i)$. A change in parameter $\gamma_0$ describes a spectral shift of the spectrum. Changing $\gamma_1$ squeezes or stretches the spectrum linearly. Parameters
\( \gamma_k \) of higher \( k \) describe a distortion of the wavelength scale of higher order. Changes in the parameter vector \( (\gamma_k) \) can be caused by different measurement conditions of the spectra, as grating spectrometers usually show a temperature drift of 1/10 of a pixel per K. A variation in air pressure, as observed in aircraft measurements, also changes the wavelength alignment due to a change in the index of refraction of air. It is, therefore, necessary to correct these effects in the analysis procedure.

Figure 6.8c shows the discrete spectrum \( I'(i) \) as was recorded and stored in a computer. One of the main components of DOAS is the analysis of \( I'(i) \) with respect to the different absorbers in the spectrum.

6.7.2 Application of the DOAS Approach in Practical Situations

Equations (6.9) and (6.10) can be combined into one equation:

\[
I^*(\lambda, L) = I(\lambda, L) * H \\
= \int_{-\Delta\lambda}^{\Delta\lambda} I_0(\lambda - \lambda', L) \exp \left( -\int_o^L \sum_j (\sigma_j(\lambda - \lambda', p, T) \cdot c_j(l)) + \varepsilon_R(\lambda - \lambda', l) \right) \\
+ \varepsilon_M(\lambda - \lambda', l) \cdot H(\lambda') d\lambda' 
\]

We have omitted the noise term in (6.13), since the following discussion focuses on a mathematical description of the DOAS method that does not consider statistical uncertainties. The noise and its influence on the results of DOAS are the topic of discussion in Chap. 8.

In order to simplify the mathematical treatment of the DOAS approach, we neglect the effect of wavelength discretisation and concentrate on the following discussion of the continuous spectra arriving at the detector, \( I^*(\lambda, L) \). The omission of the discretisation step (6.11) has no influence on the general results of our discussion. In particular, when the width of the instrument function \( H \) is much larger than the wavelength interval of one pixel, the approximation that the intensity at the centre wavelength of a pixel \( I^*(\lambda(i), L) \) is very similar to the integral over the entire pixel \( i \) is quite good. If this is not the case, other effects such as aliasing have to be considered. However, since the discussion of these effects does not aid in the understanding of DOAS, we will not consider them in this chapter, and we will assume that the integral over the pixel can indeed be approximated by the intensity of the centre wavelength of the pixel.

Although, from a purely mathematical point of view, the integration of the first integral in (6.13) should extend from \(-\infty\) to \(\infty\), in practice it is sufficient to constrain it to a small interval around the instrument function of width \( 2\Delta\lambda \). Assuming a Gaussian function \( H(\lambda') = C \cdot \exp \left[ -\left( \lambda' / \lambda_H \right)^2 \right] \) as an approximation of the instrument function, \( \Delta\lambda \) can be chosen as a small multiple of \( \lambda_H \). For example, choosing \( \Delta\lambda = 4 \cdot \lambda_H \) would result in an error
Following the general DOAS approach (see Sect. 6.3), we can simplify (6.13) by including all broadband terms in a new $I'_0(\lambda, L)$:

$$I^*(\lambda, L) = \int_{-\Delta\lambda}^{\Delta\lambda} I'_0(\lambda, p, T, L) \exp \left( \int_0^L \sum_j (\sigma'_j(\lambda, \phi, p) \cdot \rho_j(l)) \, dl \right) \cdot H(\lambda') d\lambda'. \quad (6.14)$$

It should be noted that the separation of spectrally broad and narrow terms leading to (6.14) is not an a-priori defined procedure, and there are many implementations of this separation, such as regressions and Fourier filters (see Chap. 8). Here, we treat this separation in the most general term, without giving a quantitative definition of what we consider as broad or narrow. However, one important aspect that must be mentioned is that any separation is applied to the intensity spectra $I(\lambda)$, and not to the absorption cross-section $\sigma(\lambda)$. This may, at first glance, contradict our original approach in (6.5). However, because we are free in choosing the procedure to separate broad and narrow structures, we can generalise (6.5) to:

$$\exp(-\sigma(\lambda)) = \exp(-\sigma_0(\lambda)) \cdot \exp(-\sigma'(\lambda)),$$

where any separation procedure is applied to $\exp(-\sigma(\lambda))$. The choice of separation procedure, which will be discussed in more detail in Chap. 8, will not impact our following discussion.

The DOAS problem can, in principle, be solved by a numerical model of (6.14), where the trace gas concentrations $c_j(l)$ are adjusted to optimise the agreement between $I^*(\lambda, L)$ and the measured spectrum. However, in practice, this is difficult and time consuming, since it requires a non-linear optimisation procedure. A variety of simplifications and adaptations have thus been developed.

We will now present a number of these implementations for different DOAS applications. As an initial simplification, we assume that the differential absorption cross-section $\sigma'_j(\lambda)$ is independent of temperature and pressure. For active DOAS applications, which typically measure a very small altitude interval, this restriction is applicable. For certain passive DOAS applications, this assumption is difficult to sustain and would, in principle, require a rigorous numerical solution of (6.14). There is, however, an approximate solution, which splits $\sigma'_j(\lambda, T, p)$ into a small number of different cross-sections $\sigma'_k(\lambda, T, p)$ for individual temperature/pressure combinations (note that there is a correlation between pressure and temperature in the atmosphere): $\sigma'_j(\lambda, T, p) = \sum b_k \cdot \sigma'_k(\lambda, T, p)$. With this approach, $\sigma'_j(\lambda)$ becomes independent of the integration over the path length, and the integration over $dl$ only has to be applied to $c_j(l)$.

Based on our assumption that $\sigma'_j(\lambda)$ is independent of temperature and pressure, or can be split into independent parts, we can now introduce the path-averaged gas concentration:

$$\bar{c}_j = \frac{1}{L} \int_0^L c_j(l) \, dl. \quad (6.15)$$
Equation (6.14) thus becomes:

\[ I^*(\lambda, L) = \int_{-\Delta \lambda}^{\Delta \lambda} I'_0(\lambda - \lambda', L) \cdot \exp \left( -\sum_j (\sigma'_j(\lambda - \lambda') \cdot \bar{c}_j \cdot L) \right) \cdot H(\lambda') d\lambda' . \] (6.16)

Equation (6.16) is the basis of the following discussion. It is the simplest description of a DOAS measurement containing differential absorption of multiple trace gases, a wavelength-dependent \( I'_0 \), and the convolution process representing the measurement.

Based on (6.16), we can define a number of parameters that influence the choice of DOAS implementation (see also Table 6.3):

- **The differential optical density of the trace gas absorption.** In general, we will denote differential optical densities \( D' = L \cdot \sum \sigma'_j(\lambda) \cdot \bar{c}_j \) that are below \( \sim 0.1 \) as ‘small’. It will depend on the mathematical treatment of the DOAS implementation if this limit applies to the original or convoluted absorption band. The change in differential optical density due to the convolution depends on the width of the absorption band relative to the instrument function width in the convolution. The change is more pronounced in narrow bands.

**Table 6.3. Overview of the different cases for DOAS applications**

<table>
<thead>
<tr>
<th>Case</th>
<th>Diff. OD of absorber</th>
<th>Resolution of spectrometer</th>
<th>Spectrum of source</th>
<th>Approach</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Small</td>
<td>High and low</td>
<td>Smooth</td>
<td>Linearise Lambert–Beer’s law</td>
<td>Classical case</td>
</tr>
<tr>
<td>2</td>
<td>Large</td>
<td>High</td>
<td>Smooth</td>
<td>Lambert–Beer’s Law</td>
<td>Classical case</td>
</tr>
<tr>
<td>3</td>
<td>Large</td>
<td>Low</td>
<td>Smooth</td>
<td>Nonlinear, modelling of entire equation system</td>
<td>Saturated absorber</td>
</tr>
<tr>
<td>4</td>
<td>Small or large</td>
<td>High(^a)</td>
<td>Structured</td>
<td>Divide by ( I_0(\lambda) )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Small</td>
<td>Low</td>
<td>Structured</td>
<td>High res. Model + Lambert–Beer’s Law</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Large</td>
<td>Low</td>
<td>Structured</td>
<td>Non-linear, modelling of entire equation system</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)2\Delta \lambda \ll \lambda_I \text{ and } 2\Delta \lambda \ll \lambda_B
• The spectral resolution or instrument function of the spectrograph–detector in comparison to the spectral width of the absorption bands. In general, we can distinguish between high-resolution cases, in which the natural width of the absorption band, \( \Delta \lambda_B \), is spectrally resolved, and low-resolution cases, in which the spectral width of the bands is not resolved by the measurements. In (6.16), this translates into the condition that \( 2 \Delta \lambda << \Delta \lambda_B \) for spectrally resolved bands and \( 2 \Delta \lambda \geq \Delta \lambda_B \) for unresolved bands. We would caution the reader that a band that looks resolved after a measurement may consist of a number of narrower absorption lines that are not resolved. Thus, the measurement would only show the envelope of this line system.

• The spectral structure of the light source, \( I'_0(\lambda) \). We will denote ‘smooth’ as light sources that have structures broader than the resolution of the instrument, for example incandescence or high-pressure Xe lamps have this property. ‘Structured’ light sources show spectral features that are narrower than the instrument resolution. The most important example in our case is the sun, with its narrow Fraunhofer lines. In (6.16), this leads to the condition that \( 2 \Delta \lambda \) is much smaller than the bandwidth, \( \lambda_I \), of \( I'_0(\lambda) \) for a smooth \( I'_0(\lambda) \), and larger for structured \( I'_0(\lambda) \).

Six different cases can be identified based on these three parameters (Table 6.3). We will now discuss in more detail how (6.16) has to be applied to determine the desired trace gas column densities for the different situations. The individual cases will be discussed in a general way. However, we will also give the mathematical derivation for the different implementations, wherever possible, for more details see also the ‘operator representation of DOAS’ (Wenig, 2001; Wenig et al., 2005).

Case 1: Weak Low-or High-resolution Absorbers and a Smooth Light Source

The most basic approach of DOAS applies to measurements using a smooth light source, i.e. active DOAS, where weak absorption features are measured with low or high instrumental resolution.

In this case, Lambert–Beer’s law can be linearised by taking the logarithm of the ratio of \( I^*(\lambda, L) \) and \( I'_0(\lambda, L) \), resulting in the following representation of (6.16):

\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) = \sum_j \bar{c}_j \cdot \frac{L}{\alpha_j} \cdot \ln \left[ \int_{-\Delta \lambda}^{\Delta \lambda} \exp \left( -\sigma_j' (\lambda - \lambda') \cdot \alpha_j \right) \cdot H(\lambda') \, d\lambda' \right].
\] (6.17)

Equation (6.17) states that \( \ln (I^*(\lambda, L)/I'_0(\lambda, L)) \) can be described by a sum of spectra of pure trace gas absorptions that are scaled by the average number concentration \( \bar{c}_j \) and the path length \( L \) (we will discuss the factor \( \alpha_j \) later).
However, as is made clear in the rest of this section, this mathematical approach is far more common than one may expect, and some of the other cases discussed later will also rely on it.

Since the linearisation of Lambert–Beer’s law is the most common form of DOAS implementation and is the basis of Chap. 8, we will introduce an equation that is loosely based on the discreet form of (6.17). The logarithm of the discreet form of \( I^*(\lambda, L) : J(i) = \ln(I'(i)) \) is described by:

\[
J(i) = J_0(i) + \sum_{j=1}^{m} a'_j \cdot S'_j(i) .
\]  

(6.18)

\( J_0(i) \) is the logarithm of the discretisation of \( I'_0(i) \), which was defined in (6.11). The differential absorption structures of the trace gases are described by individual ‘reference spectra’ \( S'_j(i) \), which were also discretised (6.11). \( a'_j \) are the scaling factors for the individual discretised reference spectra. We will see that, for different DOAS cases, the reference spectra calculation is different, while (6.18) can still be used. For smooth light sources, the spectra \( S'_j(i) \) are determined through the following three equations:

\[
S^*_j(\lambda) = \int_{-\Delta \lambda}^{\Delta \lambda} \exp \left( -\sigma'_j (\lambda - \lambda') \cdot \alpha_j \right) \cdot H(\lambda') d\lambda'.
\]

\[
S'_j(i) = \int_{\lambda(i)}^{\lambda(i+1)} S^*_j(\lambda) d\lambda'.
\]

\[
S'_j(i) = \frac{1}{\alpha_j} \ln(S^*_j(i))
\]

(6.19)

We have introduced a scaling parameter \( \alpha_j \) that will play a role for case 3 (see below). This parameter can be interpreted as the product of concentration and path length used in the measurement or simulation of \( S^*_j \). For case 1, where the differential optical densities are small, \( \alpha_j \) can be set to unity. In the case of small differential optical density \( (\alpha_j = 1) \), the first equation in (6.19) is taken from the sum of (6.17), and describes the convolution of the exponential of the negative differential absorption cross-section \( \sigma'_j(\lambda) \). The second equation is the discretisation according to (6.11). The last equation is then the logarithm of the discretised spectrum.

However, if the differential optical densities are not small, (6.18) and (6.19) can only be used if values for \( \alpha_j \neq 1 \) are chosen. The scaling factors

\[
a'_j = \frac{\bar{c}_j \cdot L}{\alpha_j},
\]

(6.20)
in (6.18) are the product of the average number densities and the path length, divided by the reference spectrum scaling factor \( \alpha_j \).
The solution of (6.18) is now a mathematical problem that requires the calculation of the $S'_i(i)$ through (6.19). For this calculation, the knowledge of instrument function $H(\lambda)$ and the highly resolved absorption cross-section $\sigma'_j(\lambda)$ is required. Both the mathematical approach to solve (6.18) with the goal of retrieving the $\alpha'_j$ factors and the details of the calculation in (6.18) are topics of discussion in Chap. 8. Figure 6.9 shows an example of (6.18) for a real atmospheric measurement. The top spectrum represents $J'_i(i)$ while the other spectra represent the products of the absorption cross-sections and the scaling factors: $a'_j \cdot S'_j(i)$ (in this case $\alpha_j = 1$).

After describing this ‘classical’ DOAS approach, we now discuss how this implementation can be derived mathematically from (6.16). We will use two related approximations that are directly valid for small differential optical density of the absorption structures:

$$\ln(x) \approx x - 1 \quad \text{for} \quad 1 - \varepsilon < x < 1 + \varepsilon,$$

and

$$\exp(x) \approx 1 + x \quad \text{for} \quad -\varepsilon < x < \varepsilon.$$

These approximations are good for $\varepsilon$ close to zero. At $\varepsilon = 0.1$, the error imposed by (6.21) and (6.22) is $\sim 5\%$.

We will also assume that the spectra are measured using a smooth light source. This condition leads to the approximation that $I'_0(\lambda - \lambda', L) \approx I'_0(\lambda, L)$ in the interval from $\lambda - \Delta\lambda$ to $\lambda + \Delta\lambda$. Finally, we will use the condition that the integral of the instrument function is scaled to unity. This condition can always be met by dividing the integral over $H(\lambda)$ by a constant:

$$\int_{-\Delta\lambda}^{\Delta\lambda} H(\lambda') d\lambda' = 1.$$

Mathematically, this is only true if $\Delta\lambda = \infty$. In all practical cases, however, the integral can be limited to an interval around $H$.

We will begin the derivation of (6.18) by taking the logarithm of the ratio of $I^*(\lambda, L)$ and $I'_0(\lambda, L)$ in (6.16):

$$\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) = \ln \left[ \int_{-\Delta\lambda}^{\Delta\lambda} \exp \left( - \sum_j (\sigma'_j(\lambda - \lambda') \cdot \bar{c}_j) \cdot L \right) \cdot H(\lambda') d\lambda' \right].$$

In the case of weak absorbers, the integral in (6.24) is close to unity and we can employ (6.21) to approximate the logarithm:

$$\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) \approx \int_{-\Delta\lambda}^{\Delta\lambda} \exp \left( - \sum_j (\sigma'_j(\lambda - \lambda') \cdot \bar{c}_j) \cdot L \right) \cdot H(\lambda') d\lambda' - 1.$$
Fig. 6.9. Sample of an atmospheric spectrum *(uppermost trace)* recorded in Heidelberg on August 27, 1994, with overlapping absorptions due to O$_3$, NO$_2$, SO$_2$, and HCHO (traces 2–5 from top, note different scales). The broad spectral structures were described by a fifth order polynomial. The remaining ‘residual spectrum’ after removal of the absorption structures is shown as the *bottom trace* (from Stutz and Platt, 1996)
This approximation applies to the convoluted absorption structures, which are smaller than the original absorptions before convolution. Using (6.23), this can now be transformed into:

\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \int_{-\Delta \lambda}^{\Delta \lambda} \exp \left( - \sum_j \left( \sigma_j^\prime (\lambda - \lambda') \cdot \bar{c}_j \right) \cdot L \right) \cdot H(\lambda') d\lambda' - \int_{-\Delta \lambda}^{\Delta \lambda} H(\lambda') d\lambda'.
\]

\[
= \int_{-\Delta \lambda}^{\Delta \lambda} \left[ \exp \left( - \sum_j \left( \sigma_j^\prime (\lambda - \lambda') \cdot \bar{c}_j \right) \cdot L \right) - 1 \right] \cdot H(\lambda') d\lambda'.
\]

(6.26)

Further applying the approximation for the exponential function (6.22):

\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \int_{-\Delta \lambda}^{\Delta \lambda} \left[ - \sum_j \left( \sigma_j^\prime (\lambda - \lambda') \cdot \bar{c}_j \right) \cdot L \right] \cdot H(\lambda') d\lambda'.
\]

(6.27)

This approximation applies to the absorption structures before convolution, and is thus more restrictive than the approximation used in (6.25). We can now exchange the sum and the integral. In addition, we introduced the factor \( \alpha_j \) from (6.20):

\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \int_{-\Delta \lambda}^{\Delta \lambda} \left[ \sigma_j^\prime (\lambda - \lambda') \cdot \alpha_j \right] \cdot H(\lambda') d\lambda'.
\]

(6.28)

In the next step of derivation, the approximation for the exponential function (6.22) is applied again (this time, however, in reverse direction):

\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \int_{-\Delta \lambda}^{\Delta \lambda} \left[ \exp \left( - \sigma_j^\prime (\lambda - \lambda') \cdot \alpha_j \right) - 1 \right] \cdot H(\lambda') d\lambda'.
\]

(6.29)

It is important to note here that the errors due to approximations in (6.27) and (6.29) tend to cancel each other. This counterbalance is best if \( \alpha_j \approx \bar{c}_j \cdot L \), and actually lifts the restriction to weak absorptions before convolution for the steps from (6.25) to (6.29). The derivation is finalised again using (6.23) and (6.21). The approximation of the logarithm (6.21) is again applied to the convoluted spectral structures.
\[
\ln \left( \frac{I^*(\lambda, L)}{I_0'\lambda (\lambda, L)} \right) \approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \int_{-\Delta\lambda}^{\Delta\lambda} \left[ \exp \left( -\sigma'_j (\lambda - \lambda') \cdot \alpha_j \right) \right] \cdot H(\lambda') d\lambda' - \int_{-\Delta\lambda}^{\Delta\lambda} H(\lambda') d\lambda'
\]

\[
\approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \ln \left[ \int_{-\Delta\lambda}^{\Delta\lambda} \exp \left( -\sigma'_j (\lambda - \lambda') \cdot \alpha_j \right) \cdot H(\lambda') d\lambda' \right].
\]

Equation (6.30) is equivalent to (6.17) and states that in the case of small optical densities after convolution, the DOAS approach can be solved by linearising Lambert–Beer’s law. The reference spectra used in this fit have to be calculated as the logarithm of the convolution of the exponential function of high-resolution absorption cross-sections (6.19).

It is important to comment again on the various approximations in the derivation of (6.30). Both approximations – (6.21) and (6.22) – were applied twice, in forward and backward directions. While the approximations were applied to different arguments, there is a high degree of cancellation by the twofold use, which makes the approximation better than one would expect from the single application. In particular, in the case that \( \alpha_j = \bar{c}_j \cdot L \), the twofold approximations are quite good. A detailed calculation, which uses a Tailor expansion to the second order, shows that the difference between (6.27) and (6.29) is approximately 
\[
\frac{1}{2} \sum_{j \neq k} \sigma_j \sigma_k \bar{c}_j \bar{c}_k L^2,
\]
if \( \alpha_j = \bar{c}_j \cdot L \). The derivation shown above is, therefore, more widely applicable than just for case 1, and we will come back to it in case 3. For small absorptions before the convolution, we can set \( \alpha_j = 1 \), since all the approximations apply in this case without restrictions. The preceding derivation is the basis of most DOAS applications today. Most measurements of O₃, NO₂, HCHO, NO₃, HONO, halogen oxides, etc. in the troposphere have used this approach (see Fig. 6.9).

**Case 2: Strong Absorber at High Resolution and a Smooth Light Source**

The case of strong absorbers measured with a spectral resolution that is better than the width of the absorption bands is encountered in a number of DOAS applications. The approach described in Case 1 (6.17–6.19) can also be used in this case. However, the mathematical proof is not as obvious, since the approximations of the logarithm and exponential function (6.21 and 6.22) do not apply in the case of strong absorbers. We will, therefore, use an approximation that is based on the fact that the spectral interval covering the instrument function \( H(\lambda) \), \( 2\Delta\lambda \), is smaller than the width of the absorption band. Within this interval, we can approximate the exponential function in (6.16) by a linear function, using the derivative of the exponential function as the slope. In addition, this approximation can also be made by the exponential function of the pure scaled absorption cross-section (6.30). Two new functions, \( g(\lambda) \) and \( h(\lambda) \), for these exponential functions are introduced:
\[
\exp \left( - \sum_j \left( \sigma'_j (\lambda - \lambda') \cdot c_j \cdot L \right) \right) = g(\lambda - \lambda') \approx g(\lambda) + \frac{dg}{d\lambda} \bigg|_{\lambda'} \cdot \lambda'. \tag{6.31}
\]

\[
\exp \left( -\sigma'_j (\lambda - \lambda') \cdot \alpha_j \right) = h_j(\lambda - \lambda') \approx h_j(\lambda) + \frac{dh_j}{d\lambda} \bigg|_{\lambda'} \cdot \lambda'. \tag{6.32}
\]

We again consider \( I'_0(\lambda, L) \) as being constant within \( \lambda \pm \Delta \lambda \). This is certainly true because the resolution of the instrument is very high and, as compared to the interval \( 2\Delta \lambda \), the change of \( I'_0(\lambda, L) \) is small. Applying the approximation in (6.31), the equivalent of (6.24) now becomes:

\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) = \ln \left( \int_{-\Delta \lambda}^{\Delta \lambda} g(\lambda - \lambda') \cdot H(\lambda') d\lambda' \right) \approx \ln \left( \int_{-\Delta \lambda}^{\Delta \lambda} \left( g(\lambda) + \frac{dg}{d\lambda} \right) \cdot \lambda' \cdot H(\lambda') d\lambda' \right). \tag{6.33}
\]

Equation (6.33) is now reorganised by using the fact that some of the terms under the integral are independent of \( \lambda' \):

\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) \approx \ln \left( g(\lambda) \cdot \int_{-\Delta \lambda}^{\Delta \lambda} H(\lambda') d\lambda' + \frac{dg}{d\lambda} \bigg|_{\lambda} \cdot \int_{-\Delta \lambda}^{\Delta \lambda} \lambda' \cdot H(\lambda') d\lambda' \right). \tag{6.34}
\]

The derivative of \( g(\lambda) \) can now be calculated as:

\[
\frac{dg}{d\lambda} \bigg|_{\lambda} = -g(\lambda) \cdot \frac{d}{d\lambda} \left( \sum_j \sigma'(\lambda) \cdot c_j \cdot L \right) = -g(\lambda) \cdot \sum_j \frac{d\sigma'(\lambda)}{d\lambda} \cdot c_j \cdot L. \tag{6.35}
\]

Equation (6.34) then becomes:

\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) \approx \ln \left( g(\lambda) \cdot \int_{-\Delta \lambda}^{\Delta \lambda} H(\lambda') d\lambda' - g(\lambda) \cdot \sum_j \frac{d\sigma'(\lambda)}{d\lambda} \cdot c_j \cdot L \cdot \int_{-\Delta \lambda}^{\Delta \lambda} \lambda' \cdot H(\lambda') d\lambda' \right),
\]

and after rearranging:
\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) \approx \ln \left( g(\lambda) \cdot \int_{-\Delta\lambda}^{\Delta\lambda} H(\lambda') d\lambda' \right)
+ \ln \left( 1 - \sum_j \left( \frac{d\sigma'_j(\lambda)}{d\lambda} \right)_{\lambda} \cdot \bar{c}_j \cdot L \cdot \int_{-\Delta\lambda}^{\Delta\lambda} \lambda' \cdot H(\lambda') d\lambda' \right) .
\]

(6.36)

The approximation for the logarithm from (6.21) and the fact that \( H(\lambda) \) is normalised to unity can now be used. The application of the approximation is justified because the sum over \( j \) in the above equation is small, and thus the argument of the second \( \ln \) in the equation is near unity.

\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) \approx \ln (g(\lambda)) - \sum_j \left( \frac{d\sigma'_j(\lambda)}{d\lambda} \right)_{\lambda} \cdot \bar{c}_j \cdot L \cdot \int_{-\Delta\lambda}^{\Delta\lambda} \lambda' \cdot H(\lambda') d\lambda' .
\]

(6.37)

After the following transformations,

\[
\ln (g(\lambda)) = - \sum_j (\sigma'_j(\lambda) \cdot \bar{c}_j \cdot L) = - \sum_j \left( \alpha_j \cdot \sigma'_j(\lambda) \cdot \frac{\bar{c}_j \cdot L}{\alpha_j} \right)
= \sum_j \left( \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \ln \left( \exp \left( -\alpha_j \cdot \sigma'_j(\lambda) \right) \right) \right)
= \sum_j \left( \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \ln \left( h_j(\lambda) \right) \right),
\]

(6.38)

one derives:

\[
\ln \left( \frac{I^*(\lambda, L)}{I'_0(\lambda, L)} \right) \approx \sum_j \left( \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \ln \left( h_j(\lambda) \right) \right)
- \sum_j \left( \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \frac{d\sigma_j(\lambda)}{d\lambda} \right)_{\lambda} \cdot \alpha_j \cdot \int_{-\Delta\lambda}^{\Delta\lambda} \lambda' \cdot H(\lambda') d\lambda'
= \sum_j \left( \frac{\bar{c}_j \cdot L}{\alpha_j} \cdot \ln \left( h_j(\lambda) \right) - \frac{d\sigma_j(\lambda)}{d\lambda} \right)_{\lambda} \cdot \alpha_j \cdot \int_{-\Delta\lambda}^{\Delta\lambda} \lambda' \cdot H(\lambda') d\lambda' .
\]

(6.39)

This equation can be further transformed by again employing the approximation of the logarithm (6.21) in the reverse direction. This step is followed by a number of transformations based on the properties of the logarithm in (6.23):
\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \ln \left( h_j(\lambda) \right) \approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \ln \left( h_j(\lambda) \right) + \ln \left( 1 + \int_{-\Delta\lambda}^{\Delta\lambda} \frac{d\sigma_j(\lambda)}{d\lambda} \left| \left. \frac{\alpha_j}{\lambda} \cdot \alpha_j \cdot \lambda' \cdot H(\lambda') \right\rangle \right. \right)
\]

Finally, the derivative of \( h_j(\lambda) \):
\[
\frac{dh_j(\lambda)}{d\lambda} \approx \exp \left( -\sigma_j'(\lambda) \cdot \alpha_j \right) \cdot \frac{d\sigma_j(\lambda)}{d\lambda} \cdot \alpha_j = -h_j(\lambda) \cdot \frac{d\sigma_j(\lambda)}{d\lambda} \cdot \alpha_j
\]

and the definition of \( h_j(\lambda) \) (6.32) are introduced:
\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \sum_j \frac{\bar{c}_j \cdot L}{\alpha_j} \ln \left( \frac{\Delta\lambda}{\Delta\lambda} \left( h_j(\lambda) - h_j(\lambda) \cdot \frac{d\sigma_j(\lambda)}{d\lambda} \left| \left. \frac{\alpha_j}{\lambda} \cdot \alpha_j \cdot \lambda' \cdot H(\lambda') \right\rangle \right. \right) \right.
\]

This equation is now equivalent to (6.30), showing that the approach of Case 1 is applicable. It should be emphasised that, in this derivation, the approximations were based on the fact that the convolution would change the absorption structure only slightly. In contrast to Case 1, we did not make any assumption about the strength of the absorptions.

**Case 3: Strong Absorbers at Low Resolution and a Smooth Light Source**

The case that the optical density of an absorber before the convolution in (6.16) exceeds unity is quite common in low-resolution DOAS applications.
Several molecules (e.g. O$_2$, NO, H$_2$O, halogen monoxides, some aromatics, and glyoxal) have highly resolved rotational structures in the near UV and visible spectral ranges. It is thus possible that the optical density at the centre of these lines becomes very high. If such an absorption line is measured by a low-resolution instrument, the optical density of the absorption band after convolution is not proportional to the one before convolution.

Figure 6.10 illustrates how the optical density, in this case simply calculated as the logarithm of the ratio of the intensities at the band minimum and its border, for a single narrow absorption line changes after it is convoluted with a instrument function (here assumed to be of Gaussian shape) that is broader than the initial band (see also the bands in the inserts in Figure 6.10). At low values, the optical densities of the convoluted line depend linearly on the optical density of the narrow line. This is the situation we described in Case 1. At increasing values, the two optical densities start to deviate, with the low-resolution OD becoming increasingly smaller than the high-resolution OD. The two optical densities are thus no longer linearly dependent on one another.

The straightforward solution to this problem is to model the entire function (6.16). However, the introduction of the parameter $\alpha_j$ in (6.19) expands the applicability of Case 1 to high optical densities. This is most easily seen for one absorber $j = 1$, when $\alpha_j = \tilde{c}_j \cdot L$. In this case, (6.24) and (6.30) become identical. In cases where the value of $\alpha_j$ is close to $\tilde{c}_j \cdot L$, (6.18) and (6.19)
can still be used. However, the initial value of $\alpha_j \approx \bar{c}_j \cdot L$ has to be guessed. Alternatively, a lookup table for reference spectra for different $\alpha_j$ can be used.

While it is clear that, for one strong absorber the linearisation of Lambert–Beer’s law can be applied if $\alpha_j$ is guessed correctly, one can show that, in the case of one strong absorber and various weak absorbers, (6.18) and (6.19) still apply. However, $\alpha_j$ for the strong absorber must be guessed correctly. When strong differential absorptions of several absorbers overlay each other, this approach leads to systematic errors in the analysis. This situation is, however, rather uncommon in DOAS applications.

Another effect helps in the application of (6.18) and (6.19) for strong absorbers. For many trace gases, the width of the absorption bands is larger than the width of the instrument function. In this case, the convolution does not change the optical density dramatically, as illustrated in Figure 6.10. For larger optical densities, one operates somewhere between Case 1 and Case 2. By using a good initial guess for $\alpha_j$, it is then possible to use (6.18) and (6.19), even for fairly strong absorbers. This is, for example, the case for NO$_2$ and O$_3$ absorptions, which are dominated by absorption bands that are resolved by typical DOAS instruments.

Because the numerical solution of (6.16) is slow, most DOAS applications rely on (6.18) and (6.19) in their analysis routines. Strong absorbers are taken into account by lookup tables of simulated reference spectra or some other numerical schemes to derive appropriate correction factors (Volkamer et al., 1998; Maurellis et al., 2000; Buchwitz et al., 2000; Frankenberg et al., 2004).

Case 4: Weak Absorbers, High Resolution, and a Structured Light Source

Our fourth case is that of a highly structured light source emission spectrum combined with weak trace gas absorptions and a high spectral resolution. The case of a structured light source is characteristic for the measurement of solar light, either direct or scattered, which shows narrow spectral structures due to Fraunhofer absorption bands in the photosphere of the sun. One can distinguish two situations here: If the spectral width of the instrument function is smaller than the width of the structures of $I_0(\lambda)$, we can apply Case 1. In the case that the width of the instrument function is between the width of $I_0(\lambda)$ and the bandwidth of the absorbers, Case 5 can be applied.

Case 5: Weak Absorbers, Low Resolution, and a Structured Light Source

In the case of weak absorbers, a low spectral resolution, and a structured light source, the solution shown in case 1 has to be adopted. In contrast to Case 1, however, where the convolution of the exponential of the scaled absorption cross-section can be used to describe the absorption spectrum, (6.19) does not
directly apply. The following equation must be used to calculate the absorption cross-section instead of (6.19):

\[ S_j^*(\lambda) \big|_{\text{case 5}} = \frac{\int_{-\Delta\lambda}^{\Delta\lambda} I'_0(\lambda - \lambda', L) \times \exp \left( \sum_j \sigma'_j(\lambda - \lambda') \times \alpha_j \right) \times H(\lambda') d\lambda'}{\int_{-\Delta\lambda}^{\Delta\lambda} I'_0(\lambda - \lambda', L) \times H(\lambda') d\lambda'} \]  

(6.42)

In principle, the calculation of (6.42) is very similar to that of (6.19). The only difference is that the convolution now includes \( I'_0(\lambda, L) \), and that the result, therefore, has to be normalised to the convolved \( I'_0(\lambda, L) \). It is easy to see that, in the case of a smooth light source where \( I'_0(\lambda - \lambda', L) \approx I'_0(\lambda, L) \), (6.42) is indeed equivalent to (6.19). Because \( I'_0(\lambda, L) \) is used in (6.42), the change in the absorption cross-section is often also referred to as the ‘\( I'_0 \) effect’ (Platt et al., 1997; Alliwell et al., 2002; Wagner et al., 2002c).

Before discussing the derivation of (6.42), we will introduce the convolution of \( I'_0(\lambda, L) \) with the instrument function, which helps to simplify the equations below:

\[ I^{*}_{0}(\lambda, L) = I'_0(\lambda, L) \ast H = \int I'_0(\lambda - \lambda', L) \cdot H(\lambda') d\lambda' \]  

(6.43)

Mathematically, (6.42) can be determined from (6.16). The derivation follows the approach taken in Case 1 [using the approximations from (6.21) and (6.22)], except that the assumption of a smooth light source is dropped, i.e. \( I'_0(\lambda - \lambda', L) \) cannot be taken out of the integral. We begin with transforming (6.16) in the same way as in Case 1:

\[ \ln \left( \frac{I^*(\lambda, L)}{I'^*_{0}(\lambda, L)} \right) = \ln \left( \frac{\int_{-\Delta\lambda}^{\Delta\lambda} I'_0(\lambda - \lambda', L) \times \exp \left( - \sum_j \left( \sigma'_j(\lambda - \lambda') \cdot c_j \right) \times L \right) \cdot H(\lambda') d\lambda'}{I'_0(\lambda, L)} \right) \]  

(6.44)

As in the above examples, (6.21) can now be applied to approximate the logarithm. The resulting equation can then be further reorganised to extract a factor \( [I'^*_{0}(\lambda, L)]^{-1} \):

\[ \ln \left( \frac{I^*(\lambda, L)}{I'^*_{0}(\lambda, L)} \right) \approx \left[ \int_{-\Delta\lambda}^{\Delta\lambda} I'_0(\lambda - \lambda', L) \cdot \exp \left( - \sum_j \left( \sigma'_j(\lambda - \lambda') \cdot c_j \right) \cdot L \right) \cdot H(\lambda') d\lambda' \cdot [I'^*_{0}(\lambda, L)]^{-1} - 1 \right] \]
\[ [I'_0^*(\lambda, L)]^{-1} \cdot \left[ \int_{-\Delta \lambda}^{\Delta \lambda} I'_0(\lambda - \lambda', L) \cdot \exp \left( - \sum_j \left( \sigma'_j(\lambda - \lambda') \cdot c_j \right) \cdot L \right) \cdot H(\lambda') d\lambda' \right] \]

\[ = [I'_0^*(\lambda, L)]^{-1} \cdot \left[ \int_{-\Delta \lambda}^{\Delta \lambda} I'_0(\lambda - \lambda', L) \cdot \left[ \exp \left( - \sum_j \left( \sigma'_j(\lambda - \lambda') \cdot c_j \right) \cdot L \right) - 1 \right] \cdot H(\lambda') d\lambda' \right] \]

As in Case 1, the exponential function is then approximated using (6.22):

\[ \ln \left( \frac{I^*(\lambda, L)}{I'_0^*(\lambda, L)} \right) \approx [I'_0^*(\lambda, L)]^{-1} \cdot \left[ \int_{-\Delta \lambda}^{\Delta \lambda} I'_0(\lambda - \lambda', L) \cdot \left( - \sum_j \left( \sigma'_j(\lambda - \lambda') \cdot c_j \right) \cdot L \right) \cdot H(\lambda') d\lambda' \right]. \]  

This equation is further rearranged, and (6.22) is applied again – this time, however, in reverse order. The application of (6.22) in forward and backward directions lifts the restriction of small absorptions to a certain extent, as already discussed in Case 1.

\[ \ln \left( \frac{I^*(\lambda, L)}{I'_0^*(\lambda, L)} \right) \approx [I'_0^*(\lambda, L)]^{-1} \cdot \sum_j \frac{c_j \cdot L}{\alpha_j} \cdot \left[ \int_{-\Delta \lambda}^{\Delta \lambda} I'_0(\lambda - \lambda', L) \cdot \left( \sigma'_j(\lambda - \lambda') \cdot \alpha_j \right) \cdot H(\lambda') d\lambda' \right] \]

\[ \approx [I'_0^*(\lambda, L)]^{-1} \cdot \sum_j c_j \cdot L \cdot \left[ \int_{-\Delta \lambda}^{\Delta \lambda} I'_0(\lambda - \lambda', L) \cdot \left( \exp \left( \sigma'_j(\lambda - \lambda') \cdot \alpha_j \right) - 1 \right) \cdot H(\lambda') d\lambda' \right]. \]  

In the next step, this equation is again rearranged (remembering the normalisation of \( H(\lambda) \) to unity):
\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \frac{1}{\sum_j c_j \cdot L} \cdot \left[ \int_{-\Delta\lambda}^{\Delta\lambda} I_0(\lambda - \lambda', L) \cdot \left[ \exp \left( \sigma'_j(\lambda - \lambda') \right) \cdot \alpha_j \right] \cdot H(\lambda') d\lambda' - 1 \right]
\]

Finally, (6.21) is applied to transform the last term in the sum to a logarithm:

\[
\ln \left( \frac{I^*(\lambda, L)}{I_0^*(\lambda, L)} \right) \approx \sum_j c_j \cdot L \cdot \ln \left[ \frac{\int_{-\Delta\lambda}^{\Delta\lambda} I_0(\lambda - \lambda', L) \cdot \left[ \exp \left( \sigma'_j(\lambda - \lambda') \right) \right] \cdot H(\lambda') d\lambda'}{\int_{-\Delta\lambda}^{\Delta\lambda} I_0(\lambda - \lambda', L) \cdot H(\lambda') d\lambda'} \right].
\]

It is clear from (6.49) that \( I^*(\lambda, L) \) can be analysed by a classical DOAS approach (Case 1) if the differential absorption cross-sections are calculated by (6.42). The discussion about the restrictions imposed by the multiple applications of the approximations of the logarithm and the exponential functions are applied here, in the same manner as in Case 1 (see above).

Case 6: Strong Absorbers, Low Resolution, and a Structured Light Source

This case applies to similar trace gases as those described in Case 3, however measured with passive DOAS instruments. As in Case 3, mathematically correct solution can be achieved in many cases by using (6.18) and (6.42), if \( \alpha_j \) are chosen close to \( \bar{c}_j \cdot L \). A lookup table approach, as well as a number of other numerical approximations, can also be used (e.g. Maurellis et al., 2000).

The discussion above illustrates that, in most cases, the DOAS problem can be solved by a linearisation of Lambert–Beer’s law, using (6.19) in the case of active DOAS applications and (6.42) in the case of passive DOAS applications. The non-linearity that is imposed by the convolution of strong absorbers can, in many cases, be overcame if the factor \( \alpha_j \) is close to the product \( \bar{c}_j \cdot L \). The approach shown in (6.18), (6.19), and (6.42) is thus the most important implementation of DOAS. Its numerical solution will be discussed in detail in Chap. 8.