Summary

The amount of solar radiation reaching the surface of the Earth is determined by scattering and absorption of light by particles, present in the Earth’s atmosphere. Both processes are frequency-dependent and are responsible for the attenuation - optical extinction – of the light crossing our atmosphere.

We are daily confronted with the influence of both absorption and scattering phenomena. The atmosphere is opaque for quite some wavelengths, protecting life for strong UV radiation and prohibiting ground-based astronomical observations at submillimeter wavelengths. A blue sky and a red sunset, both are a direct consequence of the fact that light with shorter wavelengths (blue) is scattered more than light with longer wavelengths (red). These observations have been known for a long time, but it took up to 1899 before Lord Rayleigh was able to quantitatively describe them as electromagnetic waves being scattered by small particles in the air. The simplicity of Rayleigh scattering theory and the prediction of the strong wavelength dependence ($\sim \lambda^{-4}$) of the molecular scattering immediately gained interest of the scientific community.

Light scattering by small molecular species has been extensively studied theoretically, but only in the last years laboratory techniques have become sensitive enough to directly determine the optical extinction due to Rayleigh scattering, addressing the scattering cross-section of single species (previously the Rayleigh scattering cross-section was indirectly assessed via the index of refraction). The majority of these studies have been focusing on frequency domains that are accessible by laser based experiments, particularly the visible part of the electromagnetic spectrum, but progress in sensitive laser detection schemes at shorter wavelengths, the ultraviolet and vacuum UV, allow detailed scattering studies at wavelengths as low as 200 nm. This is the main topic of this thesis.

Harmonic frequency generation of tunable laser radiation is used to cover the UV/VIS with high spectral purity, with a focus on the deep-UV between 198 and 270 nm. A sensitive detection scheme, based upon cavity ringdown spectroscopy applied to pressure-ramp measurements, is used to perform systematic laboratory studies of the optical extinction of a series of atmospheric
molecules (N\textsubscript{2}, O\textsubscript{2}, CO, CO\textsubscript{2}, CH\textsubscript{4}, NO and SF\textsubscript{6}). The findings directly relate to the extinction of the deep-UV electromagnetic radiation in atmospheric gases, either via Rayleigh scattering or absorption phenomena. The results are of interest for both molecular physics and atmospheric sciences. The quantitative results, reported in this thesis are needed as input in radiative transfer models, for the evaluation of the altitude-dependent concentrations of atmospheric molecular constituents via column density measurements, and the study of photochemical and ozone depletion processes.

The thesis is organized in the following way.

Chapter 1 is a general introduction and puts the work described in the following chapters in an atmospheric context, also focusing on the fundamental molecular physics behind the processes. The Earth’s atmosphere, altitude-dependent variation of physical properties and the amount of short wavelength solar radiation within the atmosphere are described, as well as the light scattering (by molecules and somewhat larger particles), linear and collisionally induced absorption phenomena.

Chapter 2 deals with the experimental approach used for the deep-UV optical extinction measurements and details of the tunable pulsed cavity ring-down setup and pressure-ramp method are given. Room-temperature optical extinction measurements in molecular CO between 198 and 220 nm are presented to illustrate the performance of the setup.

Chapter 3 is devoted to room-temperature extinction measurements of CO\textsubscript{2} between 198 and 270 nm. It is shown that the Rayleigh scattering is a dominant phenomenon that determines the optical extinction between 202 and 270 nm, whereas a clear absorption onset is found at shorter wavelengths.

Chapter 4 describes measurements to determine the absolute values of the Rayleigh scattering cross-sections of N\textsubscript{2}, CH\textsubscript{4} and SF\textsubscript{6}. Molecular scattering is found to govern the attenuation of radiation at short wavelengths. A significant part of the work described here, is devoted to a quantitative comparison of the present observations with numerical predictions that are based on dispersion of the optical properties of the gases. From the deep-UV measurements presented here, values for the refractive index and molecular polarizability are derived and compared to literature values.
Chapter 5 is a pure spectroscopic study and describes a cavity ring-down study of the heaviest NO isotopologue - $^{15}$N$^{18}$O - in its $\gamma$-system between 205 and 216 nm. Laboratory room-temperature measurements of nearly 400 individual rotational transitions, corresponding to the electronic ($A^2\Sigma^+ - X^2\Pi$) band system are fitted using a rovibronic analysis yielding for the first time accurate molecular constants for the $A^2\Sigma^+_{(v=1)}$ and $A^2\Sigma^+_{(v=2)}$ vibrational levels.

The final chapter, Chapter 6, describes cavity ring-down measurements of collision-induced absorption resonances in O$_2$−O$_2$ performed at 477 and 577 nm at different atmospheric temperatures. The observed absorption features are quantitatively analyzed for temperatures between 184 and 294 K and the temperature-dependent variation of the main parameters of the resonances are qualitatively determined and compared with data, as available from the literature.