**Rotational Raman scattering in the Earth's atmosphere**

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# Summary

A spectrum of sunlight that is backscattered by the Earth's atmosphere and surface contains a wealth of information on atmospheric constituents and surface properties. For instance, one can infer the atmospheric concentration of an important trace gas like ozone from an Earth radiance spectrum. Several satellite instruments have been launched to measure Earth radiance spectra: the first and second Global Ozone Monitoring Experiment (GOME and GOME-2), the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), and the Ozone Monitoring Instrument (OMI). It is common to take the ratio of the Earth radiance spectrum and a measured solar irradiance spectrum to reveal the information on atmospheric constituents and surface properties. This ratio, which is called the reflectivity spectrum, displays how the incident solar light has been altered by its interaction with the Earth's surface and its passage through the Earth's atmosphere. An advantage of this ratio is that many calibration errors that are shared by the Earth radiance and solar irradiance measurement cancel out.

Close examination of reflectivity spectra reveals fine structures that are caused by the Ring effect, which was discovered by Grainger and Ring in 1962. The Ring effect is observed where the solar spectrum shows lines of low intensity, the so-called Fraunhofer lines. The effect is caused by rotational Raman scattering by nitrogen and oxygen molecules in the Earth's atmosphere. This inelastic scattering process decreases the depth of the Fraunhofer lines in an Earth radiance spectrum compared to those in an extraterrestrial solar irradiance spectrum. As a result, the reflectivity spectrum contains filling-in structures. The Ring effect is most pronounced in the ultraviolet wavelength range, where many strong Fraunhofer lines are present and where molecular scattering is important. The Ring effect often interferes with absorption features in reflectivity spectra and is therefore considered as a nuisance. However, the Ring effect can also be utilized to extract information on cloud parameters from reflectivity spectra. This is because the amount of inelastic scattering is affected by the presence of clouds. In turn, this cloud information

can be used to improve trace gas retrievals for cloudy observations. At the start of this project several models were available that take the Ring effect into account to some degree. However, multiple inelastic Raman scattering and the polarization aspects of the multiple scattered light including inelastic Raman scattering needed to be investigated in more detail. This approximation in which polarization is neglected is referred to as the scalar approximation. Only the intensity $I$ is simulated instead of the full intensity vector $\mathbf{I} = [I, Q, U, V]^T$, where $Q$ and $U$ describe linear polarization and $V$ describes circulair polarization.

The work described in this thesis started with the development of a scalar radiative transfer model that is suited to describe multiple scattering in the Earth's atmosphere including multiple Raman scattering. This model is described in Chapter 2 and is based on the doubling-adding method. The doubling-adding equations were extended to include inelastic scattering. One of the questions that we were particularly interested in was to what extent higher orders of Raman scattering are important for modeling the Ring effect in the ultraviolet and visible wavelength range. Using a somewhat simplified model atmosphere that consisted of two layers and assuming an instrument spectral resolution similar to GOME, we found that the filling-in due to one order of Raman scattering can be as high as 21% at the Ca II K and H lines at 393 nm and 397 nm. The observed multiple Raman scattering contribution to the total filling-in is only 0.6% at these lines. Near 325 nm molecular scattering is stronger, but the Fraunhofer lines are less pronounced than the Ca II lines. Here, the contributions of single and multiple inelastic scattering to the total filling-in are typically 4% and 0.2%, respectively. From this we concluded that in the case of GOME-type measurements including one order of inelastic scattering is sufficient for most applications.

In Chapter 3 we investigated the polarization aspects of the light that emerges from a molecular scattering atmosphere. The impact of neglecting the polarization aspects was verified with a newly developed vector radiative transfer model. This model employs radiative transfer perturbation theory and treats inelastic rotational Raman scattering as a perturbation to elastic Rayleigh scattering (i.e. the approximation in which all light scattering is assumed to be elastic). The approach provides a perturbation series expansion for a simulated radiation quantity, where each term describes the effect of one additional order of Raman scattering. The model was worked out in detail to first order. Here, the adjoint formulation of radiative transfer reduces the numerical effort of computational applications significantly. Numerical simulations were presented for the ultraviolet part of the solar spectrum and the

effect of Raman scattering on the Stokes parameters $I$, $Q$ and $U$ of the reflected sunlight was studied. It was found that the influence of the Ring effect on a spectrum of the degree of linear polarization, $\sqrt{Q^2 + U^2}/I$, is largely determined by the filling-in structures in a spectrum of $I$. The filling-in structures in spectra of $Q$ and $U$ are less important. Two common approximations were tested for the simulation of the Ring effect structures in GOME-type measurements: the single scattering approximation and the scalar approximation. We found that the single scattering approach does not produce the correct amplitude of the Ring effect structures. For example, the filling-in of Ca II Fraunhofer lines is underestimated by a factor 2. This means that both for the simulation of the reflectivity continuum spectrum and for the calculation of the one order of Raman scattering correction the inclusion of multiple Rayleigh scattering is crucial. Next we investigated the approximation in which the Ring effect structures were calculated with a scalar model, but in which the reflectance continuum spectrum was simulated with a vector model. It was found that for most applications this approximation is justified since the biases that are introduced are typically one order of magnitude smaller than the instrument noise. Only in the case of the strong Ca II Fraunhofer lines the Ring structures on $I$ as well as on $Q$ and $U$ should be incorporated.

For the simulation of the Ring structures in GOME-type measurements it is of crucial importance to use an accurate solar irradiance spectrum as model input. In addition to the Ring structures the reflectivity spectra that are measured by GOME-type instruments contain high frequency spectral structures that are introduced by a Doppler shift between the Earth radiance and solar irradiance spectrum. These features are the result of interpolating the GOME solar irradiance spectrum to the Earth radiance spectrum wavelength grid in order to obtain the reflectivity spectrum. In Chapter 4 we introduce a novel approach that both provides the required input solar spectrum and prevents the introduction of interpolation errors. To achieve this, a solar spectrum is determined from the GOME measurements on a spectral grid that is finer than the GOME wavelength grid. When the GOME solar irradiance measurement is used to determine this solar spectrum on a fine spectral grid one ends up with errors of approximately 0.5% in the modeling of the Earth's radiance spectra. These errors are caused by the GOME undersampling error. We demonstrated that when in addition to the GOME solar irradiance measurement one GOME Earth radiance measurement is used, the undersampling errors can be effectively removed. With this approach the mean residuals are brought down to the instrument noise level. This demonstrates that the Ring effect is adequately modeled.

As mentioned before, the Ring effect contains information on cloud parameters that can be used to improve trace gas retrievals for cloudy observations. In the last chapter, *Chapter 5*, we investigated how the capability to retrieve cloud parameters from near ultraviolet spectra that contain pronounced Ring structures compares with other commonly used approaches that make use of absorption bands of oxygen and the collisional complex of oxygen. We were also particularly interested to find out which spectral window or which combination of spectral windows provides the best option to retrieve cloud parameters for present and future GOME-type instruments. We compared the retrieval of cloud top pressure, cloud fraction and cloud optical thickness from simulated reflectivity measurements in three wavelength ranges: 350–400 nm, which includes pronounced Ring structures, and 460–490 nm and 755–775 nm, which contain absorption features of oxygen and the collisional complex of oxygen, respectively. Retrieval simulations were performed for both a typical noise level of present-day space-borne spectrometers and additional random-like measurement biases. Both spectral windows 350-400 nm and 755–775 nm separately provide more information on clouds than the 460–490 nm window. The best results were obtained for the combination of the 350–400 nm and 755–775 nm windows. In this case all three cloud parameters can be retrieved independently and a high robustness was obtained to random-like measurement biases. It was found, however, that the Ring effect structures do not add significant cloud information in this combination of spectral windows. The additional information on cloud top pressure and cloud fraction is instead obtained from the $O_2$ A band, and in fact, enables a more robust and more accurate cloud retrieval. For instruments that do not measure the oxygen A band, such as OMI, both the Ring effect and the spectral continuum in the near ultraviolet wavelength range should be included in the cloud parameter retrieval scheme.

The most important conclusions of this thesis are:

1. We have developed two novel models to include rotational Raman scattering in the Earth's atmosphere. With these models we were able to assess the significance of polarization and multiple Raman scattering for the simulation of the Ring effect that is observed in GOME-type Earth reflectivity measurements. It was found that the best strategy to simulate the Ring effect in these satellite-based measurements is to solve the vector radiative transfer problem for an elastic Rayleigh scattering atmosphere and use perturbation theory to correct this base solution for one order of Raman scattering.

2. The high degree of accuracy that is reached in the simulation of the Ring effect in GOME-type reflectivity measurements demonstrates that we can accurately model atmospheric rotational Raman scattering in backscattered sunlight. For this, our radiative transfer model and the derived input solar spectrum are sufficient, interpolation errors and undersampling errors can be avoided, and the mean residuals are reduced to the instrument noise level.

3. Accurate cloud parameters can be retrieved from a combination of $O_2$ A absorption band measurements and measurements of the near ultraviolet reflectivity continuum (350–400 nm). The Ring effect does not add significant information to the cloud parameter retrieval for this combination. When $O_2$ A absorption band measurements are not available the Ring structures need to be included to accurately retrieve cloud parameters.