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Discrete-ordinate radiative transfer in a stratified medium with first-order rotational Raman scattering

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Abstract

Rotational Raman scattering (RRS) by air molecules in the Earth's atmosphere is predominantly responsible for the Ring effect: Fraunhofer and absorption-feature filling-in observed in UV/visible backscatter spectra. Accurate determination of RRS effects requires detailed radiative transfer (RT) treatment. In this paper, we demonstrate that the discrete-ordinate RT equations may be solved analytically in a multi-layer multiple scattering atmosphere in the presence of RRS treated as a first-order perturbation. Based on this solution, we develop a generic pseudo-spherical RT model LIDORT-RRS for the determination of backscatter radiances with RRS included; the model will generate output at arbitrary viewing geometry and optical thickness. Model comparisons with measured RRS filling-in effects from OMI observations show very good agreement. We examine telluric RRS filling-in effects for satellite-view backscatter radiances in a spectral range covering the ozone Huggins absorption bands. The model is also used to investigate calcium H and K Fraunhofer filling-in through cloud layers in the atmosphere.

Keywords: Inelastic radiative transfer; Rotational Raman scattering; Discrete ordinates; Pseudo-spherical

1. Introduction

The filling-in of solar Fraunhofer lines in sky spectra was first observed over 40 years ago [1]. Inelastic rotational Raman scattering (RRS) by air molecules is predominantly responsible for this effect [2,3]. The telluric filling-in of trace gas absorption features in UV and visible backscatter spectra may also be accounted for by RRS; see for example [4,5]. Fraunhofer and telluric filling-in is known collectively as the Ring effect. In ground-based and remote sensing UV/visible reflectance spectra, the Ring effect shows up as small-amplitude distortions, which follow Fraunhofer lines and absorption features. These interference structures are important sources of error in spectral fitting of trace gas column and profile amounts.

The Ring effect is generally small (RRS accounts for ~4% of all scattering events) and is often treated as a "pseudo-absorber" in inverse algorithms for the remote sensing of atmospheric trace species; amplitudes for

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Ring reference spectra are included as elements in the state vector of parameters to be retrieved. For moderate-resolution spectrometers on the ground, a single observational Ring reference spectrum may be obtained using ratios of orthogonally polarized zenith-sky measurements [6]. However, Ring reference spectra may also be obtained by a simple theoretical calculation in which a Fraunhofer spectrum is convolved with rotational Raman cross-sections, and the result convolved to instrument resolution [7]. Neglecting telluric Ring-effect interference in the ozone Huggins bands is now recognized as an important source of error in DOAS retrieval of total ozone from remote sensing instruments such as Global Ozone Monitoring Instrument (GOME), Launched in April 1995 on the ERS-2 platform). Indeed, the most recent GOME total ozone algorithms all contain effective treatments of this effect [8–10].

Fraunhofer filling-in at all wavelengths is affected by the presence of cloud and/or aerosol layers; this is most noticeable in the deep Calcium I H and II K lines, centered near 396.9 and 393.4 nm, respectively [11,12]. This dependence may be utilized to retrieve cloud information (fractional cover, cloud-top pressure and possibly cloud optical thickness) from earthshine reflectances. An operational cloud information retrieval algorithm has been developed for the Ozone Monitoring Instrument (OMI), [13,14]. This algorithm uses a look-up table approach based on inelastic-scattering calculations in a Rayleigh atmosphere, and treats clouds as reflecting surfaces in the independent pixel approximation (IPA).

In order to characterize the Ring effect in detail, a radiative transfer (RT) model is required to simulate theoretical filling-in factors defined as the ratios of backscatter radiances computed with and without RRS. A number of studies have looked at RRS of the direct beam (primary scattering), see for example [15,16]. This does not require any calculation of diffusely scattered radiation fields at Raman-shifted wavelengths, and as such is relatively easy to implement; it is often done to establish an initial estimate of the Ring effect. The first RRS filling-in computations that involved multiple scattering were performed using Monte-Carlo methods [2,17]. In recent years, RRS effects in a stratified scattering atmosphere have been modeled using successive orders of scattering [3,11,18,19].

Other models have treated RRS as a first-order perturbation [20,21]; this will be the basis for the present work.

A complete theoretical RT treatment in an atmospheric medium with elastic and inelastic scatterers would include all orders of RRS, and would require that radiances at all wavelengths be calculated simultaneously. It is not feasible to compute numerically the radiation field without substantial simplifications (see for example [22]). Instead, we regard RRS as a perturbation, in effect considering all orders of elastic scattering but only one order of RRS. With no RRS present, radiances are computed with molecular scattering described by the Rayleigh phase function and cross-section; Rayleigh scattering is taken to be *elastic* (no wavelength redistribution of scattered light). This is an approximation, however, since Rayleigh scattering is actually the sum of a pure elastic Cabannes scattering contribution and inelastic RRS terms [23].

For an RT model in which RRS treated as a first-order perturbation, we consider photons that are Raman scattered only once into and out of a given wavelength λ. Given the Rayleigh scattering solution as our starting point, we show that the sum of light scattered inelastically into this wavelength λ from Raman-shifted excitation wavelengths (the RRS gain terms) is counterbalanced by a source term representing light inelastically scattered out of this wavelength (the RRS loss term). These RRS terms are almost (but never exactly) in balance when absorption and Fraunhofer signatures show very little variation with wavelength, and under these circumstances the usual elastic-scattering RT calculation with Rayleigh scattering gives accurate results.

For multiply scattered light, we assume that diffuse fields at λ and all Raman-shifted redistribution wavelengths have first been determined using a zero-order elastic RT calculation before undergoing the first Raman scatter. We show that the radiative transfer equation (RTE) can then be solved in the usual manner, however, including a number of additional source terms due to first-order RRS. We use discrete-ordinate theory to find solutions of the RTE with first-order RRS source terms in a multi-layer multiply scattering atmosphere. The atmosphere is assumed stratified (a number of optically uniform sub-layers), and can include any number of particulates (aerosols and clouds, scattering elastically) in addition to Rayleigh and Raman molecular scattering.

The LIDORT-RRS discrete-ordinate formalism is based on methods developed for the scalar LIDORT RT model [24,25]. We have implemented many LIDORT features in the new model, including the pseudo-spherical treatment of both the solar and line-of-sight beams, and output options for upwelling and/or downwelling