



Isolating Cabannes and rotational Raman scattering to determine forward modeling error due to Rayleigh scattering in the Earth's atmosphere

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ABSTRACT

Molecular scattering in the Earth's atmosphere is commonly represented in radiative transfer (RT) models using the Rayleigh formulation. We show this to be a monochromatic approximation that incurs non-negligible bias due to spectral structure. In reality, atmospheric molecular scattering consists of two distinct physical components: elastic Cabannes scattering and inelastic Raman scattering. vSmartMOM provides a physically consistent framework to resolve Cabannes and rotational Raman (RRS) scattering individually, enabling for the first time a study of their remote-sensing sensitivities. Our previous work focused on Raman scattering with little discussion of the Cabannes component.

Here we present the formulation of Cabannes scattering by N₂, O₂ and their combined effect in air, each described by its coupling with Rayleigh scattering and RRS. Rayleigh and RRS parameters derived from Placzek's quantum-mechanical treatment of molecular polarizability are used to determine the exact Cabannes single scattering albedo and depolarization ratio critical to its accurate vector RT simulation. This is of particular importance for hyperspectral observations from the ultraviolet (UV) to the near-infrared (NIR).

We focus on the O₂ A-band, where spectral structure causes significant Rayleigh bias despite weaker RRS relative to the UV. This has implications for GHG retrievals that widely use the O₂ A-band to constrain airmass, and for FLEX SIF retrievals aiming to determine the SIF spectrum from the A-band. We examine the dependence of the Rayleigh bias on surface brightness, pressure, viewing geometry, and post-cloud-screened residual aerosol, with a LuT-based recommendation to correct it.

1. Introduction

Molecular scattering is one of the fundamental radiative processes governing the propagation of sunlight in the Earth's atmosphere. In atmospheric radiative transfer models, this process is commonly represented using the Rayleigh formulation [1], which describes monochromatic scattering by molecules whose sizes are much smaller than the wavelength of incident radiation. Rayleigh's description is very successful in explaining large-scale optical phenomena such as the color, polarization and spatial distribution of skylight, and remains a standard component of forward models used in atmospheric remote sensing.

However, molecular scattering is not strictly monochromatic. In addition to purely elastic scattering, molecules undergo inelastic Raman transitions [2,3]. In solids and liquids, the only modes of inelastic scattering are (dominant) vibrational Raman scattering (VRS) and electronic Raman scattering (not considered here). This makes the central elastic scattering line spectrally distinct from the significantly displaced modes of VRS, allowing the monochromatic definition of Rayleigh scattering (for scatterers that are small compared with the wavelength) to accurately describe the central elastic component. Gases, however,

possess the rotational degree of freedom not available to solids and liquids – this unlocks rotational Raman scattering (RRS) and rovibrational Raman scattering (RVRS) [4,5]. Because pure RRS produces much smaller wavelength shifts than vibrational or rovibrational Raman scattering, its spectral structure lies close to the central elastic component and was often treated within the broader “Rayleigh scattering” signal rather than as a separately resolved redistribution process [6]. The terminology currently adopted in RT applications restricts Rayleigh scattering to an unshifted component, casting it as a “monochromatic approximation”, while it actually contains both the elastic component of molecular scattering more precisely described as Cabannes scattering [7–9] and RRS which redistributes photons in the immediate spectral neighborhood of the incident light.

The importance of Raman redistribution in atmospheric remote sensing was first established in Earth-atmosphere spectroscopy, where anomalous Fraunhofer line profiles in skylight were identified as the Ring effect [10] and interpreted in terms of noncoherent molecular scattering [11]. Subsequent Earth-science studies treated RRS in

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zenith-sky spectra, satellite backscatter ultraviolet measurements, and absorption-band infilling [12–16]. The same redistribution physics has also long been used in planetary-atmosphere RT: Belton et al. [17] treated short-wavelength Uranus and Neptune albedos using Rayleigh and Raman scattering by H_2 , and later Uranus calculations explicitly modeled Raman filling of solar absorption-line cores [18]. These Earth and planetary studies establish the long use of Raman scattering in atmospheric RT, without naming the elastic component as a separately isolated Cabannes term. The combined action of these processes gives rise to complex spectral signatures, including the well-known Ring effect, in which RRS causes an infilling of Fraunhofer lines in the solar spectrum.

The monochromatic Rayleigh approximation has typically been used as a convenient representation of molecular scattering, while Raman processes have been treated primarily in connection with specific spectroscopic phenomena such as the Ring effect. Several mature RT tools include either exact or approximate treatments of RRS and elastic molecular scattering, including LIDORT-RRS [19], SCIATRAN [20,21], and vSmartMOM [22,23]. Broader atmospheric RT frameworks such as SASKTRAN [24,25] and libRadtran [26] provide flexible elastic-scattering calculations for a wide range of remote-sensing applications. These models make RRS calculations possible, but they cannot identify the forward-model error introduced when a Rayleigh-only forward model is used in a spectrally structured retrieval band. As a result, the purely elastic Cabannes component has rarely been treated explicitly in atmospheric radiative transfer formulations. Reintroducing Cabannes scattering explicitly into atmospheric radiative transfer restores the physical separation between elastic and inelastic molecular scattering that is implicit in the underlying quantum-mechanical description of molecular polarizability [27,28], re-arranged in a form amenable to standard radiative transfer modeling by Sanghavi [29]. While the Rayleigh approximation can be adequate for broadband radiative transfer calculations, it becomes increasingly problematic for modern hyperspectral observations, where the redistribution of radiance by Raman scattering produces measurable effects in high-resolution spectra from the ultraviolet (UV) through the near-infrared (NIR).

Recent studies have demonstrated that Raman scattering introduces additive radiance contributions that can bias retrievals from hyperspectral satellite observations of the Earth [23,30]. These effects are particularly relevant in spectral regions such as the O_2 A-band, which is used by missions such as OCO-2/3, GOSAT/TANSO-FTS, GOSAT-2/TANSO-FTS-2, GOSAT-GW/TANSO-3, MicroCarb, TanSat/Carbon-Spec, Sentinel-5P/TROPOMI, Sentinel-5/MetOp-SGA, and upcoming missions such as CO2M/Sentinel-7 A/B/C and FLEX/FLORIS [31] to constrain photon path lengths in greenhouse gas (GHG) retrievals [32–34] and/or to retrieve solar-induced chlorophyll fluorescence [35–37]. In such applications, the use of Rayleigh scattering to represent molecular scattering obscures the physical separation between elastic and inelastic processes and complicates the interpretation of Raman-induced radiance contributions. Explicitly separating elastic and inelastic molecular scattering provides a framework in which these processes can be treated independently within radiative transfer simulations, allowing corrections for multi-wavelength Raman scattering effects in hyperspectral observations in the form of pre-computed look-up tables (LuTs).

RRS simulations are computationally expensive because of their multi-wavelength mapping, making them difficult to include directly in real-time forward models. We can, however, precompute the dependence of Rayleigh, Cabannes and RRS components on scene parameters, allowing efficient LuT-based corrections for RRS in hyperspectral observations. The LuT discussed here currently covers a wavelength range of 740–785 nm at a constant spectral resolution of 0.1 cm^{-1} (0.0055–0.0062 nm). It includes an expanded set of precomputed correction files, covering a wider range of viewing geometries and split into separate downloadable files, available at ftp://fluio.gps.caltech.edu/XYTZ_RRS_LUT/ using guest login.

In this work we present a detailed formulation of purely elastic (Cabannes) scattering by the dominant atmospheric molecules N_2 and O_2 and place it within the framework of vector radiative transfer. Fundamental conservation rules given by Equations (3) of Sanghavi and Frankenberg [23] are used to reconstruct Rayleigh-analogous Cabannes single scattering albedos and depolarization ratios. This formulation provides a physically consistent representation of molecular scattering in which the purely elastic Cabannes remains intimately coupled with inelastic Raman processes, and yet both components can be quantified independently of each other.

The paper is organized as follows. Section 2 describes the construction of Cabannes scattering properties from Rayleigh and Raman scattering parameters. Section 3 shows how Rayleigh scattering as currently interpreted in RT applications becomes more approximate as spectral structure increases. Section 4 describes the sensitivity of the error due to the monochromatic Rayleigh approximation to variables such as surface albedo, surface pressure, viewing geometry, and post-cloud-screened residual aerosol.

2. Single scattering properties of Cabannes scattering

The single scattering properties of Rayleigh and rotational Raman scattering [29] are derived by mapping the quantum mechanical treatment of molecular scattering based on the polarizability tensor by Placzek [27] to the radiative transfer formalism of Chandrasekhar [38]. We expanded the familiar template of Rayleigh scattering to various types of Raman scattering, resulting in inelastic scattering cross-sections and phase matrices for O_2 and N_2 that could be easily incorporated into conventional analytic RT modeling frameworks. In this work, we present a similar formalism for Cabannes scattering, this time using simply Eqs.(3) of Sanghavi and Frankenberg [23] (henceforth called SF23), which require that the Cabannes single scattering albedo,

$$\varpi_{\text{Cab}} = 1 - \frac{\sum_i \sigma_{\text{RRS},i}}{\sigma_{\text{Rayl}}}, \quad (1)$$

and

$$\mathbf{Z}_{\text{Rayl}} = \varpi_{\text{Cab}} \cdot \mathbf{Z}_{\text{Cab}} + (1 - \varpi_{\text{Cab}}) \cdot \mathbf{Z}_{\text{RRS}}, \quad (2)$$

where the subscripts “Rayl”, “Cab”, and “RRS” denote Rayleigh, Cabannes and rotational Raman scattering, respectively. All cross-sections on the right hand side of Eq. (1) are obtained directly from Eq. (16) and Eq. (22) of Sanghavi [29]. The index i denotes individual rotational Raman transitions. In Eq. (2), $\mathbf{Z}$ denotes the normalized scattering phase matrix. Requiring Cabannes scattering to have a Rayleigh-analogous phase matrix $\mathbf{Z}_{\text{Cab}}$ by substituting $\gamma_{\text{C, Rayl}}$ in Eq. (3) of Sanghavi [29] with $\gamma_{\text{C, Cab}}$, Eq. (2) yields

$$\gamma_{\text{C, Cab}} = \frac{1}{2} \frac{2\gamma_{\text{C, Rayl}}(2 + 3\varpi_{\text{Cab}}) - 3(1 - \varpi_{\text{Cab}})}{(3 + 2\varpi_{\text{Cab}}) - 4\gamma_{\text{C, Rayl}}(1 - \varpi_{\text{Cab}})}, \quad (3)$$

where $\gamma_{\text{C, Rayl}}$ is obtained directly from Eq.(12) of Sanghavi [29] as

$$\gamma_{\text{C, Rayl}} = \frac{3\gamma^2}{45\alpha^2 + 4\gamma^2}, \quad (4)$$

where α and γ are respectively the mean polarizability and the polarizability anisotropy of the molecule. The subscript C in γ_{C} refers to Chandrasekhar’s phase-matrix formulation: γ_{C} is the parameter that quantifies molecular depolarization in the Rayleigh/Cabannes phase matrix and is related to the conventional depolarization ratio by $\rho = 2\gamma_{\text{C}}/(1 + \gamma_{\text{C}})$. This should not be confused with the molecular polarizability anisotropy γ .

Writing the Rayleigh cross-section of a molecule ‘x’ as

$$\sigma_x = \kappa_x \cdot \frac{1 + 2\gamma_{\text{C},x}}{3 - 4\gamma_{\text{C},x}} \cdot \lambda^{-4} \quad (5)$$

and its phase matrix as given in Box I, the factor κ_x absorbs the molecular polarizability and number-density constants in the standard

$$\mathbf{Z}_x = \frac{3}{8\pi} \frac{1}{(1 + 2\gamma_{C,x})} \cdot \begin{bmatrix} \frac{1}{2}(1 - \gamma_{C,x})(\cos^2 \Theta + 1) + 2\gamma_{C,x} & \frac{1}{2}(1 - \gamma_{C,x})(\cos^2 \Theta - 1) & 0 & 0 \\ \frac{1}{2}(1 - \gamma_{C,x})(\cos^2 \Theta - 1) & \frac{1}{2}(1 - \gamma_{C,x})(\cos^2 \Theta + 1) & 0 & 0 \\ 0 & 0 & (1 - \gamma_{C,x}) \cos \Theta & 0 \\ 0 & 0 & 0 & (1 - 3\gamma_{C,x}) \cos \Theta \end{bmatrix}, \quad (6)$$

Box I.

Cabannes/King-corrected Rayleigh cross-section [6,38,39]. This allows us to write the following equation for air (ignoring for simplicity the presence of species like CO₂ and Ar):

$$\sigma_{\text{air}} = \sum_{x \in \{O_2, N_2\}} \text{VMR}_x \sigma_x \quad (7)$$

and

$$\sigma_{\text{air}} \cdot \mathbf{Z}_{\text{air}} = \sum_{x \in \{O_2, N_2\}} \text{VMR}_x \sigma_x \cdot \mathbf{Z}_x, \quad (8)$$

where VMR_x denotes the partial pressure or the volume mixing ratio of gas 'x.' For Rayleigh scattering, $\kappa = 128\pi^5 \alpha^2$, so that Eqs. (7)–(8) simplify to

$$\gamma_{\text{air, Rayl}} = \frac{3}{4 + \frac{\sum_{x \in \{O_2, N_2\}} \text{VMR}_x \kappa_x}{\sum_{x \in \{O_2, N_2\}} \frac{\text{VMR}_x \kappa_x \gamma_{C,x}}{3 - 4\gamma_{C,x}}}} \quad (9)$$

The subscript 'Rayl' for σ_x , κ_x , and $\gamma_{C,x}$ is implicit in Eqs. (7)–(9). Substituting $\kappa_{x, \text{Rayl}}$ with $\kappa_{x, \text{Cab}} = \varpi_{\text{Cab}} \sigma_{x, \text{Rayl}} \cdot \frac{3 - 4\gamma_{C,x, \text{Cab}}}{1 + 2\gamma_{C,x, \text{Cab}}}$, and $\gamma_{C,x, \text{Rayl}}$ with

$\gamma_{C,x, \text{Cab}}$ yields the corresponding value for $\gamma_{\text{air, Cab}}$. The resulting constants for air are listed in Table 1 at 395 nm and 760 nm, respectively. A comparison of the two depolarization factors shows that $\gamma_{C, \text{Cab}} \ll \gamma_{C, \text{Rayl}}$. This is expected because Rayleigh scattering includes the highly depolarizing RRS component in addition to purely elastic Cabannes scattering. A similar comparison between depolarization factors shows that N₂ is more polarizing than O₂. N₂ also has a larger Rayleigh cross-section with a larger proportion of elastic (Cabannes) scattering. Asymmetrically distributed unpaired electrons in the outer orbital of O₂ give it a smaller mean polarizability ($\alpha_{O_2} = 1.5658 \cdot 10^{-24} \text{ cm}^3$, $\alpha_{N_2} = 1.7406 \cdot 10^{-24} \text{ cm}^3$, Asawaroengchai and Rosenblatt [40]) and greater polarizability anisotropy ($\gamma_{O_2} = 1.080 \cdot 10^{-24} \text{ cm}^3$, $\gamma_{N_2} = 0.71 \cdot 10^{-24} \text{ cm}^3$, Asawaroengchai and Rosenblatt [40]) than N₂, whose paired electrons are more diffuse, and thus symmetrically distributed.

In the discussion above we choose $\mathbf{Z}$ as described for Rayleigh scattering in Eq.(23) of SF23. We choose this form over Eq.(3) of Sanghavi [29] because of the more widespread use of the $[I, Q, U, V]$ -representation of the Stokes vector over $[I_{\parallel}, I_{\perp}, U, V]$. Both forms yield the same result.

The quantity expressed in Eq. (4) above was mis-attributed to $\gamma_{C, \text{Cab}}$ in Eq. (24) of SF23. This error had no implications on the purely inelastic simulations. The Rayleigh scattering cross-section σ_{Rayl} and Cabannes single scattering albedo ϖ_{Cab} also remained unchanged. However, it affected the phase matrices of both Rayleigh and Cabannes scattering, viz., $\mathbf{Z}_{\text{Rayl}}$ and $\mathbf{Z}_{\text{Cab}}$, making both appear more isotropic than their actual forms, as illustrated for air in Fig. 1. The effect on the resulting simulations, especially the I component of the Stokes vector, is minor enough to be imperceptible.

While Rayleigh scattering is fully described by σ_{Rayl} and $\gamma_{C, \text{Rayl}}$, the quantities σ_{Rayl} , ϖ_{Cab} and $\gamma_{C, \text{Cab}}$ fully define the radiative properties of Cabannes scattering by a given molecule, and are listed in Table 1. Struck out values represent values of $\gamma_{C, \text{Cab}}$ and $\gamma_{C, \text{Rayl}}$ arising from the mis-attribution in SF23. The λ^{-4} dependence of σ_{Rayl} drives its strong spectral gradient, which mostly cancels out in ϖ_{Cab} , with a negligible effect on $\gamma_{C, \text{Cab}}$. $\gamma_{C, \text{Rayl}}$ is given by Eq. (4), where the mean

polarizability α of the molecule has a weak spectral dependence at wavelengths longer than $\sim 300 \text{ nm}$ [41]. The molecular polarizability anisotropy γ is treated as constant in the numerical values tabulated here. This is an approximation: measurements and parameterizations show that polarizability anisotropy also disperses with wavelength [42,43]. The 760 nm O₂ A-band values are therefore best understood as a physically consistent Cabannes/RRS separation within the molecular-constant set used in SF23, while future versions of the LuT will incorporate wavelength-dependent anisotropy without changing the formalism.

The depolarization ratios $\rho = \frac{2\gamma_C}{1+\gamma_C}$ corresponding to the corrected $\gamma_{C, \text{Cab}}$ and $\gamma_{C, \text{Rayl}}$ values are given in Table 2. Our computations incorporate the temperature and wavelength dependence of the mean polarizabilities $\bar{\alpha}$ of O₂ and N₂ given by Buldakov et al. [41], resulting in different values for air at 395 nm and 760 nm, which respectively differ by 6.04% and 1.01% from the value $\rho = 0.0279$ put forth by Young [6]. However, it should also be noted that we currently do not account for the presence of CO₂ and Argon in the Earth's atmosphere, crudely assigning all scattering to only O₂ and N₂.

A simple dry-air composition estimate shows that this simplification is small for the present O₂ A-band sensitivity study. Argon contributes about 0.9% of the dry-air number density and, because it is monatomic, adds only elastic, nearly non-depolarizing scattering. In spite of its larger molecular polarizability, CO₂ accounts for about 420 ppm by volume, so that its contribution to the bulk molecular scattering optical depth is of the order of $\sim 10^{-3}$. If the omitted Ar and CO₂ scattering is treated as elastic, the bulk Cabannes fraction at 760 nm changes by only a few 10^{-4} in absolute value and the Rayleigh depolarization ratio changes by less than about 1%. These values are much smaller than the scene-dependent Rayleigh-approximation errors examined below. The omission is therefore not expected to affect the conclusions for OCO-2/3-like A-band calculations, although our LuT will incorporate the complete dry-air composition in the future.

These results revise those of SF23: considering Cabannes scattering to be the more fundamental process, and assuming a general mislabeling of Cabannes scattering as Rayleigh scattering, the author had misguidedly applied all molecular constants to Cabannes scattering, and then derived the Rayleigh parameters using a process similar to the one described in this section. In the absence of rotational Raman scattering, Rayleigh becomes identical to Cabannes scattering for the central elastic line, explaining some of the confusion in nomenclature: Rayleigh scattering remains interchangeable with Cabannes scattering for solids and liquids, which do not possess a rotational degree of freedom, and hence exhibit only Rayleigh and vibrational Raman scattering. This statement concerns molecular or small-particle scattering in the Rayleigh limit, where the scatterer is much smaller than the wavelength [6,39] - it should not be interpreted as applying Rayleigh theory to bulk solids or liquids such as ocean water or ice sheets.

3. Limitations of the monochromatic Rayleigh approximation in the earth's atmosphere

RRS causes a redistribution of energy in the immediate spectral neighborhood of the incident light. The Rayleigh approximation, which

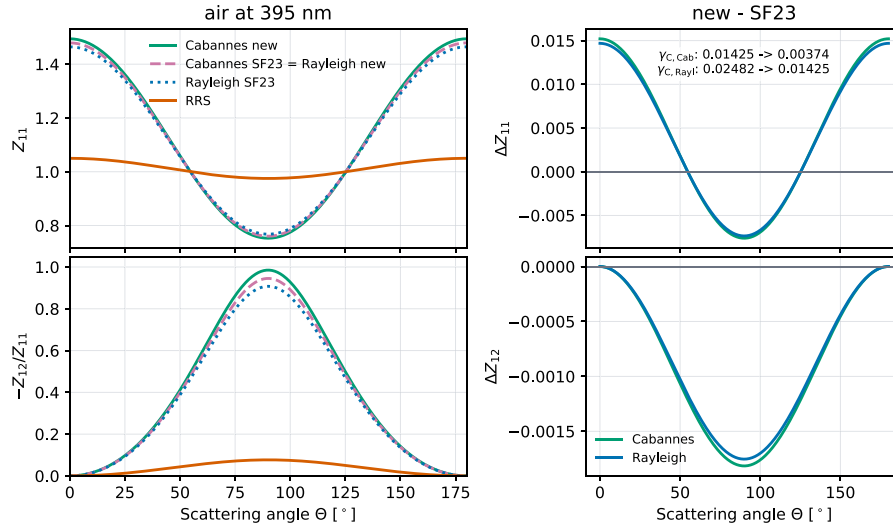


Fig. 1. Analogous to Fig. 1 of SF23. The left panels show new and SF23 computations of Cabannes and Rayleigh scattering alongside rotational Raman scattering: normalized (to 4π) phase function, Z_{11} (top), and degree of linear polarization given by $-Z_{12}/Z_{11}$ (bottom). The right panels show the difference between the corrected and the SF23 computations of Z_{11} and Z_{12} .

Table 1

Constants defining Cabannes and Rayleigh scattering for N_2 , O_2 , and air at 395 nm and 760 nm. Struck out values represent values of $\gamma_{C,Cab}$ and $\gamma_{C,Rayl}$ arising from the mis-attribution in SF23. New values replacing them follow the formulation presented in this paper. Note: the values of ϖ_{Cab} are slightly larger than those in Table 1 of SF23, because the latter included VRS and RVRS cross-sections in addition to RRS in Eq. (1) of the current paper.

	395 nm				760 nm			
	σ_{Ray} $\cdot 10^{-26}$ [cm ²]	ϖ_{Cab}	$\gamma_{C,Cab}$	$\gamma_{C,Ray}$	σ_{Ray} $\cdot 10^{-26}$ [cm ²]	ϖ_{Cab}	$\gamma_{C,Cab}$	$\gamma_{C,Ray}$
O_2	1.58970	0.93547	~~≈ 0.02769~~ 0.00746	~~≈ 0.04813~~ 0.02769	0.10864	0.93120	~~≈ 0.02967~~ 0.00805	~~≈ 0.05154~~ 0.02967
N_2	1.80159	0.97523	~~≈ 0.01021~~ 0.00265	~~≈ 0.01780~~ 0.01021	0.12526	0.97406	~~≈ 0.01073~~ 0.00280	~~≈ 0.01868~~ 0.01073
air	1.75921	0.96804	~~≈ 0.01328~~ 0.00349	~~≈ 0.02314~~ 0.01328	0.12194	0.96642	~~≈ 0.01400~~ 0.00370	~~≈ 0.02437~~ 0.01400

Table 2

Depolarization ratios $\rho = 2\gamma_C/(1 + \gamma_C)$ corresponding to the corrected $\gamma_{C,Cab}$ and $\gamma_{C,Ray}$ values. Young's reference value for Rayleigh scattering in air is $\rho = 0.0279$.

	395 nm		760 nm	
	$\rho_{C,Cab}$	$\rho_{C,Ray}$	$\rho_{C,Cab}$	$\rho_{C,Ray}$
O_2	0.01481	0.05388	0.01596	0.05764
N_2	0.00529	0.02021	0.00559	0.02122
air	0.00695	0.02622	0.00737	0.02762

subsumes both Cabannes and RRS under a monochromatic umbrella, strictly holds when the RT problem is completely devoid of spectral features, implying a white light source function propagating through a gray atmosphere over a gray surface as the exact limiting case. It becomes increasingly inaccurate as spectral structure is introduced. In Fig. 2, we consider a thin slice between 761–764 nm of the O_2 A-band to show:

1. a gray surface with no atmospheric spectral absorption and a spectrally flat, assumed solar function (left column),
2. then introduce spectral variations in the form of the actual solar function (middle column), and
3. finally add absorption due to the O_2 A-band (right column).

The green line represents the intensity of light that undergoes purely inelastic RRS scattering, I_{RRS} normalized by the solar function, F_0 . The

red line represents the monochromatic difference between Cabannes and Rayleigh scattering intensities $\Delta I_{mono} = I_{Cab} - I_{Rayl}$ normalized by F_0 . The sum of these two terms, shown in blue, represents the intensity deficit incurred by our use of the Rayleigh approximation, $\Delta I = (I_{Cab} + I_{RRS}) - I_{Rayl}$, again normalized by F_0 .

The left hand panels illustrate how Rayleigh scattering exactly simulates the combined effect of Cabannes and Raman scattering in the first case: Starting at a Lambertian surface albedo $\rho = 0$ for a black surface in the bottom panel, proceeding through $\rho = 0.3$ for a surface of intermediate brightness in the middle panel to $\rho = 1$ for a white surface at the top, the monochromatic ΔI_{mono} and inelastic I_{RRS} components cancel out exactly to yield $\Delta I = 0$ at all wavelengths.

In the middle column, we relax the first condition to replace a perfectly white Sun with the actual solar source function replete with Fraunhofer lines. While the ratio of the monochromatic component (red) relative to F_0 remains unaffected, the inelastic component I_{RRS}/F_0 (green) reveals spikes because of the net infilling of Fraunhofer lines of absorption by RRS from their immediate spectral neighborhood, which shows small wavelike structures due to redistribution between wavelengths of unequal intensities. These spikes and wavelike structures persist in the sum of the green and red lines represented by $\Delta I/F_0$ (blue).

In the right column, we replace the conservatively scattering gray atmosphere with the Earth's atmosphere featuring absorption due to the O_2 A-band. Now, both the monochromatic (red) and inelastic (green) components follow spectral absorption patterns – nearing zero as the

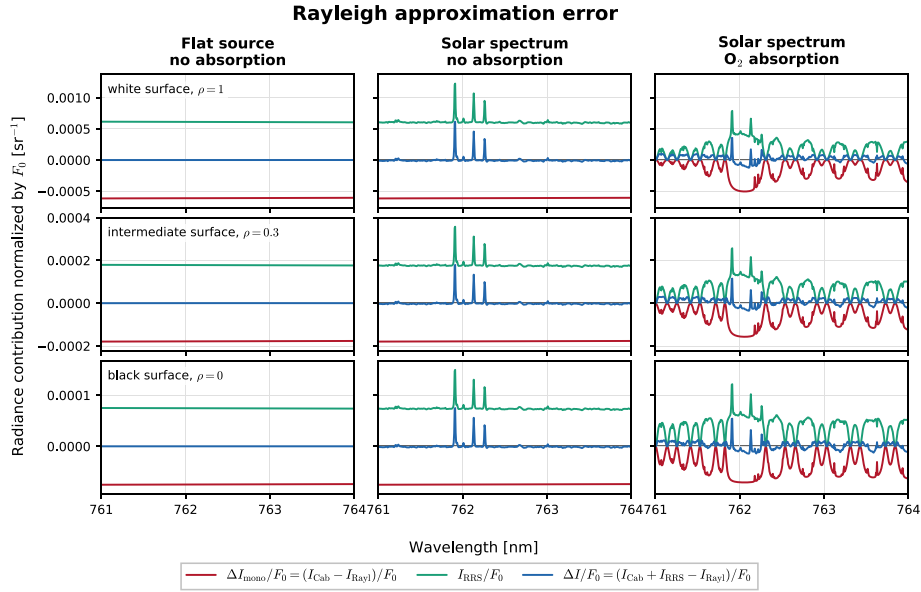


Fig. 2. The ability of Rayleigh scattering to describe molecular scattering in the atmosphere varies with the spectral complexity of the scene. This is illustrated by constructing three distinct cases: a gray surface with no atmospheric spectral absorption and a spectrally flat solar function (left), the same surface and atmosphere with the actual solar function bearing lines of Fraunhofer absorption (middle), and the same surface but with the actual solar function and the typical Earth atmosphere with O₂ A-band absorption (right). The actual molecular scattering signal consists of the sum of pure elastic and pure inelastic scattering, i.e. $I_{\text{Cab}} + I_{\text{RRS}}$, which differs from the Rayleigh approximation I_{Rayl} by an amount ΔI , shown in blue. This error can be resolved into its monochromatic ($I_{\text{Cab}} - I_{\text{Rayl}}$, red) and multi-wavelength (I_{RRS} , green) components, respectively. Three different Lambertian surface albedos have been considered, varying from $\rho = 0$ (bottom) through $\rho = 0.3$ (middle) to $\rho = 1$ (top). In each case, the blue line coincides with $\Delta I = 0$ only for the leftmost case devoid of all spectral structure. As spectral structure increases from left to right, so does the deviation of blue line from zero.

absorption strength increases, and growing in absolute magnitude as the absorption weakens. While the monochromatic signal is affected only by the absorption strength of one wavelength, the inelastic signal is affected by the observed wavelength as well as the absorption strength of its immediate spectral neighborhood. Thus, Raman scattered light observed at a strongly absorbing wavelength in a spectral neighborhood of weakly absorbing lines will undergo less extinction than its monochromatic counterpart. Conversely, a weakly absorbing line surrounded by wavelengths of stronger absorption will undergo more extinction in its inelastic component. This causes the resulting blue line to undulate around $\Delta I = 0$: when a wavelength receives more light from its spectral neighborhood than it loses to inelastic scattering, $\Delta I > 0$. This happens when the spectral neighborhood is brighter than the given wavelength (either due to a brighter source or due to weaker absorption). $\Delta I < 0$ at wavelengths that lose more light to inelastic scattering than they receive from their immediate spectral neighborhood. This occurs when the source function is brighter or absorption is weaker at the wavelength in question than its spectral neighborhood.

In the following, we show how an accurate computation of Rayleigh, Cabannes and RRS scattering allows us to determine the spectral bias introduced by the use of Rayleigh scattering in forward models. We focus here on the O₂ A-band, which is relevant to sensitive measurements of GHGs like CO₂ from instruments such as OCO-2/3, GOSAT, GOSAT-2, TanSat, CO2M, MicroCarb, and GeoCarb, and to retrievals of solar induced fluorescence (SIF) from instruments such as OCO-2/3, GOSAT, TROPOMI, PACE, and FLEX. It should be noted that the O₂ A-band exhibits significantly weaker errors due to Rayleigh scattering than simulations at shorter wavelengths because molecular scattering contributes less strongly in the near-infrared than in the UV and visible.

4. Forward model bias in O₂ A-band simulations using Rayleigh scattering

Operational retrievals in current missions like OCO-2/3 and GOSAT use the Rayleigh formalism to simulate molecular scattering in their

forward models. Spectral structures due to Fraunhofer lines in the solar source function and absorption in the Earth's atmosphere introduce a spectral bias ΔI in O₂ A-band simulations, as demonstrated in the previous section. Multi-wavelength RRS computations are currently too computationally expensive to include in an operational forward model. However, adding precomputed ΔI to the Rayleigh simulation of a given O₂ A-band measurement would minimize its forward modeling error. Shortwave infrared (SWIR) spectra longward of 1500 nm, including for example, the weak ($\sim 1.6 \mu\text{m}$) and strong ($\sim 2 \mu\text{m}$) CO₂ bands, are negligibly affected by inelastic biases because molecular scattering contributes much less strongly there than in the O₂ A-band and at shorter wavelengths.

In the following, we carry out fully polarized, GPU-accelerated vSmartMOM simulations [22,44] of Cabannes, RRS and Rayleigh scattering in the O₂ A-band to study the effects of surface albedo, surface pressure, and viewing geometry on ΔI , first assuming a clear sky devoid of aerosols. Subsequently, we introduce residual aerosols to study the effect of aerosol optical depth (AOD) on ΔI after cloud-screening. A detailed study of aerosols, including microphysical properties and, more importantly, vertical distribution will be covered in future work. We use the OCO-2 Müller matrix to convert our simulated Stokes vector into the radiance measured by the instrument. We convolve the resulting high resolution spectrum ($\delta\lambda \approx 0.01 \text{ nm}$) using the OCO-2 O₂ A-band instrument slit function (FWHM $\sim 0.04 \text{ nm}$) [45,46], resampling it to the wavelength grid of the instrument.

Normalization by F_0 is useful to highlight the infilling of Fraunhofer lines by RRS, and hence is used in Fig. 2. However, we retain radiance units in Figs. 3–7 because ΔI is an additive forward-model residual that is useful to understand the changes in the overall shape of the O₂ A-band due to RRS.

Fig. 3 shows the dependence of the Rayleigh error ΔI (left panel) due to an increase in the assumed Lambertian surface reflectance ρ from 0 through 1 in steps of 0.2. The black lines represent simulated OCO-2 measurements, superposed on color-coded high resolution vSmartMOM simulations. The middle and right panels show the monochromatic and

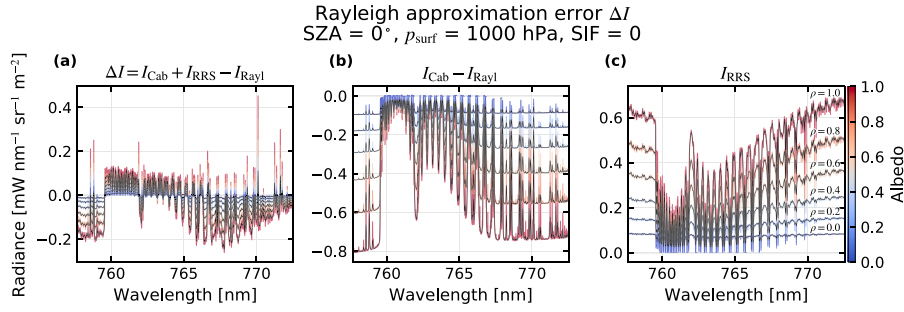


Fig. 3. The dependence on surface albedo of the forward modeling error, ΔI , due to a Rayleigh scattering assumption (left). This error can be separated into a monochromatic ($\Delta I_{\text{mono}} = I_{\text{Cab}} - I_{\text{Rayl}}$ (middle)) and an inelastic (I_{RRS} , right) component. We consider here a nadir-viewing geometry with $\text{SZA} = 0^\circ$ and a surface pressure of 1000 hPa.

inelastic components of this error. Individually, these components show a stronger dependence on the surface albedo than ΔI . $I_{\text{Cab}} - I_{\text{Rayl}}$ and I_{RRS} appear to grow in nearly equal and opposite directions away from the x -axis. However, Fraunhofer lines that form a prominent feature of $I_{\text{Cab}} - I_{\text{Rayl}}$, for example shortward of 760 nm, are blurred beyond recognition in I_{RRS} as light gets redistributed across neighboring wavelengths. Telluric lines of absorption grow deeper as increasing surface brightness leads to longer light paths and more multiple scattering. Spectrally, it should be noted that surface reflection has a weaker, non-monotonic dependence on wavelength, and does not fall off as λ^{-4} . At a given wavelength, a greater albedo increases both the photon path length and the relative molecular contribution. In this case, the redistribution of radiation between neighboring wavelengths by RRS causes the lines of strongest absorption to be shallower and the near-continuum wings to slope more steeply towards the strongly absorbing core of the A-band in the I_{RRS} component. The combined effect of the two components is a significant albedo-dependent deviation of ΔI from zero. These biases limit the ability of Rayleigh scattering to reproduce the exact shape of the observed spectrum, resulting in induced biases on other state parameters which have to play a compensating role towards achieving an acceptable fit in retrieval algorithms.

Surface pressure, indicative of the airmass contained in the atmospheric column, also increases the amount of molecular scattering in the atmosphere. Its effects on ΔI and its monochromatic and inelastic components are shown in Fig. 4, as the surface pressure increases from 500 hPa through 750 hPa to 1000 hPa. As surface brightness increases from a black surface in the bottom row to a white surface in the top row, the effect of surface pressure can be seen to be significantly amplified.

Fig. 5 shows the effect of varying the solar zenith angle (SZAs) as the Sun moves from zenith through angles of 18° , 37° , and 53° to 70° . We do not consider angles beyond 70° to avoid the effects of the Earth's curvature. The incoming solar flux varies as $\cos \text{SZA}$, as a result of which the continuum wavelengths get closer to zero in ΔI and both its components as SZAs increase. Within the absorption lines, increasing slantness of the incoming light leads to more extinction at larger angles.

Increasing the viewing zenith angle (VZA), however, has the opposite effect, as seen in Fig. 6. An increase in VZA increases the light path (roughly as a function of $\cos \text{VZA}$) and the amount of multiple scattering without affecting the amount of light entering the atmosphere. Absorption at larger VZAs is significantly stronger, dwarfing that at smaller VZA. However, these absorption effects, easily observable in the $I_{\text{Cab}} - I_{\text{Rayl}}$ and I_{RRS} components, largely cancel out in ΔI . Especially for brighter surfaces, greater sensitivity in ΔI is seen at weakly absorbing and continuum wavelengths, where the differences in light path affect the spectral shape.

The sensitivity of ΔI was examined only for clear sky scenes so far. However, aerosols cannot be ruled out in real scenes observed from satellite-borne instruments. The OCO-2 cloud-screening algorithm [47], for example, allows for an aerosol optical depth at 760 nm of 0.1–0.3.

In vSmartMOM, aerosols are included as elastic scatterers defined by a complex refractive index, a lognormal size distribution, and a lognormal vertical distribution [48–50]. Mie theory is used to compute the resulting optical depth, single-scattering albedo and phase matrix [51,52]. We simulated aerosols of AOD between 0–0.5 at 760 nm, lognormal median radius r_0 between 0.1–0.5 μm , and a lognormal vertical distribution with median height between 2–12 km. In this parametric range, we found that ΔI and its components were most sensitive to the AOD. Fig. 7 shows the sensitivity to an aerosol with median radius 0.1 μm and median height 2 km over Lambertian surfaces of albedo 0 (bottom), 0.1 (second from bottom), 0.5 (second from top) and 1 (top), respectively. Aerosols, with optical depths increasing from 0 (light blue), through 0.1 (orange) to 0.5 (red), add to the light path by increasing elastic scattering events in the atmosphere. The monochromatic and inelastic components move away from zero with increasing AOD, but the net ΔI changes only weakly even as AOD increases by more than a factor of five. This partial cancellation indicates that residual elastic aerosol scattering can reduce the relative Rayleigh-approximation error even while modifying the absolute radiance. The combined spectral effect is familiar: an infilling due to RRS in lines of strong telluric/Fraunhofer absorption, and a net loss of radiation from weakly absorbing and near-continuum wavelengths. This brief study is intended to explore the effect of aerosols in cloud-screened scenes. A more in-depth exploration of the effect of clouds/aerosols exceeds the scope of this paper.

While previous studies quantified in-filling due to RRS in the O_2 A-band [16,21,23,53], we isolate the signed O_2 A-band radiance error incurred by a Rayleigh-only approximation as a function of surface albedo, surface pressure and geometry. We recognize ΔI as the forward modeling error that can lead to a retrieval bias in surface pressure, P_{surf} , or any other metric affecting the observed airmass – the main purpose for the inclusion of the O_2 A-band in most GHG retrievals [34,54–58]. A biased estimation of airmass directly propagates into X_{GHG} biases. ΔI also has clear implications for SIF retrievals from the planned FLEX mission [31], which aims to use the full O_2 A-band to determine not only the magnitude but also the spectral shape of SIF. SIF-specific retrieval impacts and a LuT-based correction strategy have been investigated in dedicated companion work [30], while corresponding quantification for X_{CO_2} and surface-pressure retrievals is ongoing.

5. Conclusion

We have presented a radiative transfer formulation that separates molecular scattering in the Earth's atmosphere into its purely elastic Cabannes component and its inelastic rotational Raman component. Using conservation relationships between Rayleigh, Cabannes, and RRS scattering, we derived the Cabannes single scattering albedo and depolarization ratio for N_2 , O_2 , and dry air, and corrected the assignment of the Cabannes and Rayleigh depolarization factors used in previous work. The resulting framework preserves the familiar structure

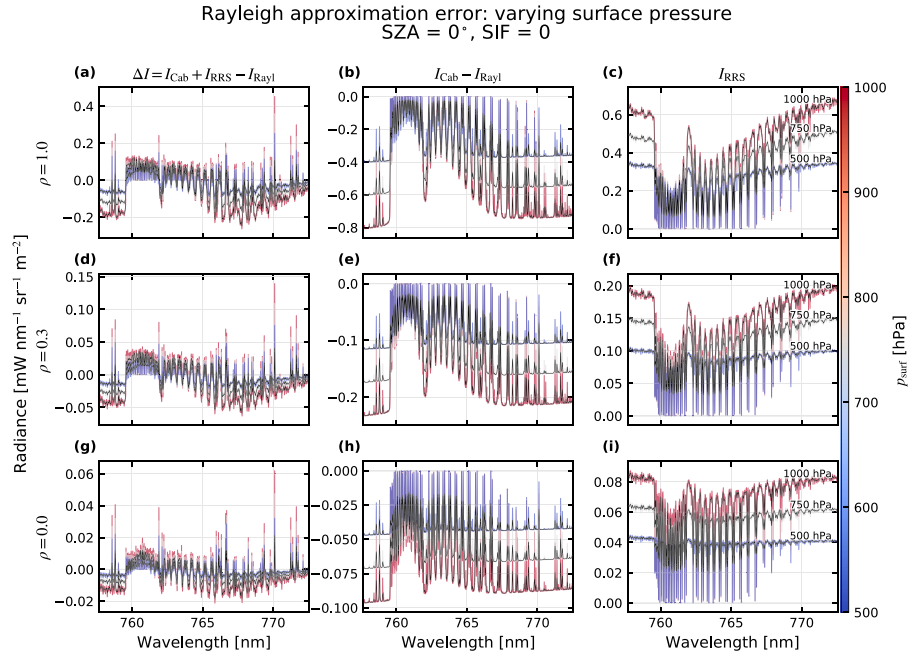


Fig. 4. The same as Fig. 3, but now we examine the dependence of the Rayleigh error and its components with respect to the surface pressure. We consider three surface albedos: a black surface ($\rho = 0$) in the bottom, a surface of intermediate brightness ($\rho = 0.3$) in the middle, and a white surface ($\rho = 1$) in the top panels.

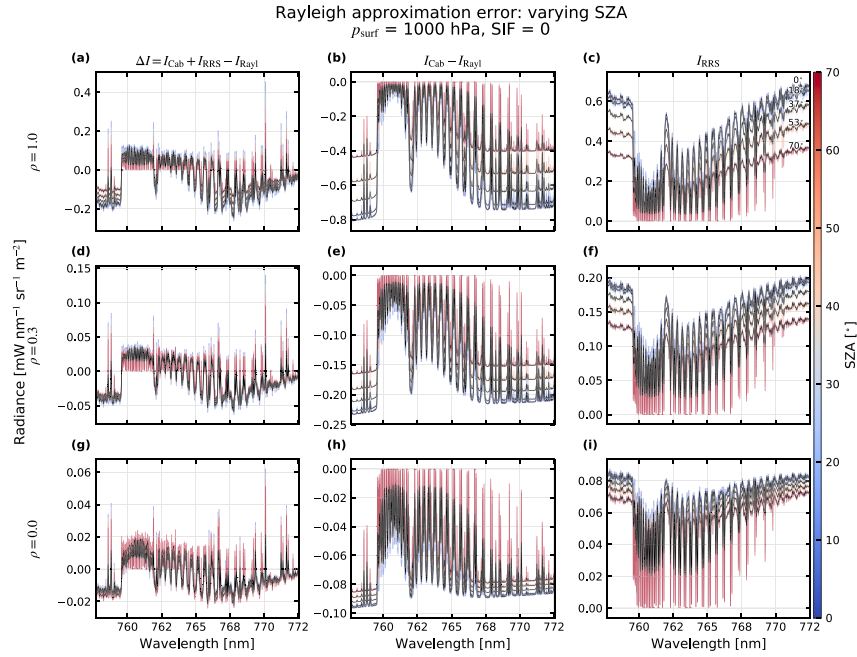


Fig. 5. The same as Fig. 4, but with respect to the solar zenith angle.

of Rayleigh-like vector radiative transfer while making explicit the physical distinction between elastic and inelastic molecular scattering.

This has important implications for hyperspectral remote sensing. In spectrally smooth scenes, the conventional Rayleigh treatment reproduces the combined effect of Cabannes and RRS scattering. In the presence of spectral structure, however, the monochromatic Rayleigh approximation produces a signed radiance error, $\Delta I = I_{\text{Cab}} + I_{\text{RRS}} - I_{\text{Rayl}}$. This error reflects the partial cancellation between the monochromatic Cabannes-Rayleigh difference and the multi-wavelength RRS contribution, and therefore depends on the spectral contrast of the scene as well

as on the atmospheric photon path.

Fully polarized vSmartMOM simulations in the O_2 A-band show that this Rayleigh-approximation error depends systematically on surface albedo, surface pressure, viewing geometry, solar zenith angle, and residual aerosol optical depth. Larger molecular columns amplify the molecular-scattering contribution, viewing geometry modifies the effective light path, and bright surfaces and aerosols do both, each affecting the balance between line infilling and continuum loss. Although the O_2 A-band is less affected than shorter wavelength bands because molecular scattering contributes more weakly in the near-infrared than at

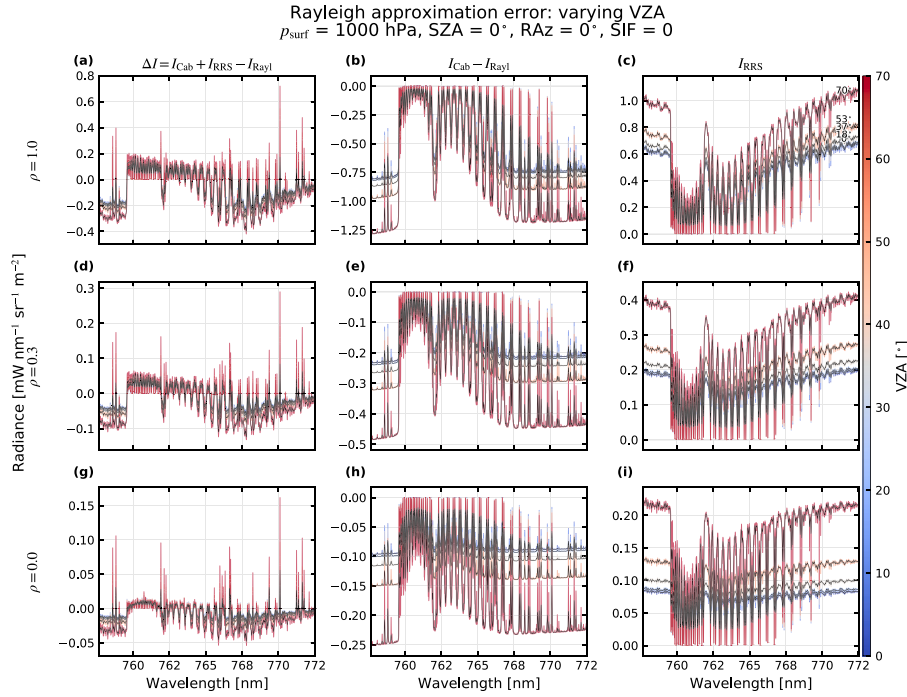


Fig. 6. The same as Fig. 4, but with respect to the viewing zenith angle.

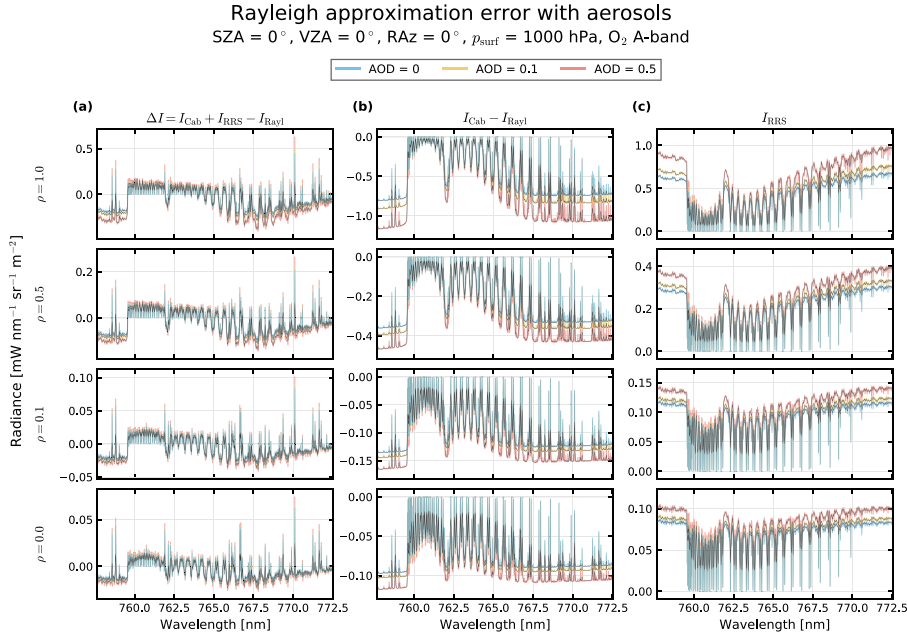


Fig. 7. Sensitivity of the O_2 A-band Rayleigh-approximation error to residual aerosol optical depth. The left column shows the forward modeling error due to the monochromatic Rayleigh approximation, $\Delta I = I_{\text{Cab}} + I_{\text{RRS}} - I_{\text{Rayl}}$, the middle column shows the monochromatic component, $I_{\text{Cab}} - I_{\text{Rayl}}$, and the right column shows the inelastic RRS contribution, I_{RRS} . Rows correspond to Lambertian surface albedos $\rho = 1.0, 0.5, 0.1$, and 0.0 from top to bottom. Colors indicate aerosol optical depth at 760 nm : $\text{AOD} = 0, 0.1$, and 0.5 , for an aerosol layer with median radius $r_0 = 0.1 \mu\text{m}$ and median height 2 km . Simulations use $\text{SZA} = 0^\circ$, $\text{VZA} = 0^\circ$, $\text{RAZ} = 0^\circ$, and $p_{\text{surf}} = 1000 \text{ hPa}$. Increasing AOD enhances both the monochromatic and inelastic components, altering the net spectral error in absorption lines and continuum regions.

shorter wavelengths, the resulting biases are relevant for retrievals that use the A-band to constrain airmass, surface pressure, GHG columns, or the spectral shape of SIF.

RRS, and hence ΔI , is sensitive to the same scene and atmospheric parameters that control the photon path length through the Earth's atmosphere. These are precisely the quantities that the O_2 A-band is used to constrain in GHG retrievals, and that must be accurately characterized for SIF retrievals from missions such as FLEX. Leaving ΔI

unaccounted for thus risks biasing the path-length information that the O_2 A-band is intended to provide, with corresponding induced biases in retrieved X_{GHG} and in the inferred SIF spectrum.

Because exact RRS simulations require multi-wavelength coupling, they remain too expensive for routine operational forward modeling. The decomposition developed here provides a practical alternative: the Rayleigh-only forward model can be retained, while precomputed corrections for ΔI are applied as a function of scene parameters.

An expanded LuT archive is now available as separate downloadable files at ftp://fluo.gps.caltech.edu/XYZT_RRS_LUT/ using guest login. These LuT-based corrections offer a path towards reducing Raman-related forward-model errors in hyperspectral observations without requiring full multi-wavelength RRS calculations in every retrieval. The SIF implications of this approach have already been developed in [30]. Quantifying the corresponding impact on X_{CO_2} and surface pressure retrievals remains ongoing. Future work should also extend this sensitivity analysis to a larger number of realistic aerosol and cloud vertical distributions and shorter wavelength spectral regions where Raman effects are expected to be stronger.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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