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Discussion Paper

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# Retrieval of aerosol parameters from the oxygen A band in the presence of chlorophyll fluorescence

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# Abstract

We have investigated precision of retrieved parameters for a generic aerosol retrieval algorithm over vegetated land using the  $O_2$  A band. Chlorophyll fluorescence is taken into account in the forward model. Fluorescence emissions are modeled as isotropic

- <sup>5</sup> contributions to the upwelling radiance field at the surface and they are retrieved along with aerosol parameters. Precision is calculated by propagating measurement noise using the forward model's derivatives. We assume that measurement noise is dominated by shot noise; thus, results apply to grating spectrometers in particular. In a number of retrieval simulations, we describe precision for various atmospheric states, ob-10 servation geometries and spectral resolutions of the instrument. Our results show that
- aerosol optical thickness, aerosol pressure, fluorescence emission and surface albedo can be simultaneously retrieved from the  $O_2$  A band. We also show that most of the fluorescence signal is provided by filling-in of the  $O_2$  A band and to a lesser extent by filling-in of Fraunhofer lines.

#### 15 **1** Introduction

Chlorophyll in terrestrial vegetation exhibits fluorescence in the red and near-infrared wavelength range. The oxygen A band around 760 nm is located in the fluorescence wavelength region and is often used for cloud retrieval (e.g. Koelemeijer et al., 2001; Rozanov and Kokhanovsky, 2004) but increasingly also for aerosol retrieval. Current and future operational algorithms employ the O<sub>2</sub> A band for retrieval of aerosol parameters per se (e.g. Sanders et al., 2012; Dubuisson et al., 2009) or for aerosol correction as part of a more convolved trace gas retrieval (e.g. O'Dell et al., 2012; Butz et al., 2012; Reuter et al., 2010; Yoshida et al., 2011). Recently, advancements have been made into remote sensing of fluorescence emissions from space using the Greenhouse Gases Observing Satellite's (GOSAT; Kuze et al., 2009) hyperspectral radiance measurements (Frankenberg et al., 2011a; Joiner et al., 2011; Guanter et al., 2012).





If the relatively small fluorescence signal is strong enough to enable fluorescence retrieval from space, the question arises whether fluorescence emissions will interfere with aerosol retrieval from the  $O_2$  A band and, if so, how to account for fluorescence in an aerosol retrieval algorithm.

- <sup>5</sup> Photosynthesis in chlorophyll pigments is driven by absorption of visible solar radiation between about 400 and 700 nm (photosynthetically active radiation). Part of the energy absorbed by chlorophyll that is not used for carbon fixation is re-emitted at longer wavelengths in the 650 to 800 nm wavelength range (fluorescence). Interest in remote sensing of solar-induced chlorophyll fluorescence arises, because it is an in-10 dicator of photosynthetic activity (e.g. Maxwell and Johnson, 2000; Krause and Weis,
- 1991). Frankenberg et al. (2011b) indeed show a strong linear correlation between satellite retrievals of fluorescence and gross primary production from vegetation models. Satellite-based remote sensing of fluorescence would thus offer a way to measure carbon fluxes associated with gross primary production on a global scale.
- <sup>15</sup> For the present study, it is important to know typical values of fluorescence emissions at the  $O_2$  A band. Guanter et al. (2012) retrieved fluorescence emissions at 755 nm, which is near the start of the  $O_2$  A band. They report monthly 2° by 2° average values up to 1.8 mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>. This range agrees with Frankenberg et al. (2011b), who also use GOSAT measurements but employ a different retrieval method. Around
- the O<sub>2</sub> A band, fluorescence emissions typically decrease with wavelength. Laboratory measurements of leaf fluorescence as well as leaf and canopy models show that emissions at 770 nm can be up to a factor of two smaller than emissions at 755 nm (e.g. Amoros-Lopez et al., 2008; Guanter et al., 2010). A linear wavelength dependence seems sufficient to describe the spectral behavior across the O<sub>2</sub> A band.
- Fluorescence emissions are a slowly varying function of wavelength. There are basically two mechanisms for retrieving fluorescence emissions from space: filling-in of solar absorption lines and filling-in of atmospheric absorption bands (e.g. oxygen bands). These mechanisms make it possible to distinguish light reflected by the atmospheresurface from fluorescence emissions.



Firstly, for solar absorption lines (i.e. Fraunhofer lines), the mechanism is straightforward and well known: relative depths of Fraunhofer lines in the (continuum of the) radiance spectrum decrease in case of fluorescence emissions. Filled-in Fraunhofer lines can be easily recognized in reflectance spectra. Figure 1 shows monochromatic reflectance spectra and simulated measurements at a spectral resolution of 0.1 nm and

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- 0.5 nm. The atmosphere contains aerosols (aerosol optical thickness of 0.4 and a layer pressure of 700 hPa) over vegetated land (albedo of 0.20) with a representative fluorescence emission  $(1.2 \text{ mW m}^{-2} \text{ sr}^{-1} \text{ nm}^{-1})$ . Simulated measured reflectance spectra in the right panel of Fig. 1 correspond to retrievals in Fig. 4: for details of these simula-
- <sup>10</sup> tions, see Sect. 4.2. One can recognize filled-in Fraunhofer lines in the monochromatic reflectance spectrum between 755 nm and 759 nm (continuum), but note that filling-in of Fraunhofer lines inside the  $O_2$  A band occurs as well. Individual Fraunhofer lines, hence filling-in effects, are hardly resolved at spectral resolutions of 0.1 and 0.5 nm. The dependence of the fluorescence *signal* on spectral resolution, however, can best
- be evaluated using retrieval simulations. Note that for this representative scenario the increase in continuum reflectance (hence in radiance) due to the fluorescence emission is about 2 %.

Secondly, absorption bands of atmospheric constituents, such as oxygen, can also provide information on fluorescence emissions. Photons emitted at the surface pass the atmosphere only once, whereas photons reflected by the surface pass the atmosphere twice before reaching the detector. Thus, fluorescence emissions will contribute relatively more to the top-of-atmosphere radiance at atmospheric absorption bands compared to the continuum (filling-in). For the present study, our interest is in filling-in of the oxygen A band. The  $O_2$  A band consists of many closely spaced absorption

<sup>25</sup> lines, which, like Fraunhofer lines, are not resolved with most current remote sensing instruments. In this paper, we investigate the effect of spectral resolution on retrieval of fluorescence and aerosol parameters in a retrieval simulation study.

If the objective of retrieval is to estimate fluorescence emission itself and if extinction by aerosols can be ignored, using filling-in of Fraunhofer lines outside atmospheric





absorption bands is most efficient (but perhaps not most accurate). Frankenberg et al. (2011a), Joiner et al. (2011) and Guanter et al. (2012) do so when applying their respective retrieval methods to GOSAT radiance spectra to retrieve emissions at 755 nm or 770 nm. The retrieval methods differ with respect to the way the

- <sup>5</sup> fluorescence-free part of the radiance spectrum is modeled. In all cases, complicated radiative transfer calculations are not needed, which enables retrieval of the fluorescence emission at the top of the atmosphere in a fast way. Frankenberg et al. (2012) perform an analysis showing that total atmospheric transmission is typically well above 0.8 for aerosol optical thicknesses (at 760 nm) smaller than 1.0, so that the difference between fluorescence and at the top of the approximation of the atmosphere in a fast way.
- between fluorescence emissions at canopy level and at the top of the atmosphere is rather small. Guanter et al. (2012) apply a post-retrieval correction for aerosol extinction and Rayleigh scattering to arrive at values at canopy level.

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On the other hand, if the objective is retrieval of aerosol parameters from the  $O_2$  A band, the question is whether filling-in of Fraunhofer lines across the  $O_2$  A band as well as filling-in of the  $O_2$  A band itself provides sufficient independent information to

simultaneously retrieve fluorescence and aerosol parameters. (The effect of fluorescence on cloud retrieval from the  $O_2$  A band will be much smaller and we will therefore only consider aerosol retrieval in this paper.)

Frankenberg et al. (2011a) have shown that if fluorescence is not taken into account (i.e. zero emissions assumed in retrieval, emissions not fitted), significant biases in retrieved aerosol parameters (optical thickness, height of the Gaussian layer), surface albedo and surface pressure occur. We have confirmed this finding: for the forward model described in Sect. 2 we find aerosol pressure biases up to 100 hPa and biases in optical thickness up to 2.0 as well as non-convergent retrievals. Apparently, errors

<sup>25</sup> in aerosol and fluorescence parameters are correlated and so part of the fit residue caused by ignoring fluorescence is absorbed by other retrieval parameters. This finding, however, does not prove that it is actually impossible to simultaneously retrieve aerosol and fluorescence parameters. Nevertheless, based on the observation that "if based only on O<sub>2</sub> lines [meant is: if the O<sub>2</sub> A band is fitted], the Jacobians with respect





to scattering properties and fluorescence are not linearly independent", Frankenberg et al. (2011a) conclude that "from space-borne measurements of the  $O_2$  A-band, fluorescence cannot be distinguished from the impacts of aerosols".

- Even if derivatives are to some extent linearly dependent, which they are in this case as well as in many other retrieval problems, parameters may still be fitted with acceptable precision levels. Figure 2 shows normalized derivatives (i.e. normalized to one at 755 nm) of reflectance with respect to surface albedo, aerosol optical thickness and fluorescence emission. Derivatives are calculated at a spectral resolution of 0.5 nm for the same atmospheric scenario as in Fig. 4. Overall, one can see that spectral shapes of the derivatives have similar features. Hence, fluorescence will indeed disturb retrieval of aerosol optical thickness and surface albedo, if it is present and not taken into account. The spectral shapes of the derivatives outside the O<sub>2</sub> A band suggest that we can fit fluorescence but can not distinguish between aerosol optical thickness and surface albedo from the continuum reflectance (red and blue lines coinciding).
- <sup>15</sup> However, the differences in spectral shape inside the O<sub>2</sub> A band are significant, which shows that it is possible to simultaneously fit the three parameters.

In this paper we take a different approach to answering the question how well we can distinguish between fluorescence and aerosol parameters when fitting the  $O_2$  A band. For a number of atmospheric states and instrument properties, we fit fluorescence and aerosol parameters simultaneously and investigate errors in retrieved parameter val-

- aerosol parameters simultaneously and investigate errors in retrieved parameter values. If spectral shapes of derivatives with respect to certain fit parameters become similar (given a particular noise level), precision of these parameters will be poor. In the end, the question whether or not aerosol and fluorescence parameters can be simultaneously fitted should of course be understood in terms of meeting scientific user
- requirements: precision levels reported in this paper can be compared with such requirements to decide whether or not precision levels are indeed acceptable. The focus of this paper is the effect of fitting fluorescence on retrieval precision of aerosol parameters. However, we will also report and analyze retrieval precision of fluorescence emissions.



The instrument noise model that we use for our simulations assumes that measurement noise is dominated by shot noise. Results are thus particularly relevant for missions carrying grating spectrometers for which the shot noise assumption is reasonable. This includes future satellite instruments such as the Tropospheric Monitoring Instrument on the Sentinel-5 Precursor mission (TROPOMI; Veefkind et al., 2012), spectrometers on the Sentinel-5 and Sentinel-4 missions (Ingmann et al., 2012), the

- Orbiting Carbon Observatory-2 instrument (OCO-2; Crisp et al., 2004), and instruments on the Earth Explorer 8 candidate missions Carbon Monitoring Satellite (CarbonSat; Meijer et al., 2012; Bovensmann et al., 2010) and Fluorescence Explorer (FLEX; Kraft
  et al., 2012; ESA, 2008). Current satellite instruments include the Scanning Imaging
- Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY; Bovensmann et al., 1999) and the Global Ozone Monitoring Experiment-2 (GOME-2; Callies et al., 2000).

The paper is structured as follows: Sect. 2 gives a detailed description of the forward
 <sup>15</sup> model. Section 3 describes in more detail the method to calculate retrieval precision.
 Section 4 presents results from the simulations. Section 5 provides a discussion of these results. The main purpose of this paper is to describe precision of aerosol parameters for a generic aerosol retrieval algorithm over vegetated land using the O<sub>2</sub>
 A band and to investigate effects of changing the spectral resolution of the observations. In all cases, fluorescence emission is included as a fit parameter.

#### 2 Forward model

#### 2.1 Overview

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The forward model used to calculate reflectance spectra and derivatives is part of a software package developed at KNMI called DISAMAR. The abbreviation DISAMAR stands for Determining Instrument Specifications and Analyzing Methods for Atmospheric Retrieval. It is a comprehensive tool to support the development at KNMI of





Level-2 algorithms for satellite measurements of backscattered solar radiation. We will only use DISAMAR modules to simulate measured reflectance spectra and calculate their derivatives.

Measured reflectance is defined as

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$$R(\lambda_i) = \frac{\pi I(\lambda_i)}{\mu_0 E_0(\lambda_i)}$$

where  $\mu_0$  is the cosine of the solar zenith angle  $\theta_0$ , and  $I(\lambda_i)$  and  $E_0(\lambda_i)$  are the radiance and solar irradiance measured in the *i*th spectral bin, respectively (the *i*th bin is assigned nominal wavelength  $\lambda_i$ ). When simulating reflectance spectra, measured radiance  $I(\lambda_i)$  and irradiance  $E_0(\lambda_i)$  result after convolving monochromatic (or high-resolution) radiance  $I(\lambda)$  and irradiance  $E_0(\lambda)$  with their respective slit functions. Monochromatic radiance, in turn, is calculated by multiplying monochromatic reflectance from the radiative transfer model with the high-resolution solar irradiance spectrum and adding a fluorescence term. The radiative transfer model also provides derivatives of high-resolution reflectance spectra. These derivatives are appropriately 15 convolved with the radiance slit function to give derivatives of measured reflectance spectra (matrix **K**, see below).

Hence, key elements of the forward model are a *high-resolution solar irradiance spectrum*, an *atmospheric model*, including oxygen absorption cross section data, to describe the atmosphere-surface system, a *radiative transfer model* to calculate <sup>20</sup> monochromatic reflectance and an *instrument model* to describe the physics of the instrument. These elements will be discussed in more detail below.

# 2.2 High-resolution solar irradiance spectrum

We use the high-resolution solar reference spectrum by Chance and Kurucz (2010), which has a full width at half maximum (FWHM) of 0.04 nm and is oversampled by

<sup>25</sup> a factor of four. A correction for the finite resolution of the solar reference spectrum is made by artificially reducing the width of the instrument's slit functions. In addition, we



(1)

only investigate effects of spectral resolution of the observation for FWHMs of 0.1 nm and larger to further avoid artifacts due to the finite resolution of the solar reference spectrum.

We also perform a number of simulations in which we assume a constant irradiance spectrum. When using a flat irradiance spectrum, filling-in of Fraunhofer structure cannot occur.

# 2.3 Atmospheric model

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We choose a simple but generic atmospheric model to describe an atmosphere in which Rayleigh scattering, oxygen absorption, and scattering and absorption by aerosols takes place.

The ground surface is modelled as an isotropically reflecting (Lambertian) surface. Since we are interested in the effect of chlorophyll fluorescence, we only consider a vegetated land albedo  $A_s$  of 0.20 (Koelemeijer et al., 2003). The albedo is assumed to be independent of wavelength across the spectral window.

- <sup>15</sup> Chlorophyll fluorescence is modeled as an isotropic contribution to the upwelling radiance field at the surface in units of photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>. The maximum fluorescence emission near the start of the O<sub>2</sub> A band as retrieved by Guanter et al. (2012) is 1.8 mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> (monthly 2° by 2° average). This value corresponds to 7.0 × 10<sup>11</sup> photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> at the start of the spectral window (758 nm). The fluorescence emission  $F_s$  is fully incorporated in the radiative transfer model: upon transmission to the top of atmosphere, the emission may undergo absorption by oxygen but also Rayleigh scattering and aerosol extinction. The fluorescence emission (in photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>) is assumed to be independent of wavelength
- across the spectral window.
   The conventional unit of fluorescence in the literature is mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>. Fluorescence emissions in our simulations depend on wavelength in that unit. We therefore report simulation results in units of photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>. For comparison with





previous studies, we convert results into units of mW  $m^{-2} sr^{-1} nm^{-1}$  where appropriate, taking 758 nm as the reference wavelength.

An aerosol layer is modelled as a layer of particles with an associated optical thickness  $\tau$  (constant volume extinction coefficient within the layer). Aerosols have a single

- <sup>5</sup> scattering albedo of 0.95 and a Henyey–Greenstein phase function with asymmetry parameter of 0.7. This represents an average aerosol model as compared to long-term AERONET observations by Dubovik et al. (2002). Optical thickness, single scattering albedo and phase function are assumed to be independent of wavelength across the spectral window. Optical thicknesses reported in this paper thus hold for wavelengths of the Q. A hand and are dependent on a function are assumed to be independent of the dependent of the dependen
- $_{\rm 10}~$  of the O\_2 A band and are denoted as  $\tau$  (760 nm).

Furthermore, we take a simplified aerosol profile that consists of a single layer with a fixed pressure difference between top and base of 20 hPa - pressure is the independent height variable. Hence a layer with a mid pressure  $P_{\text{mid}}$  of 700 hPa is located between 710 hPa and 690 hPa.

<sup>15</sup> Finally, we use a Mid-Latitude Summer temperature profile. Rayleigh scattering is specified according to Bodhaine et al. (1999). The surface pressure is 1013 hPa. Oxygen is assumed to have a constant volume mixing ratio of 21 %. Oxygen absorption cross section data are taken from the HITRAN 2008 data base (Rothman et al., 2009).

#### 2.4 Radiative transfer model

- <sup>20</sup> Monochromatic reflectances are calculated with the layer-based orders of scattering method. This is a variant of the doubling-adding method (e.g. De Haan et al., 1987; Hovenier et al., 2004) in which the adding of the different layers is replaced by orders of scattering for the atmospheric layers. Multiple scattering is taken into account, but polarization is ignored. Rotational Raman scattering is ignored as well (see Sect. 5).
- A pseudo-spherical correction is used as in Caudill et al. (1997). The spectral window extends from 758 nm to 770 nm, which covers almost the entire  $O_2$  A band. Wave-lengths beyond 770 nm do not contribute additional information content (Siddans et al.,





2007). Calculations are done accurately using nine Gaussian points for integration over the polar angle (eighteen streams). Other settings for the radiative transfer calculations are optimized for accuracy as well.

It is essential that derivatives are calculated accurately, when assessing whether aerosol and fluorescence parameters can be simultaneously determined from the measurement. Derivatives of monochromatic reflectance with respect to the fit parameters are calculated in a semi-analytical manner using reciprocity (equivalent to the adjoint method; e.g. Landgraf et al., 2001). Such an approach is preferred over numerical techniques (e.g. finite-difference methods), because derivatives can be calculated faster and much more accurately.

#### 2.5 Instrument model

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The instrument model contains slit functions for the convolution of high-resolution radiance spectra, irradiance spectra and derivatives. It also contains a noise model to associate radiance and irradiance spectra with mean noise spectra. These spectra can then be used to calculate mean noise spectra associated with reflectance spectra (measurement covariance matrices  $\mathbf{S}_{s}$ ).

We assume that measurement noise can be characterized by shot noise. In that case, the signal-to-noise ratio (SNR) of the radiance L is proportional to the square root of the radiance (in photons):

<sup>20</sup> SNR( $L(\lambda_i)$ ) =  $f(\lambda_i) \cdot \sqrt{L(\lambda_i)}$ 

In addition, we assume the proportionality factor  $f(\lambda_i)$  to be independent of wavelength. If we know the signal-to-noise ratio for some reference radiance level  $L^{\text{ref}}$  at some reference wavelength  $\lambda_i^{\text{ref}}$ , we can calculate the signal-to-noise ratio for any other radiance level at any other wavelength following



(2)

$$SNR(L(\lambda_i), \Delta \lambda) = SNR(L^{ref}(\lambda_i^{ref}); \Delta \lambda^{ref}) \cdot \sqrt{\frac{L(\lambda_i)}{L^{ref}(\lambda_i^{ref})}} \cdot \sqrt{\frac{\Delta \lambda}{\Delta \lambda^{ref}}}$$

Here, we have also explicitly accounted for the dependence of signal-to-noise ratio on spectral sampling interval  $\Delta\lambda$  (spectral bin). Finally, we assume the signal-to-noise ratio of the irradiance to be a factor of ten higher than the signal-to-noise ratio of the <sup>5</sup> radiance.

The default instrument model for this study consists of anticipated instrument characteristics for TROPOMI (Veefkind et al., 2012). The TROPOMI instrument model will be used in a set of simulations investigating the dependence of retrieval precision on atmospheric parameters. The radiance and irradiance slit functions *S* at the O<sub>2</sub> A band are flat-topped functions with a full width at half maximum of 0.5 nm:

$$S(\lambda_i, \lambda) = \text{const} \cdot 2^{-\left(\frac{\lambda_i - \lambda}{\text{FWHM}/2}\right)^4}$$

The constant const normalizes the slit function to unit area. The spectral sampling interval is 0.1 nm. The signal-to-noise ratio at 758 nm (continuum) is 500 for a reference radiance  $L^{\text{ref}}$  (758 nm) of  $4.5 \times 10^{12}$  photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>. The reference radiance spectrum, which is used for specification of the SNR within the Sentinel-5 and Sentinel-5 Precursor projects, corresponds to a dark scene ("tropical dark", meaning a pure molecular atmosphere with a surface albedo of 0.02, a solar zenith angle of 0° and a viewing zenith angle of 0°). Hence, if clouds or aerosols are present, or if the surface albedo is larger than 0.02, the actual SNR will be (much) larger than 500.

In subsequent simulations, we investigate the dependence of retrieval precision on spectral resolution and signal-to-noise ratio. When decreasing the FWHM, we keep the spectral sampling ratio constant (i.e. five) and adjust the spectral sampling interval  $(\Delta \lambda)$  accordingly (e.g. spectral bin of 0.02 nm at a FWHM of 0.1 nm). We also keep the number of photons entering the detector constant. Hence, signal-to-noise ratio will



(3)

(4)



be scaled according to Eq. (3). Signal-to-noise ratios reported in this paper always are reference values that hold for the default TROPOMI spectral sampling interval of 0.1 nm and the TROPOMI reference radiance at 758 nm mentioned above.

# 3 Error propagation

- For various atmospheric states, observation geometries and instrument properties, we simulate reflectance spectra of the O<sub>2</sub> A band using the forward model described in Sect. 2. We associate these reflectance spectra with corresponding mean noise spectra. The forward model also provides derivatives of reflectance spectra with respect to the various fit parameters (e.g. aerosol and fluorescence parameters). We then calcu-
- <sup>10</sup> late 1- $\sigma$  errors in fit parameters by propagating the measurement noise using these derivatives. Throughout this paper, the term *precision* is used to indicate the random error component (1- $\sigma$  error).

In symbols: let's assume that the forward model F can be linearized for the purposes of an error analysis. We write

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$$\boldsymbol{R} \approx \boldsymbol{F}(\hat{\boldsymbol{X}}) + \boldsymbol{K}(\boldsymbol{X} - \hat{\boldsymbol{X}})$$

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where *R* is the vector of measured reflectances, *x* is the state vector containing the fit parameters and  $\mathbf{K} = \partial F(x)/\partial x$  is the Jacobian matrix (evaluated here at  $\hat{x}$ ). The *i*th element of *R* is the reflectance at wavelength  $\lambda_i$ . The reflectance is subject to measurement noise. The measurement error covariance matrix  $\mathbf{S}_{\varepsilon}$ , describing this random error in *R*, is assumed to be diagonal:

$$S_{\varepsilon})_{ij} = \begin{cases} \sigma_{\varepsilon}^2(R_i), & i = j \\ 0, & i \neq j \end{cases},$$

where  $\sigma_{\varepsilon}^2(R_i)$  is the variance in  $R_i$ . Elements  $\sigma_{\varepsilon}^2(R_i)$  are calculated according to the noise model described in Sect. 2.5. The optimal retrieval solution  $\hat{x}$  is, for example,



(5)

(6)

given by the weighted least-squares solution. The covariance matrix S describing the error in retrieved parameters  $\hat{x}$  due to the measurement error in *R* follows from Eq. (5) using conventional rules for error propagation:

$$\mathbf{S}_{\varepsilon} = \mathbf{K}\hat{\mathbf{S}}\mathbf{K}^{\mathsf{T}} \Rightarrow \hat{\mathbf{S}} = (\mathbf{K}^{\mathsf{T}}\mathbf{S}_{\varepsilon}^{-1}\mathbf{K})^{-1}.$$

Note that **Ŝ** generally has off-diagonal elements: 5

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$$\hat{S})_{ij} = \begin{cases} \sigma^2(\hat{x}_i), & i = j \\ r_{ij}\sigma(\hat{x}_i)\sigma(\hat{x}_j), & i \neq j \end{cases},$$

where  $r_{ii}$  is the correlation coefficient between errors in retrieved parameters  $\hat{x}_i$  and  $\hat{x}_i$ . An alternative retrieval solution is the weighted least-squares solution constrained by a priori knowledge of the atmosphere and surface (e.g. Rodgers, 2000). We will not investigate the role of a priori information, since the focus of the present analysis is the information content of the measurement in absence of a priori knowledge.

A column of **K** corresponds to the derivative of reflectance with respect to a particular fit parameter as a function of wavelength (after appropriate convolution with the slit function). If columns of **K** become strongly linearly dependent, the matrix  $\mathbf{K}^{T}\mathbf{S}_{c}^{-1}\mathbf{K}$  will be nearly singular and the error in some retrieved parameters (diagonal elements of  $\hat{S}$ )

15 will be large. Note that if columns of K become nearly linearly dependent, the solution  $\hat{x}$  will typically also become more sensitive to systematic errors, such as numerical inaccuracies, model biases or calibration errors.

We choose a basic set of fit parameters that would be representative for any typical aerosol retrieval algorithm employing absorption by oxygen in the A band. The set of 20 fit parameters comprises the mid pressure of the aerosol layer ( $P_{mid}$ ), aerosol optical thickness ( $\tau$ ), fluorescence emission ( $F_{c}$ ) and surface albedo ( $A_{c}$ ).



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# 4 Results

# 4.1 Dependence on atmospheric parameters

In a first set of simulations, we investigate the dependence of retrieval precision on atmospheric parameters and solar and viewing zenith angles. We have used the TROPOMI instrument model described in the previous section. Figure 3 shows the dependence of precision of all four fit parameters on aerosol optical thickness for three values of the mid pressure of the aerosol layer. Results are presented for a solar zenith angle of 50° and nadir viewing direction. Each panel corresponds to a different fit parameter: aerosol optical thickness (at 760 nm), mid pressure, fluorescence emission and surface albedo. We will summarize the main findings.

Dependence on fluorescence emission. Fluorescence emissions ranged between zero emission and a maximum emission of  $7.0 \times 10^{11}$  photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> (or  $1.8 \text{ mW m}^{-2} \text{ sr}^{-1} \text{ nm}^{-1}$  at 758 nm). Absolute errors in all four fit parameters are the same when varying fluorescence emissions between zero emission and maximum emission. The results presented in Fig. 3 therefore hold for fluorescence emissions in this range. Relative errors in retrieved fluorescence emission of course decrease with increasing emissions.

Dependence on aerosol optical thickness. Precision of retrieved aerosol optical thickness and aerosol mid pressure improves with increasing  $\tau$  (stronger aerosol signal).

<sup>20</sup> Precision of retrieved fluorescence emission and surface albedo deteriorates with increasing  $\tau$  (shielding of the surface below the aerosol layer).

Dependence on mid pressure. Precision of aerosol parameters improves with decreasing pressure (increasing altitude). At larger pressure differences between aerosol layer and ground surface, it is easier to distinguish aerosol contributions from surface contributions. There is a tendency for precision of fluorescence emission to improve with increasing aerosol pressure (decreasing altitude).

Dependence on solar zenith angle. We have tested retrieval precision for solar zenith angles of  $0^{\circ}$ ,  $50^{\circ}$  and  $75^{\circ}$  (not shown). Precision of aerosol parameters generally





improves with increasing solar zenith angle. If the solar zenith angle increases, a unit area of surface receives less light (weaker aerosol signal) but path lengths through the aerosol layer are longer (stronger aerosol signal). Apparently, the former effect dominates. As for the dependence of precision of retrieved fluorescence emissions on

solar zenith angle, we cannot make any statements with our forward model. We have modeled fluorescence emission at canopy level as being independent of solar zenith angle. However, the broadband downwelling flux of photosynthetically active radiation depends on solar zenith angle and hence so must the fluorescence yield.

Dependence on viewing zenith angle. We have tested retrieval precision for viewing zenith angles of 0°, 50° and 70° (not shown). Precision of aerosol parameters generally improves with increasing viewing zenith angle (longer path lengths through aerosol layer, hence stronger aerosol signal). Precision of retrieved fluorescence emission typically deteriorates with increasing viewing zenith angle (longer path lengths through aerosol layer, more extinction of fluorescence emission, hence weaker fluorescence signal).

#### 4.2 Dependence on instrument properties

In a second set of simulations we investigate the dependence of retrieval precision on spectral resolution and signal-to-noise ratio. We also investigate the relative contributions to the fluorescence signal of filling-in of Fraunhofer lines and filling-in of  $O_2$  lines.

- <sup>20</sup> We assume an atmospheric scenario of an aerosol layer with optical thickness of 0.4 between 710 hPa and 690 hPa, vegetated land with an albedo of 0.20 and a fluores-cence emission of  $4.6 \times 10^{11}$  photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> (or 1.2 mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> at 758 nm). The solar zenith angle is 50° and the viewing direction is nadir. Recall that reported signal-to-noise ratios are reference values that hold for a spectral sampling
- interval of 0.1 nm and the TROPOMI reference radiance at 758 nm. The spectral resolution (FWHM) is varied while keeping the spectral sampling ratio constant (i.e. five). Signal-to-noise ratios are scaled with the square root of the spectral sampling interval (amount of light entering detector is constant).



Figure 4 shows the dependence of retrieval precision on resolution for three values of the signal-to-noise ratio. Precision of all four parameters varies almost linearly with spectral resolution. However, the improvement of precision when going to finer resolutions is modest. Precision levels for every parameter at a FWHM of 0.1 nm are roughly two-thirds of precision levels at a FWHM of 0.5 nm. Furthermore, a change of

the signal-to-noise ratio by a factor of two results in a change of precision levels with a factor of two (we are only considering random errors here).

Figure 5 compares retrieval precision for a true solar irradiance spectrum with retrieval precision if the irradiance spectrum is flat. In the former case, both filling-in of

- <sup>10</sup> the  $O_2$  A band and filling-in of Fraunhofer lines provide information. In the latter case, Fraunhofer lines are not present and only filling-in of the  $O_2$  A band can contribute to the fluorescence signal. We show results for the reference signal-to-noise ratio of 500 (blue dashed lines in Figs. 4 and 5 are the same). One can see that if filling-in of Fraunhofer lines is added, precision improves for all parameters except for mid pressure.
- <sup>15</sup> The decrease of the error is 19% on average for retrieved fluorescence emissions. The improvement of the error in retrieved  $\tau$  is smaller (12% on average). As expected from the previous figure, the relative improvement in precision when adding filling-in of Fraunhofer lines is the same for all three signal-to-noise ratios tested (not shown).

# 5 Discussion

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- In this study, we have investigated precision of retrieved parameters for a generic aerosol retrieval algorithm over vegetated land using the  $O_2$  A band. Chlorophyll fluorescence is taken into account in the forward model. Fluorescence emissions are modeled as isotropic contributions to the upwelling radiance field at the surface and they are retrieved along with aerosol parameters. The set of fit parameters comprises
- the pressure of the aerosol layer, aerosol optical thickness, fluorescence emission and surface albedo. Precision is calculated by propagating measurement noise using the forward model's derivatives.





In a number of retrieval simulations, we have described retrieval precision for various atmospheric states, observation geometries and instrument properties. Our results show that we can, indeed, retrieve fluorescence emission, aerosol optical thickness, aerosol pressure, and surface albedo simultaneously. This finding disagrees with the 5 conclusion drawn by Frankenberg et al. (2011a).

Frankenberg et al. (2012) investigated the sensitivity of the ACOS (Atmospheric Carbon Observations from Space)  $CO_2$  retrieval algorithm (O'Dell et al., 2012) to chlorophyll fluorescence by taking an ensemble approach simulating many atmospheric and observation scenarios. The ACOS algorithm includes the  $O_2$  A band to account for aerosol extinction – but note that trace gas retrieval algorithms typically discard retrieved mixing ratios if retrieved aerosol optical thickness is above a certain threshold (e.g. O'Dell et al., 2012). Frankenberg et al.'s (2012) results show a significant decrease of biases in retrieved  $CO_2$  volume mixing ratios and aerosol parameters when fluorescence is included in the fit. This finding, which is consistent with our results, stands

- <sup>15</sup> in marked contrast with Frankenberg et al.'s (2012) conclusion that "using the potentially added information contained in the O<sub>2</sub> absorption structures seems to do more harm than good for the fluorescence retrieval because interferences are introduced". It seems unlikely that an improved retrieval of CO<sub>2</sub> when fitting fluorescence will at the same time yield biased fluorescence values. Although they acknowledge that these
- interferences "may be due to deficiencies in [their] chosen implementation" (e.g. simplified atmospheric transmission and spectral parameterization of fluorescence emissions in the forward model for retrieval), Frankenberg et al. (2012) conclude that a "fluorescence fit using Fraunhofer lines only (Frankenberg et al., 2011a) results in a much more stable and accurate fit of the NIR chlorophyll fluorescence signal". A fit using
- Fraunhofer lines is fast, but it is not shown whether such a fit is indeed more accurate and more stable. After all, a retrieval based on Fraunhofer lines can only retrieve the fluorescence signal at the top of the atmosphere. Our findings indicate that using the  $O_2$  A band yields an accurate retrieval and that there is no reason in this respect to determine fluorescence from spectral regions outside the  $O_2$  A band.





Whether errors in retrieved parameters are acceptable depends on scientific user requirements. We have reported retrieval errors so that the reader can evaluate their magnitudes. Note that systematic errors, such as model biases and calibration errors, are not included in these error estimates. Errors in retrieved mid pressure, aerosol op-

- tical thickness and fluorescence emission may be put into perspective by comparing them against the benchmark numbers provided in Table 1. If we compare these numbers to retrieval precision for the first set of simulations (TROPOMI instrument model; see Fig. 3), we can make the following observations. Precision of retrieved pressure always is below the TROPOMI target requirement of 50 hPa. For solar zenith angles
- <sup>10</sup> approaching 0° and optically thin layers ( $\tau$  of about 0.2), the error may increase above 50 hPa (not shown) but it remains below the threshold requirement of 100 hPa. Precision of retrieved  $\tau$  compares well with the total uncertainty in MODIS optical thickness (at 550 nm) as found in the large-scale validation study by Levy et al. (2010). Finally, precision of retrieved fluorescence emission is in the same range as the precision re-15 ported by Guanter et al. (2012). For viewing zenith angles approaching 70°, however,
- precision may increase up to  $3 \times 10^{11}$  photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> (not shown).

We have described the dependence of retrieval precision on optical thickness, aerosol pressure, fluorescence emission, and solar and viewing zenith angles. We remark that exceptions to the overall trends described in Sect. 4 exist. We have noticed

- in our work on the O<sub>2</sub> A band that retrieval precision can significantly deteriorate for very specific combinations of aerosol pressure, optical thickness, aerosol properties (phase function and single scattering albedo), surface albedo and observation geometry. These singular cases often occur for optically thin layers over land and may be related (but not limited) to situations of a so-called critical surface albedo (e.g. Seidel
- <sup>25</sup> and Popp, 2012). This illustrates the importance of a proper error analysis: by calculating derivatives we know whether for a specific retrieved state the system is becoming singular.

In addition, we have described the dependence of retrieval precision on spectral resolution and signal-to-noise ratio. Table 2 provides instrument specifications for





a number of satellite grating spectrometers that will be operational in the coming years. We have also calculated the respective reference signal-to-noise ratios (indicated in bold) that hold for the TROPOMI spectral sampling interval and TROPOMI reference radiance (as in Fig. 4). Prospective retrieval precision for the Sentinel-4/5 instruments,

<sup>5</sup> OCO-2 and CarbonSat can be directly evaluated in Fig. 4 using values for the spectral resolution and reference SNR from Table 2. Note that all instruments mentioned in Table 2 are oversampled.

Finally, we have investigated the relative contributions to the fluorescence signal of filling-in of Fraunhofer lines and filling-in of  $O_2$  lines. We have calculated retrieval precision for a true solar irradiance spectrum (filling-in of Fraunhofer lines and  $O_2$  lines) and for a flat irradiance spectrum (filling-in of  $O_2$  lines). Precision of retrieved fluorescence emission improves by 19% on average if we use a solar irradiance spectrum. Hence,

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assuming that the fluorescence signals due to filling-in of Fraunhofer lines and due to filling-in of O<sub>2</sub> lines are uncorrelated (cf. Fig. 1), we see that filling-in of Fraunhofer lines provides a fluorescence signal that is approximately five times weaker than the fluores-

- cence signal due to filling-in of O<sub>2</sub> lines. The contribution of filling-in of Fraunhofer lines to precision of aerosol parameters is even smaller. Note that the relative improvement of precision when adding filling-in of Fraunhofer lines is the same across the range of spectral resolutions (0.1 nm to 0.5 nm). At finer spectral resolutions, not only Fraunhofer lines are better resolved but the O<sub>2</sub> A band is better resolved as well. Also note
- that even at a spectral resolution of 0.5 nm, filling-in effects related to Fraunhofer lines are still resolved to some extent and provide information on fluorescence.

Rotational Raman scattering is not taken into account in this study. There are indications that for typical observation geometries and significant fluorescence emis-

sions (larger than approximately 0.5 mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>) the contribution to the top-ofatmosphere radiance due to Rotational Raman scattering is smaller than the contribution due to fluorescence (Vasilkov et al., 2012; Sioris et al., 2003). At first glance, spectral shapes of the two filling-in effects seem comparable (Vasilkov et al., 2012) but there are slight differences: after all, origins of the respective signals are different.



Rotational Raman scattering is well known and can, at least in principle, be included in the radiative transfer calculations. In that case, rotational Raman scattering does not need to be fitted and fluorescence emissions can still be retrieved. It remains to be investigated what the precise effect of neglecting rotational Raman scattering on retrieval of aerosol from the O<sub>2</sub> A band is.

In our analysis, we assume that the retrieval solution  $\hat{x}$  was found so that we could perform an error analysis. However, the forward model is typically highly non-linear and the retrieval solution has to be found in an iterative manner. Hence, the question is raised what the effect of including fluorescence emission as a fit parameter on the stability of retrieval is. The stability of a retrieval algorithm is difficult to assess in a simulation environment. We did some preliminary tests, which indicated that even with starting values differing strongly from true values retrieval is stable. However, one needs real data in the end to determine the stability and convergence of a retrieval algorithm.

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# **Table 1.** Benchmark numbers for comparing precision of retrieved mid pressure, aerosol optical thickness and fluorescence emission as found in this study.

Param.	Benchmark	Description	Reference
P <sub>mid</sub>	50 hPa (100 hPa)	TROPOMI target (threshold) requirement on precision of retrieved Aerosol Layer Height	Veefkind et al. (2012)
τ <sup>a</sup>	±(0.05 + 15 %) <sup>b</sup>	Large-scale global validation of MODIS aerosol retrievals over "dark" land (e.g. veg- etation) with AERONET sunphotometer mea- surements; error envelope containing two- thirds of all collocations	Levy et al. (2010)
F <sub>s</sub>	$0.4 \times 10^{11}$ -1.5 × 10 <sup>11</sup> photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1c</sup>	Precision of monthly 2° by 2° average $F_s$ values at 755 nm retrieved from GOSAT observations; error estimate includes only measurement noise (similar to Eq. 7)	Guanter et al. (2012)
a at 760 pp	<b>^</b>		

<sup>a</sup>  $\tau$  at 760 nm. <sup>b</sup>  $\tau$  at 550 nm.

 $^{\circ}$  0.1–0.4 mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> at 758 nm.





Table 2	2. Instrument	specifications	of the O <sub>2</sub>	A band	channel for	r a numbei	r of spac	e-borne
grating	spectrometer	s that will be	operational	in the co	oming years	. Numbers	printed b	old can
be used	d to interpret F	<sup>-</sup> ig. 4.						

Instrument	FWHM	Δλ	SNR	L <sub>ref</sub> (758 nm)	Reference	SNR-ref. <sup>a</sup>
TROPOMI <sup>b</sup>	0.5 nm	0.1 nm	500	$4.5 \times 10^{12}$ photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1</sup>	Veefkind et al. (2012)	500
Sentinel-5	0.4 nm <sup>c</sup>	0.13 nm	500	$4.5 \times 10^{12}$ photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1</sup>	ESA (2012)	570
Sentinel-4	<b>0.12 nm</b> <sup>d</sup>	0.04 nm	566	$1.3 \times 10^{13}$ photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1</sup>	ESA (2012)	526
OCO-2	0.042 nm	0.014 nm	814	$3.5 \times 10^{13}$ photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1</sup>	Boesch et al. (2011)	780
CarbonSat	0.045 nm	0.015 nm	340	$2.0 \times 10^{13}$ photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1</sup>	Bovensmann et al. (2010)	416
CarbonSat <sup>e</sup>	0.1 nm	0.033 nm	507	$2.0 \times 10^{13}$ photons s <sup>-1</sup> cm <sup>-2</sup> sr <sup>-1</sup> nm <sup>-1</sup>	Meijer et al. (2012) and	620
					Bovensmann et al. (2010)	

 $^{a}$  Reference SNR under the assumption of shot noise: holds for  $\Delta\lambda$  of 0.1 nm and TROPOMI reference radiance at 758 nm.

<sup>b</sup> Sentinel-5 Precursor.

<sup>c</sup> Threshold value.

<sup>d</sup> Goal value.

<sup>e</sup> Spectral resolution and sampling ratio are taken from Meijer et al. (2012); signal-to-noise ratio and corresponding radiance are taken from Bovensmann et al. (2010) and scaled to the sampling interval of 0.033 nm assuming shot noise.







**Fig. 1.** Left panel: high-resolution reflectance spectrum (left y-axis) with fluorescence emission (" $F_s$ ": blue line) and without fluorescence emission ("no  $F_s$ ": red line), and a high-resolution solar irradiance spectrum (right y-axis, black line). Right panel: the high-resolution reflectance spectrum containing fluorescence emission of the left panel after convolution with the slit function at resolutions (full width at half maximum) of 0.1 nm (magenta line) and 0.5 nm (cyan line). The atmosphere contains aerosols ( $\tau$  of 0.4 and  $P_{mid}$  of 700 hPa) over vegetated land ( $A_s$  of 0.2) with a representative fluorescence emission ( $F_s$  of 1.2 mW m<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup>). The solar zenith angle is 50° and the viewing direction is nadir. Zoom windows highlight filled-in Fraunhofer lines in the continuum; the magenta line in the zoom window of the right panel is given an artificial vertical offset to better reveal small filling-in peaks still visible at this spectral resolution. Simulated measurements in the right panel correspond to retrievals in Fig. 4 described in Sect. 4.2. Note that the fit window extends from 758 nm to 770 nm.



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**Fig. 2.** Derivatives of reflectance with respect to surface albedo ( $A_s$ ), fluorescence emission ( $F_s$ ) and aerosol optical thickness ( $\tau$ ) at a spectral resolution of 0.5 nm and normalized to the respective derivative at 755 nm. Derivatives are for the same atmospheric scenario as in Figs. 1 and 4, which is described in Sect. 4.2. The derivative of reflectance with respect to mid pressure is not shown for clarity.





**Fig. 3.** Precision of all four fit parameters as a function of optical thickness for three values of the mid pressure of the aerosol layer. Top left: aerosol optical thickness ( $\tau$ ); top right: mid pressure ( $P_{mid}$ ); bottom left: fluorescence emission ( $F_s$ ); bottom right: surface albedo ( $A_s$ ). Aerosols have a single scattering albedo of 0.95 and a Henyey-Greenstein phase function with asymmetry parameter of 0.7; the aerosol layer has a pressure thickness of 20 hPa; the surface has an albedo of 0.20 and exhibits fluorescence emissions. Absolute errors were the same across the range of fluorescence emissions investigated (see text). The solar zenith angle is 50° and the viewing direction is nadir. Results hold for the TROPOMI instrument model (FWHM of 0.5 nm). Note that precision values for  $F_s$  and  $A_s$  are scaled with factors  $1 \times 10^{11}$  and  $1 \times 10^{-3}$ , respectively.







**Fig. 4.** Precision of all four fit parameters as a function of spectral resolution for three values of the signal-to-noise ratio. Top left: aerosol optical thickness ( $\tau$ ); top right: mid pressure ( $P_{mid}$ ); bottom left: fluorescence emission ( $F_s$ ); bottom right: surface albedo ( $A_s$ ). Results are for the following atmospheric scenario: aerosol layer at 700 hPa with optical thickness of 0.4, default aerosol model, surface albedo of 0.20, and a fluorescence emission of  $4.6 \times 10^{11}$  photons s<sup>-1</sup> cm<sup>-2</sup> sr<sup>-1</sup> nm<sup>-1</sup> (or  $1.2 \text{ mW m}^{-2} \text{ sr}^{-1} \text{ nm}^{-1}$  at 758 nm). The solar zenith angle is 50° and the viewing direction is nadir. The reference signal-to-noise ratios hold for the TROPOMI reference radiance at 758 nm and spectral sampling interval of 0.1 nm. When varying spectral resolution, signal-to-noise ratios are scaled with the square root of the spectral sampling interval (amount of light entering detector is constant). For details, see Sect. 2.5. Note that precision values for  $F_s$  and  $A_s$  are scaled with factors  $1 \times 10^{11}$  and  $1 \times 10^{-3}$ , respectively.







**Fig. 5.** Precision of all four fit parameters as a function of spectral resolution when Fraunhofer structure is present in the solar irradiance spectrum (" $O_2 + FH$  lines") and when it is not (" $O_2$  lines only"). Top left: aerosol optical thickness ( $\tau$ ); top right: mid pressure ( $P_{mid}$ ); bottom left: fluorescence emission ( $F_s$ ); bottom right: surface albedo ( $A_s$ ). Results are for the same atmospheric scenario and observation geometry as in Fig. 4. The reference signal-to-noise ratio is 500. (Blue dashed lines in this figure and in Fig. 4 are the same.) Note that precision values for  $F_s$  and  $A_s$  are scaled with factors  $1 \times 10^{11}$  and  $1 \times 10^{-3}$ , respectively.

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