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Disentangling chlorophyll fluorescence from atmospheric scattering effects in O_2A-band spectra of reflected sun-light.

C. Frankenberg,[1] A. Butz,[2] G.C. Toon,[1]

[1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, USA
[2]SRON Netherlands Institute for Space Research, Sorbonnelaan 2, NL-3584 CA Utrecht, The Netherlands

Retrieval interferences between fluorescence and scattering properties

We perform a retrieval simulation on (1) how the fluorescence emission F_s^{TOA} affects the retrieval of surface and scattering parameters from space-based observations of the O_2A-band and on (2) how the retrieval of such parameters can mask the fluorescence signal. Here, we consider as retrieval parameters surface pressure p_s, Lambertian surface albedo r, the aerosol optical density τ (AOD in main text) and the center height z of an aerosol layer. We simulate a measurement $\vec{y}$ by a forward model $\vec{f}(F_s^{rel} > 0, p_{true}, r_{true}, \tau_{true}, z_{true})$ that takes fluorescence emission into account. Given the synthetic measurement, we retrieve the target parameters by a retrieval forward model $\vec{f}(F_s^{rel} = 0, p, r, \tau, z)$ that neglects fluorescence.

For the full physics retrieval, the forward model $\vec{f}$ is based on the radiative transfer (RT) model developed by *Hasekamp and Landgraf* (2002, 2005) and extensively used for CO_2 and CH_4 retrievals by *Hasekamp and Butz* (2008), *Butz et al.* (2009), and *Butz et al.* (2010). The RT model calculates spectra of sunlight backscattered by the Earth's surface and atmosphere considering absorption and (multiple) scattering by molecules and particles in a multi-layer, plane parallel atmosphere. The RT model also provides the Jacobians with respect to the parameters p, r, τ, and z and thus allows for their retrieval.

Fluorescence emission is simulated by adding $\vec{F}_s^{TOA}$ as given by equation (1) to the RT modeled spectra. Thereby, we explicitly consider re-absorption of the fluorescence emission by O_2 between the surface and top-of-the-atmosphere (TOA), but we neglect scattering of the emitted fluorescence for simplicity. The modeled spectra and Jacobians are convolved by an instrument line shape that mimics the spectral resolution of a GOSAT-like observer (Fourier transform spectrometer with 2.5 cm optical path difference and 15.8 mrad full-angle field-of-view). Measurement noise is assumed vanishing. In analogy to equation (2), we use a non-linear weighted least-squares method to find the retrieval parameters p, r, τ, and z or a subset of these. In contrast to the simplified fluorescence retrieval, the full-physics retrieval is performed in intensity space as, due to noise and the sinc-type instrumental line-shape, negative radiances can be observed.

The simulation is performed for a scene (p_{true} = 1013 hPa, r_{true} = 0.4) with a moderate aerosol load (τ_{true} = 0.15 at 765 nm) of fine aerosol particles in a layer close to the surface (Gaussian layer centered at z_{true} = 2 km, full-width-at-half-maximum 1 km). The assumed composite aerosol consists of non-absorbing Mie-particles with a refractive index of 1.43 following a power-law size distribution according to *Mishchenko et al.* (1999) with size parameter $\alpha = 4.5$. A GOSAT-like instrument observes the scene at exact nadir and solar zenith angle (SZA) 45°. The input solar irradiance (Fig. S1, panel a) is modeled as described below and then normalized to a continuum value of 1. The assumed plant fluorescence emission at the surface (Fig. S1, panel b) amounts to roughly 1.5% of the reflected radiance (Fig. S1, panel c) with a smooth spectral dependence as suggested by *Meroni et al.* [2009]. The fluorescence signal at TOA $\vec{F}_s^{TOA}$ (Fig. S1, panel d) clearly shows re-absorption by O_2 along the light-path from the surface to TOA.

We undertake 5 retrieval simulations. Fig. S1, panels e through i, illustrate the results and spectral fitting residuals. In a first exercise (Fig. S1 panel e), we allow for the retrieval of the albedo parameter r only. Next, we simultaneously retrieve albedo r and aerosol optical density τ (Fig. S1 panel f). Then, we further add aerosol height z as retrieval parameter (Fig. S1 panel g). These three panels correspond to the lower three panels of Fig. 1 in the

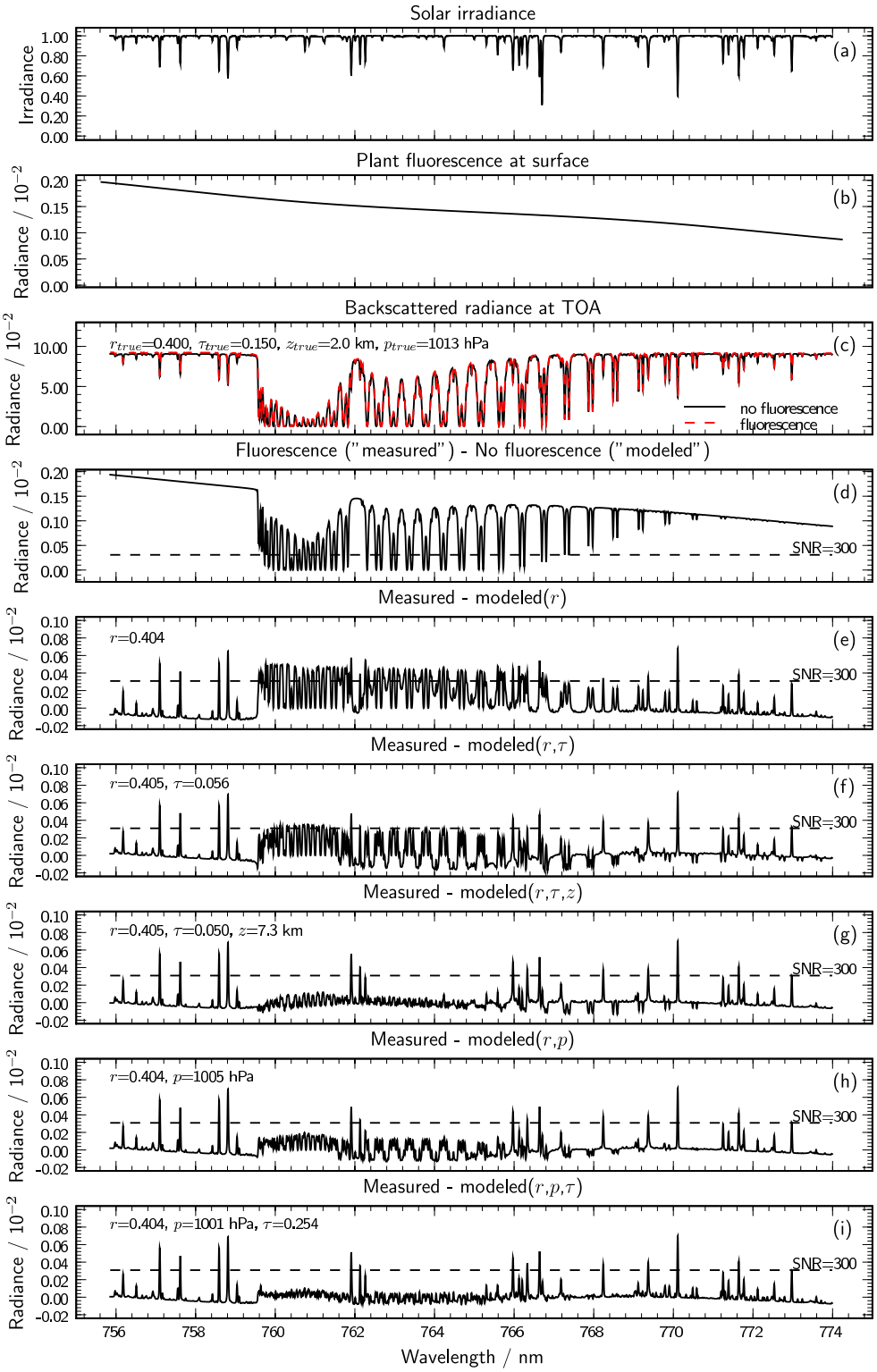

Figure S1: Retrieval simulations of a typical O_2A-band fit neglecting the impact of a $\approx 1.5\%$ fluorescence emission. Different fit parameters are used and the respective fit residuals shown in panels e-i. See text for details.

main text. In addition to those cases, we allow for simultaneously retrieving albedo r and surface pressure p (Fig. S1 panel h) and additionally aerosol optical density (Fig. S1 panel i).

These exercises reveal that fluorescence emission amounting to 1.5% of the backscattered radiance can induce substantial errors in retrieved surface pressure (error ∼10 hPa) and aerosol optical density (error ∼0.1) as well as errors in aerosol layer height and surface albedo. Thus, fluorescence emission is not negligible when aiming at retrieving surface and aerosol parameters from the O_2A-band. Further, the spectral fitting residuals illustrate that surface and scattering parameters can efficiently mask the fluorescence signal. Given a signal-to-noise of 300, all retrieval exercises tried here - with exception of the albedo-only retrieval (Fig. S1 panel e) - reduce the spectral fluorescence signal below the noise level in the O_2 absorption lines. In particular, a simultaneous retrieval of albedo, aerosol optical density, and aerosol layer height yields virtually vanishing residual fluorescence features in the O_2 absorption lines. In reverse, a retrieval of the fluorescence signal using the filling-in of O_2 absorption lines would require highly accurate *a priori* knowledge of surface and scattering properties which is typically not available. Although the O_2 features can be fitted nicely using a forward model that neglects F_s, it is impossible to fit the solar Fraunhofer lines.

Solar model

An empirical model of the solar transmission spectrum is used to calculate the depths and shapes of the Fraunhofer absorption lines. This uses a solar linelist containing the positions, strengths and widths of the absorption lines, together with a subroutine encoding the assumed functional form of the lineshape. As preparatory work for the OCO mission, the solar spectrum in the A-band region was carefully tested and the linelist generated from high resolution spectra acquired by the Kitt peak FTS, both disk-center and disk-integrated. The solar model was validated in the A-band region using high resolution solar occultation spectra measured from balloons (courtesy of Sebastian Payan and Claude Camy-Peyret, CNRS, Paris, and Ron Blatherwick and Frank Murcray, Denver University). Since the isolated solar lines used in this study are also isolated from telluric lines in Kitt peak spectra, their depth and shape is especially well known. This solar model has been widely used for analysis of ground-based FTS spectra (e.g., TCCON).

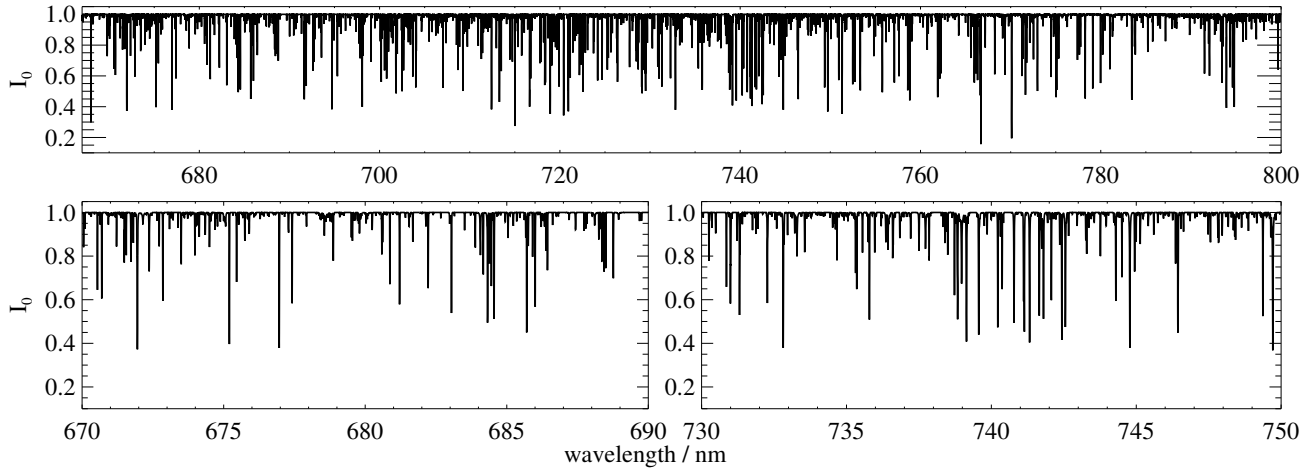

Figure S2: Solar transmission spectra at full spectral resolution for the whole wavelength region where fluorescence occurs (top panel) as well as a zoom on the fluorescence peak region around 680 and 750 nm in the lower two panels.

Fig. S2 shows the solar transmission spectrum for the entire wavelength range, where chlorophyl fluoresces. The lower panels depict zooms on the regions of peak fluorescence emission. There is a tremendous wealth of Fraunhofer lines in the entire spectrum and a retrieval based on Fraunhofer lines only should be feasible in the entire range when recorded with high spectral resolution (and sufficient SNR). In general, the precision error of the least-squares fit largely decreases with a) the strength (depth) of the Fraunhofer lines and b) the amount of lines within a retrieval window. Since the relative fluorescence signal F_s^{rel} in the 680 nm region is far higher than in the O_2A-band, high

resolution spectra in this region, as proposed in FLEX, will yield higher precision. However, for FLEX we would recommend higher spectral resolution and focus on Fraunhofer lines, not only O_2 absorption features.

Least-squares retrieval approach

In contrast to the formulation of the full-physics forward model and retrieval problem described earlier, the F_s retrieval can be greatly simplified as no radiative transfer scheme is necessary. Our approach is based on standard non-linear weighted least-squares fits, solving an overdetermined problem with far more measurements than unknowns in the presence of measurement error. In the following, we briefly describe the methods employed in the paper.

The simplified forward model as described in the main text is

$$\vec{f}(F_s^{rel}, a, b) = \log\left(< \vec{I_0} + F_s^{rel} >_{b_1,b_2}\right) + \sum_{i=0}^{n} a_i \cdot \lambda^i \,.$$

Strictly speaking, F_s^{rel} is not exactly the relative contribution to the continuum radiance but almost identical at low percentage levels. $F_s = F_s^{rel}/(1 + F_s^{rel}) \cdot R_{cont}$ properly takes this into account. The convolution $<>$ with the instrumental line-shape function ϕ is defined as

$$< I(\lambda) >= \int_{-\infty}^{\infty} I(\lambda') \cdot \phi(\lambda - \lambda') d\lambda'$$

The convolution has to be performed at very high spectral resolution, fully resolving the Fraunhofer lines of the incoming solar radiation. The convolution is the most time-consuming step in our retrieval and we use Fast Fourier Transform convolution routines to enable an efficient and fast retrieval. The convolved spectrum (at high spectral resolution, $\Delta\lambda \approx 0.0005 - 0.001\, nm$) then has to be mapped to the spectrometer wavelength grid $\lambda_i, ..., n$, (lower spectral resolution, $\Delta\lambda \approx FWHM/3$ in our case in order to sample ϕ), which can be defined as

$$\lambda_i = b_1 + b_2 \cdot i$$

where b_1 represents a spectral shift and b_2 a spectral stretch. For the sake of simplicity, $<>$ as used in the paper denotes the combination of convolution and mapping. In order to solve the non-linear least squares problem, the Jacobians of $\vec{f}$ are needed. $\partial\vec{f}/\partial b_i$ are computed with finite differences, $\partial\vec{f}/\partial a_i$ is λ^i and

$$\frac{\partial \vec{f}}{\partial F_s^{rel}} = \frac{1}{< \vec{I_0} + F_s^{rel} >} \approx \frac{1}{< \vec{I_0} >} \,.$$

Given the measurement vector $\vec{y} = \log(R(\lambda))$, the solution to the problem (minimizing spectral residuals) solve the normal equation (minimizing the squared differences) in a non-linear way:

$$x_{i+1} = x_i + (K_i^T \, S_\epsilon^{-1} \, K_i)^{-1} K_i^T \, S_\epsilon^{-1} \cdot (\vec{y} - \vec{f}(x_i)) \,,$$

where K_i is the Jacobi matrix $\frac{\partial f}{\partial x}$ evaluated at x_i and the state vector x reads

$$x = \begin{pmatrix} F_s^{rel} \\ a_1 \\ \vdots \\ a_n \\ b_1 \\ b_2 \end{pmatrix} \,.$$

The inverse problem with respect to F_s^{rel} is almost linear but b_1 and b_2 are highly non-linear, requiring iterations (convergence is typically achieved within 2-5 iterations). A physical origin of a shift and/or squeeze is not only spectrometer calibration (e.g. shift due to changes in optical bench temperature). The relative velocity of the Earth and the Sun caused by the Earths rotation and the ellipticity of the Earth's orbit about the Sun also produces daily and seasonal Doppler shifts in the solar lines.

As in standard weighted least-squares methods, $(K^T \, S_\epsilon^{-1} \, K)^{-1}$ represents the error covariance matrix $\hat{S}$ of the retrieved state vector x, directly providing the statistical error estimates as presented in the main text.

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