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Journal Pre-proof

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Highlights

- New radiative transfer and retrieval pipeline designed for occultation data.
- Able to correct for uncertainties in multiple instrumental parameters.
- Results validated to be within 2% of existing radiative transfer codes.

Journal Pre-proof

The RISOTTO radiative transfer and retrieval pipeline for the analysis of occultation spectra

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Abstract

We present a new radiative transfer and retrieval pipeline, referred to as RISOTTO, designed for observations made in occultation geometry. RISOTTO can retrieve accurate vertical profiles of the constituents of a planetary atmosphere using a Bayesian approach while simultaneously correcting for instrumental artefacts and uncertainties. The algorithm makes use of a rapid Abel integration scheme involving matrix multiplication, using pre-calculated gaseous cross-section data to calculate the integration along the line of sight, while also separating out any effects of transmission baseline variation. We assess its accuracy using synthetic solar occultation spectra of Mars and comparing it with the older more established NEMESIS radiative transfer and retrieval pipeline (Irwin et al. 2008, *J. Quant. Spec. Radiat. Transf.* 109, 1136-1150), and show that it can match its accuracy while also being able to more easily retrieve gases with substantial continuum absorption.

Keywords: Radiative transfer, Retrievals, Atmospheres, composition

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1. Introduction

Solar and stellar occultation observations of a planetary atmosphere using high-resolution spectroscopy provide a valuable means of measuring vertically resolved atmospheric abundance profiles of different gaseous species[1], with the geometry of the spacecraft designed to detect radiation that passes through the atmosphere tangentially to the surface. This geometry maximises the optical path of radiation that passes through the atmosphere, and thus the total absorption of a given gaseous species, allowing for the detection of trace gases at quantities far lower than ground-based or nadir observations are able to achieve. The occultation process involves viewing a bright source with a very well-characterised emission spectrum, such as the sun or a distant star, providing a simple baseline reference from which the transmission of radiation through the atmosphere can be calculated. To extract scientific information out of these spectral data, a radiative transfer and retrieval pipeline is required. The aim of the radiative transfer model is to simulate gaseous absorption along the line of sight, while the retrieval stage then uses this model to convert input values of transmission into realistic vertical gas profiles and, where applicable, to extract information on vertical temperature and pressure variations.

In this work, we present the code for Retrievals in the Infrared of Solar Occul- TaTiOns (RISOTTO), a new retrieval algorithm based on Bayesian inference with an implemented forward model that can retrieve atmospheric profiles using a rapid and optimised matrix inversion scheme. This code is also capable of simultaneously correcting for minor instrumental artefacts in the data, together with any distortions of the spectral baseline (for instance due to aerosol absorption), and can provide a first-order quantification of the signal-to-noise ratio (SNR) of each spectrum in the occultation without needing any prior information on sources of noise. Unlike many other similar radiative transfer and retrieval tools, it is gen-

28 eralisable and does not rely on large amounts of prior information on technical
29 instrumental parameters. This therefore makes it run more efficiently, have a sim-
30 pler user interface, and is easier to tailor and customise to the instrument or the
31 spectral domain at hand.

32 Occultation observations usually have two main aims: firstly, to find evidence
33 of trace gases in a planetary atmosphere and provide accurate detection limits in
34 the case of non-detection; and secondly to constrain the climatology of the planet
35 through vertically-resolved observations of known gases in the atmosphere. These
36 two objectives require very different retrieval techniques. In the former case, the
37 retrieval algorithm has to be robust to a very large uncertainty on *a priori* vertical
38 variations of gaseous abundances (if the molecule has never been detected on the
39 planet before, there is by definition no prior information on the vertical profile of
40 the gas, and so the *a priori* uncertainty is close to infinite) while also having to
41 clearly distinguish a detection from a non-detection. In the latter case, there is less
42 uncertainty on the prior profile but the algorithm has to produce vertical profiles
43 of gaseous compounds to very high accuracy and precision.

44 In Section 2 we describe how the code estimates the signal-to-noise ratio of
45 the spectrum, together with reference molecular absorption data and instrumental
46 parameters, and thereby calculates a forward model of the spectrum through path
47 integration along the line of sight. In Section 3 we then describe the inversion
48 algorithm that results in atmospheric profiles that provide an optimal fit to the
49 observed spectra given the aforementioned forward model. We show that the re-
50 sults obtained using this method are accurate by comparing them with the results
51 obtained from similar data using a different, more established, radiative transfer
52 and retrieval code called NEMESIS [2] in Section 4. Finally, we provide some
53 concluding remarks in Section 5.

2. Forward model

2.1. Definition

The aim of a forward model is to be able to compute a simulated set of transmission values given a vector of known variables that we refer to as the *state vector*. We distinguish two sets of variables that make up the state vector: *scientific* variables which define the properties of the atmosphere that we wish to investigate in the first place, and *instrumental* variables which define properties of the spectra that are related to calibration defects or uncertainties. We focus on three of these corrections in particular: those due to uncertainties in the transmission baseline (continuum modelling), those due to uncertainties in the instrumental line shape (ILSF modelling), and those due to uncertainties in the spectral registration (spectral law derivation). We assume the following model to derive the corrected transmission values T_{cor} from a set of transmission values T_{mod} modelled according to the wavenumber grid λ_{mod} with respect to which the molecular cross-sections are stored:

$$T_{cor}(\lambda_{cor})_i = C(\lambda_{cor})_i \sum_j K(\lambda_{cor}, \lambda_{mod})_{ij} T_{mod}(\lambda_{mod})_j \quad (1)$$

where C is the continuum model and K is the instrument line shape model. This parameter K takes into account both the modelled wavenumber grid λ_{mod} and the estimated wavenumber grid of the observed data λ_{cor} (both in units of cm^{-1}). We discuss these three instrumental variables individually in section 2.2, and then describe how scientific variables are used to calculate T_{mod} in sections 2.3 - 2.5.

2.2. Instrumental variables

2.2.1. Spectral Law Derivation

A first guess of spectral registration can be made using reference solar or stellar lines that are present in the spectrum (eg. [3]), but is not usually sufficient

78 for accurate fitting of high-resolution spectra, especially in wavenumber regions
 79 where these reference lines are lacking. This means that a second spectral reg-
 80 istration process is needed to further refine the first guess. The forward model
 81 assumes a polynomial relationship between λ_{mod} and λ_{cor} :

$$\lambda_{cor} - \lambda_{ref} = \begin{pmatrix} a_0 & a_1 & a_2 & \dots & a_n \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_{mod} - \lambda_{ref} \\ (\lambda_{mod} - \lambda_{ref})^2 \\ \vdots \\ (\lambda_{mod} - \lambda_{ref})^n \end{pmatrix} \quad (2)$$

82 where the polynomial coefficients $\begin{pmatrix} a_0 & a_1 & a_2 & \dots & a_n \end{pmatrix}$ are variables of the
 83 model to be retrieved. For relatively small wavenumber ranges, a linear relation-
 84 ship ($n = 1$) is usually sufficient, while retrievals of higher-order terms may be
 85 required for larger wavenumber ranges. The wavenumber λ_{ref} is a single arbitrary
 86 wavenumber value (usually fixed to the average of λ_{mod}) that acts as a centralising
 87 factor for when the wavenumber values in λ_{mod} are of several orders of magnitude
 88 larger than zero (e.g. in the near-infrared where $\lambda_{mod} \sim 10^5 \text{ cm}^{-1}$), and to thereby
 89 make the retrieval of higher-order polynomial coefficients more efficient.

90 This spectral shift correction process only works when λ_{mod} and λ_{cor} are al-
 91 ways close enough that a modelled gas absorption peak cannot be fully resolved
 92 spectrally from an observed gas absorption peak, that is to say that $\lambda_{mod} - \lambda_{cor}$ can-
 93 not be greater than the full-width half maximum (FWHM) of a given absorption
 94 line. In cases where this is not satisfied, an approximate correction may need to
 95 be made manually after a single forward model, which the retrieval algorithm can
 96 then refine further as necessary.

2.2.2. Instrument Line Shape Function model

The finite spectral resolution of an instrument usually results in an instrumental signature, or Instrumental Line Shape Function (ILSF) that distorts an observed spectrum through convolution in a manner that is often, but not always, well-characterised. The algorithm is currently equipped to model an ILSF according to a simple Gaussian, although additional types of ILSF can easily be added to the algorithm according to the instrument at hand. The term $K(\lambda_{cor}, \lambda_{mod})_{ij}$ in Equation 1, which solely depends on a single retrievable parameter p_{gauss} defined as the spectral resolution in units of $R = \frac{\lambda}{\Delta\lambda}$, would therefore be represented as follows:

$$K(\lambda_{cor}, \lambda_{mod})_{ij} = \frac{1}{\sigma N_i} \exp\left(-\frac{1}{2} \left(\frac{\lambda_{cor(j)} - \lambda_{mod(i)}}{\sigma}\right)^2\right) \quad (3)$$

where $\sigma = \frac{\bar{\lambda}_{mod}}{2\sqrt{2\ln(2)}p_{gauss}}$ describes the standard deviation of the Gaussian in wavenumber units, and $N_i = \sum_j K(\lambda_{cor}, \lambda_{mod})_{ij}$ is a normalisation factor.

2.2.3. Continuum model

Often the baseline, or continuum level, of a given transmission spectrum can exhibit unwanted distortions due to a number of factors such as instrumental noise, poor calibration or the presence of aerosol. This provides an additional source of uncertainty particularly when measuring the abundances of certain molecules that exhibit substantial continuum absorption at the given spectral resolution.

A prior continuum model is therefore found by linearly interpolating over local maxima in a spectrum and then smoothing the resulting line [4], which we usually find provides a better first guess to the baseline level than the more established convex and concave hull methods [5]. Although the shape of the baseline level is refined further in the retrieval process, a constraint must be placed on it to prevent it from overfitting the spectra. This is done by multiplying a diagonal matrix of the continuum uncertainties σ_i^2 with a kernel function to give a prior continuum

121 covariance matrix \mathbf{C}_{cont} that induces a correlation between neighbouring points on
 122 the continuum. Empirically we find that a Matérn kernel [6] provides the best fit:

$$C_{contij} = \sigma_i \left(\frac{2^{1-\nu}}{\Gamma(\nu)} \left(2 \frac{|\sqrt{(i-j)^2} \sqrt{2\nu}}{\rho} \right)^\nu K_\nu \left(2 \frac{|\sqrt{(i-j)^2} \sqrt{2\nu}}{\rho} \right) \right)_{ij} \sigma_j \quad (4)$$

123 where $\Gamma(\nu)$ is the Gamma function, K_ν is the modified Bessel function of the
 124 second kind and ν is an integer that controls how the correlation changes with
 125 distance from a given point. The parameter ρ is the key constraint on the fitting
 126 of the continuum - the lower the value the higher the frequency of the baseline
 127 variation in wavenumber space. Hence a value of ρ that is too large may underfit
 128 the spectrum by neglecting medium-frequency variations in the baseline, while a
 129 value of ρ that is too small may overfit the spectrum and mistake any instrumental
 130 artefacts or genuine gas absorption features for variations in the baseline.

131 The advantage of this method is that it allows greater flexibility in the con-
 132 tinuum level for a given retrieval while minimising the possibility of overfitting.
 133 This enables a much more efficient fitting procedure of species with substantial
 134 continuum absorption where the baseline level is uncertain - upper limits on these
 135 species can be derived directly through a single retrieval without the need for
 136 a complex continuum subtraction procedure, as explained further in section 4.2.
 137 However, if total flexibility of the continuum over all wavenumbers and tangent
 138 heights is required, the speed of the retrieval may be much slower since the num-
 139 ber of state vector variables required will be equal to the total number of spectral
 140 points.

141 2.3. Scientific variables

142 Given the information available in the mid-infrared, we distinguish three sets
 143 of scientific variables in the model: vertical gaseous abundance profiles, vertical
 144 temperature profiles and a reference pressure value P_0 known *a priori* at a fixed

altitude, usually the surface ($z_0 = 0$ km). In order to calculate the vertical pressure profile $P(z)$, we make two assumptions. Firstly, we assume that the atmosphere is an ideal gas. Secondly, we assume that the relationship between temperature and pressure at a given altitude grid z_j can be described according to the hydrostatic approximation:

$$P(z_j) = P_0 \exp \left(- \sum_{i=0}^{j-1} \frac{z_{i+1} - z_i}{2} \left(\frac{Mg(z_{i+1})}{RT_{i+1}} + \frac{Mg(z_i)}{RT_i} \right) \right) \quad (5)$$

where N is the total number of altitude gridpoints, M is the molar mass of the planetary atmosphere (assumed constant with altitude and location), $g(z_i)$ is the gravitational acceleration, R is the universal gas constant and T_i is the temperature at altitude z_i .

If there is some uncertainty in the ILSF, gaseous abundance retrievals may be degenerate with temperature and pressure. In this case, either a fixed pressure-temperature profile must be assumed (using a prior obtained either from a separate instrument or from a theoretical model) or the profile of another gas (such as CO_2 in the case of Mars or CH_4 in the case of Jupiter and Saturn) must be assumed to be fixed and relatively well-mixed in the atmosphere at the required altitudes. An example of the latter case will be discussed further in section 4.1.

2.4. Molecular cross-sections

For a given molecule, a Humlíček algorithm [7] is used to calculate molecular absorption cross-sections $\sigma(p_i, t_j, \lambda_k)$ as a function of wavenumber λ_k from a set of source line data (e.g. the HITRAN 2016 database [8]), assuming a Voigt line-shape. These are calculated independently for a set of n_i pressure grid values (p_i , in units of Pascals) and n_j temperature grid values (t_j , in units of Kelvin), chosen to efficiently sample the variation in molecular absorption for a temperature and pressure parameter space suitable for the planetary atmosphere in question. The

cross-sections could then be linearly interpolated to intermediate temperature and pressure values during the forward modelling process, but this is both slow and increases the probability of inducing errors in the optical path integration due to aliasing or undersampling.

If we therefore assume that, for a given molecule, the molecular absorption cross-section at a given wavenumber λ_k can be represented as a quartic surface with respect to temperature T and the logarithm of pressure $\ln(P)$:

$$\sigma_k(P, T) \approx C_{00(k)} + C_{10(k)} \ln(P) + C_{01(k)} T + C_{11(k)} \ln(P) T + C_{20(k)} \ln(P)^2 + C_{02(k)} T^2 \dots + C_{44(k)} \ln(P)^4 T^4 \quad (6)$$

or equivalently:

$$\sigma_k(P, T) \approx \text{trace}(\mathbf{C}_k \mathbf{M}) \quad (7)$$

with \mathbf{M} defined as follows:

$$\mathbf{M} = \begin{pmatrix} \ln(P)^0 \\ \ln(P)^1 \\ \vdots \\ \ln(P)^4 \end{pmatrix} \begin{pmatrix} T^0 & T^1 & \dots & T^4 \end{pmatrix} \quad (8)$$

then one can solve a set of $n_i \times n_j$ simultaneous equations for the coefficients in \mathbf{C}_k substituting the cross-section values pre-calculated at the aforementioned temperature and pressure grid into equation 6:

$$\left\{ \begin{array}{l} \sigma_k(p_1, t_1) = C_{00(k)} + C_{10(k)} \ln(p_1) + C_{01(k)} t_1 + C_{11(k)} \ln(p_1) t_1 \\ \quad + C_{20(k)} \ln(p_1)^2 + C_{02(k)} t_1^2 \dots + C_{44(k)} \ln(p_1)^4 t_1^4 \\ \sigma_k(p_2, t_1) = C_{00(k)} + C_{10(k)} \ln(p_2) + C_{01(k)} t_1 + C_{11(k)} \ln(p_2) t_1 \\ \quad + C_{20(k)} \ln(p_2)^2 + C_{02(k)} t_1^2 \dots + C_{44(k)} \ln(p_2)^4 t_1^4 \\ \vdots \quad \quad \quad \vdots \\ \sigma_k(p_{n_i}, t_{n_j}) = C_{00(k)} + C_{10(k)} \ln(p_{n_i}) + C_{01(k)} t_{n_j} + C_{11(k)} \ln(p_{n_i}) t_{n_j} \\ \quad + C_{20(k)} \ln(p_{n_i})^2 + C_{02(k)} t_{n_j}^2 \dots + C_{44(k)} \ln(p_{n_i})^4 t_{n_j}^4 \end{array} \right. \quad (9)$$

181 These coefficients C_k can be pre-calculated once and then stored in look-up ta-
 182 bles as a function of wavenumber. The look-up tables can then be directly loaded
 183 into the forward model when needed, and then the cross-section values calcu-
 184 lated at the required temperature and pressure grid using the matrix multiplication
 185 scheme in equation 7. We find that this method is usually around 3-4 times faster
 186 than linear interpolation.

187 2.5. Path integration through an Abel approximation scheme

188 Our forward model relies on two major assumptions. Firstly, we assume that
 189 all radiation from the sun passes directly through the atmosphere into the detector
 190 without any diffuse component from scattering in the atmosphere or from surface
 191 reflection. This is often an assumption made for solar occultation retrievals con-
 192 ducted in the mid-infrared (e.g. [9, 10]) and a further analysis on the applicability
 193 of this assumption to planetary solar occultation spectra can be found in [11]. Any
 194 extinction due to the presence of aerosol in the atmosphere is assumed to be broad
 195 relative to the observed gas absorption peaks given the spectral resolution, and is
 196 therefore removed during the baseline correction process. Secondly, we assume
 197 that the atmosphere is spherically symmetric and that gas abundances only vary

with altitude. Since we are observing the atmosphere at the limb, we can assume an optical path that is exactly perpendicular to a tangent point at a distance z_T directly above the planetary surface, and therefore simplify the calculation of slant opacity using the Beer-Lambert Law to an Abel integral equation (e.g. [12]):

$$\tau_{T\lambda} = 2 \int_{R_T}^{\infty} \sum_{m=1}^{N_m} \frac{\rho(z)x_m}{M} \sigma_{m\lambda}(z) \frac{R_T + z}{\sqrt{(R_T + z)^2 - (R_T + z_T)^2}} dz \quad (10)$$

where σ is the extinction cross-section of a molecule (of volume mixing ratio x_m) at a given wavenumber λ and as a function of altitude z from the surface, and R_T is the planetary radius below the observed tangent height. M is the molar mass of the planetary atmosphere which is assumed to be constant with altitude. The factor of 2 in the integral is to account for both the incoming and outgoing stream of radiation through the atmosphere, which is illustrated further in figure 1.

We assume that the total number density of molecules ρ in the atmosphere at each altitude gridpoint z_j can be described according to the Ideal Gas Law:

$$\rho(z_j) = \frac{P_j}{k_B T_j} \quad (11)$$

with k_B referring to the Boltzmann constant.

We also assume that the molecular absorption cross-sections $\sigma_{m\lambda}(z)$ vary continuously with altitude z :

$$\sigma_{m\lambda}(z) = \sum_{p=0}^{n_p} a_{mpj\lambda} z^p \quad (12)$$

The values $a_{mpj\lambda}$ are found by calculating sample reference values $\sigma_{m\lambda u}$ at discrete altitude gridpoints z_u (with associated pressure values P_u and temperature values T_u), and then performing an interpolation of degree n_p to an arbitrary intermediate altitude z_j :

$$a_{mpj\lambda} \equiv \sum_{u=1}^N C_{ju}^{(p)} \sigma_{m\lambda u} \quad (13)$$

217 The set of matrices $C_{ju}^{(n_p)}$ therefore represents a function for linear interpolation
 218 (if $n_p = 1$) or cubic spline interpolation (if $n_p = 3$) of $\sigma_{m\lambda}$ from one set of altitude
 219 gridpoints z_u to another set of altitude gridpoints z_j . This has two purposes: firstly,
 220 to remove an integration singularity when $z = z_T$, and secondly to account for
 221 the fact that the cross-sections are dependent on pressure and temperature which
 222 themselves vary continuously with altitude. We find empirically that cubic spline
 223 interpolation provides the best trade-off between accuracy and speed.

224 We can therefore define a matrix A_{Tu} , referred to as the *Abel kernel*, which is
 225 derived from the substitution of equations 12-13 into equation 10:

$$A_{Tu} = 2 \sum_{j=1}^{N-1} \sum_{p=0}^3 C_{ju}^{(p)} \int_{\delta_{jt} z_T + (1-\delta_{jt}) z_j}^{z_{j+1}} z^p \frac{R_T + z}{\sqrt{(R_T + z)^2 - (R_T + z_T)^2}} dz \quad (14)$$

226 Hence, equation 10 can be approximated through quadrature as follows:

$$\tau_{\lambda T} \approx \sum_{u=1}^N \sum_{m=1}^{N_m} \frac{\rho_u}{M} A_{Tu} \sigma_{m\lambda u} x_{mu} \quad (15)$$

227 and so:

$$T_{mod}(\lambda_{mod})_j = \exp(-\tau_{\lambda T}) \quad (16)$$

228 where t in this equation is equal to the index of the altitude gridpoint that is
 229 located just below z_T , and δ_{jt} is the Kronecker delta function. The integral in
 230 equation 14 is solved through global adaptive quadrature.

231 Equation 15 can therefore allow us to calculate modelled transmission spectra
 232 $\exp(\tau_{\lambda T})$ from a series of vertical profiles of gas abundance x_{mu} through a simple
 233 matrix multiplication, where the Abel kernel A_{Tu} only needs to be calculated once

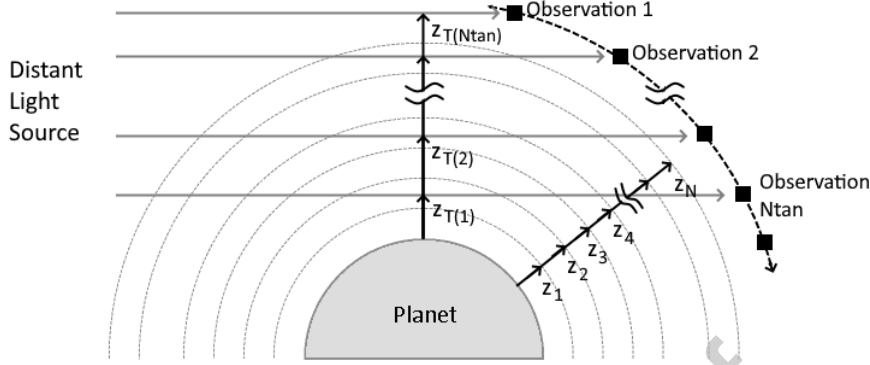


Figure 1: A diagram of a given occultation consisting of N_{tan} individual observations of the atmosphere of a planet, adapted from Figure 1 of Takagi et al. [13]. A spacecraft in orbit around the planet performs multiple observations of a distant light source directly through the atmosphere, with the optical path of the radiation for each observation, marked in grey, passing through the atmosphere parallel to the surface at a given tangent point. The altitude of the path above the tangent point is referred to as a ‘tangent height’ z_T , with each observation associated with a unique tangent height. This is not to be confused with the designation z which refers to the height above the surface of a given atmospheric layer (marked in the semicircular dotted lines) at which a gas abundance or temperature value is evaluated.

at the beginning of the retrieval. We find an altitude grid sampling $z_{i+1} - z_i$ comparable to the difference in altitude between adjacent observations in the occultation is sufficient to provide adequate vertical resolution without compromising on speed.

2.6. Estimation of the signal-to-noise ratio

In order to accurately constrain detection limits for minor species, a reasonable estimation of the signal-to-noise ratio (SNR) of the spectrum at each diffraction order and tangent height is required. We intend to approximately estimate the total SNR of a spectrum without any prior information either on sources of instrumental noise (eg. thermal dark current) or on the forward model. To this end, we compared three different noise quantification models:

Method 1 Calculate the standard deviation of the difference between the original spectrum and the spectrum smoothed by a Gaussian filter of a set number

of pixel widths, removing anomalous values of the difference greater than 3 sigma. The estimate of the SNR is then calculated by dividing the median of the unsmoothed spectrum by the difference value extrapolated to a filter width of 0.

Method 2 Calculate the difference between the original spectrum and the spectrum smoothed by a Gaussian filter, and then derive the SNR through the inverse of a robust estimate of the difference value ($1.4826 * \text{mean absolute deviation}(\text{unsmoothed spectrum} - \text{smoothed spectrum})$)

Method 3 Find all the local maxima present in the spectrum smoothed by a Gaussian filter, and then estimate the SNR from the median of the spectrum divided by the average variance in the spectrum around each local maximum.

In Figure 2 we compare the accuracy of these three methods for a number of synthetic occultations fixed to a given SNR. We find that Method 3 generally provides the most accurate estimations of SNR over the widest range of noise values, especially for solar occultation spectra of Mars like those observed by the Trace Gas Orbiter/Atmospheric Chemistry Suite (ACS) instrument with SNR values in the thousands [14]. However, Method 2 may be more accurate for values of SNR ~ 10 -100 as can be found more typically in mid-ultraviolet observations of stellar occultations of Mars by the SPICAM instrument [15] on board Mars Express, as well as of similar observations by the SPICAV instrument on board Venus Express [16].

The main advantage in our quantification of SNR compared with other retrieval models is that it does not either require any prior knowledge of the instrumentation nor does it require multiple retrievals to accurately refine. However, it cannot easily take into account wavenumber dependency in SNR. In addition, the noise profile cannot account for either large individual artefacts or systematic

offsets in the spectrum, perhaps resulting from uncertainties in the forward model or errors in background correction.

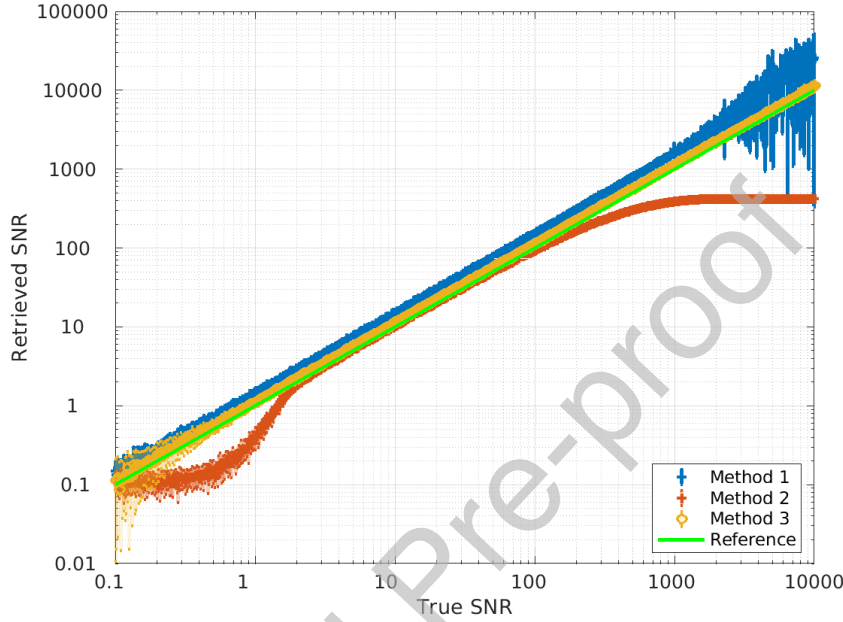


Figure 2: SNR estimation for a number of synthetic transmission spectra, with random Gaussian noise of a given SNR added to the spectrum as shown on the x-axis, and then re-evaluated using the three different methods explained in the text as shown on the y-axis. The green line shows the optimal case where the SNR is calculated to perfect accuracy and precision. We find that method 2 tends to provide the most accurate estimates for SNR values of ~ 10 -100, but method 3 can provide reasonable estimates over a much wider range of SNR values.

3. Retrieval model

3.1. Gauss-Newton iteration scheme

The aim of a retrieval algorithm is to find a set of atmospheric parameters for which the forward model results in a set of simulated transmission values that provides the best fit to the observed transmission data. In practice, this is complicated by the presence of noise and systematics in the spectrum and by the

fact that the problem does not always have a unique solution. For instance, a gas profile that oscillates wildly over a characteristic length that is smaller than the vertical resolution will result in the same observed spectrum as a gas profile that varies smoothly with altitude. Indeed, if too little constraint is placed on the retrieval this is exactly what will occur, in a process known as *ill-conditioning* [2]. We therefore implement a Bayesian optimal estimation approach that relies on some prior constraints on the atmospheric parameters we wish to retrieve. As we essentially follow a similar procedure to the one described by equations 2.16 - 2.31 in Rodgers et al. [17], we will only summarise the main steps here and leave the reader to consult said work for a more detailed derivation of each equation.

Let x be a state vector and y be a vector of observed transmission values (the *measurement vector*), so that $P(y|x)$ describes the likelihood function of the transmission values calculated using the forward model. To provide some constraint on the retrieval, we provide an initial state vector (also known as the *prior state vector*) consisting of educated guesses of each of the scientific and instrumental variables to be retrieved. In addition, we provide a corresponding set of *prior covariance* values that estimate the degree of certainty on each of the initial guessed values and the degree to which they correlate with each other. These prior state vector and covariance values therefore describe an *a priori* probability function $P(x)$. We can therefore easily derive an *a posteriori* probability function $P(x|y)$, that is to say the probability of obtaining a set of instrumental and scientific variables given a set of observed transmission values, according to Bayes' theorem:

$$P(x|y)P(y) = P(y|x)P(x) \quad (17)$$

where $P(y)$ is a normalisation factor.

Let S_y be a covariance matrix where the diagonal values give the estimated spectral uncertainty as calculated according to the signal-to-noise estimation method

previously described in section 2.6 (we generally do not assume spectral correlation and so set non-diagonal values to zero). If the probability functions are all assumed to follow a Gaussian distribution, it can be shown that the most likely value of x , that is to say the maximum value of $P(x|y)$, involves minimising a cost function ϕ :

$$\phi = (y - \mathbf{K}_n \mathbf{x}_n)^T \mathbf{S}_y^{-1} (y - \mathbf{K}_n \mathbf{x}_n) + (\mathbf{x}_n - \mathbf{x}_0)^T \mathbf{S}_0^{-1} (\mathbf{x}_n - \mathbf{x}_0) \quad (18)$$

The left-hand side ensures a good fit to the spectrum by minimising the difference between the measurement vector y and the forward model $\mathbf{K}_n \mathbf{x}_n$ computed following the n th iteration of the retrieval, while the right-hand side prevents ill-conditioning by using the prior state vector \mathbf{x}_0 (of covariance \mathbf{S}_0) as a constraint on the optimal retrieved state vector solution \mathbf{x}_n .

Nonetheless, if the optimal state vector is too far from the prior, the problem becomes non-linear. Assuming low non-linearity, the optimal solution can be found through a Gauss-Newton iteration scheme:

$$\mathbf{x}_{i+1} = \mathbf{x}_0 + \mathbf{S}_0 \mathbf{K}_i^T (\mathbf{K}_i \mathbf{S}_0 \mathbf{K}_i^T + \mathbf{S}_y)^{-1} (y - \mathbf{K}_i \mathbf{x}_i + \mathbf{K}_i (\mathbf{x}_i - \mathbf{x}_0)) \quad (19)$$

and the *a posteriori* covariance on the final state vector can then be found as follows:

$$\mathbf{S}_n = (\mathbf{S}_0^{-1} + \mathbf{K}_n^T \mathbf{S}_y^{-1} \mathbf{K}_n)^{-1} \quad (20)$$

where the derivation of the Jacobian matrix $\mathbf{K}_n = \frac{dy}{dx_n}$ is described in the Appendix for each variable type.

The quality of each forward model is quantified by a reduced χ^2 parameter, which is equal to the left-hand side of the cost function described in equation 18:

$$\frac{\chi^2}{n_y} = \frac{1}{n_y} (\mathbf{y} - \mathbf{K}_i \mathbf{x}_i)^T \mathbf{S}_y^{-1} (\mathbf{y} - \mathbf{K}_i \mathbf{x}_i) \quad (21)$$

where n_y is the total number of data points. Ideally, the value of the reduced χ^2 parameter should decrease with each iteration of equation 19, however this may not be the case if the problem is highly non-linear. Hence, if the reduced χ^2 increases after a single iteration, a step damping procedure is conducted where a fraction of the nominal step $\mathbf{x}_{i+1} - \mathbf{x}_i$ is chosen that minimises the reduced χ^2 .

The iteration scheme ends either when a local minimum in the reduced χ^2 is found, when the maximum number of iterations has been exceeded, or when the change between two subsequent forward models is below a threshold value $\sqrt{F_{tol}}$:

$$\frac{1}{n_y} (\mathbf{K}_{i+1} \mathbf{x}_{i+1} - \mathbf{K}_i \mathbf{x}_i)^T \mathbf{S}_i^{-1} (\mathbf{K}_{i+1} \mathbf{x}_{i+1} - \mathbf{K}_i \mathbf{x}_i) < F_{tol} \quad (22)$$

3.2. Constraints on the prior likelihood function

In this model, we are dealing with two separate aims, as previously described in Section 1, that require a different treatment of the prior likelihood function described by \mathbf{x}_0 and \mathbf{S}_0 . The first aim is to constrain vertical profiles of gases that are known to exist in the atmosphere. In this case, gas abundance profiles extracted from theoretical models usually provide an adequate prior. Empirically we find that the standard deviation on the prior abundance of each gas m can usually be set to equal around 100% as shown in Figure 3. Non-diagonal covariances are derived by convolving the diagonal terms of the covariance matrix ($\sigma(z)$) with a Gaussian kernel:

$$S_{0m(ij)} = \sigma_i \exp\left(\frac{-4 \ln(2)(z_i - z_j)^2}{\rho^2}\right) \sigma_j \quad (23)$$

where the term ρ is referred to as a ‘correlation length’ (in km), a higher value of which results in a smoother profile. The value of this term should be set accord-

ing to the vertical sampling of the occultation data. The second aim is to derive stringent upper limits in the case of a non-detection of a particular gas species. Since these species are undetected, we have zero prior information on their abundances by definition. In this case, we wish to make the prior abundances equal to 0 at all altitudes, with diagonal variances $S_{0m(ii)}$ made as large as possible and non-diagonal covariances $S_{0m(i \neq j)}$ derived through a similar kernel convolution.

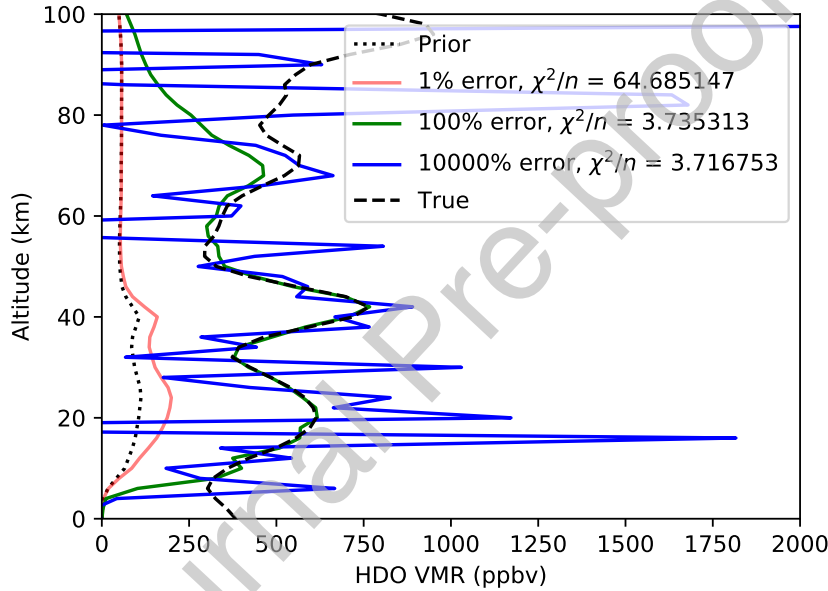


Figure 3: The effect of changing the prior uncertainty on a retrieved profile of HDO to best fit a set of synthetic spectra produced by a forward model of a synthetic ‘true’ profile of HDO (black, dashed). In the case of the retrieved profile marked in red, the prior uncertainty is only 1%, resulting in insufficient flexibility in the HDO profile to enable it to fit the observed spectra and hence a very poor χ^2/n value. In the case of the retrieved profile in blue, you have the opposite extreme, where the prior error is 10,000% and for which there is insufficient constraint on the retrieval to converge to a physical solution, resulting in an ill-conditioned, highly oscillating profile. A 100% prior error results in the most realistic profile that provides the best fit to the occultation.

In the case of a non-detection of a gaseous species, the probability distribution of retrieved abundances should approximate a Gaussian around a mean volume mixing ratio of zero. The standard deviation would roughly equal the instrumen-

tal detection limit of the species, which itself would be dependent on both the presence of noise in the spectrum and the sensitivity of the spectrum to that particular species. A consequence of this Gaussian probability assumption is that the retrieved abundance of a gas that is not present in the atmosphere would be equally likely to be negative as it would to be positive. Negative gas abundances are of course unphysical, but are nonetheless useful when assessing the sensitivity of a spectrum to a particular gas. A retrieved VMR that is negative is usually an indication either of ill-conditioning or of a genuine lack of sensitivity at a given altitude. For this reason, we do not choose to restrict our gas volume mixing ratios to be exclusively positive by performing retrievals in logarithmic space. This also removes a source of bias and allows smoother convergence to a solution.

4. Validation

4.1. Comparison with the NEMESIS radiative transfer and retrieval tool

We validated the retrieval model by generating a set of synthetic spectra for a Mars-like atmosphere using the forward model of a well-established radiative transfer and retrieval tool known as NEMESIS [2, 18], and then attempting to retrieve them using RISOTTO starting from a relatively distant prior. In this section we present two sets of retrievals that demonstrate the accuracy of RISOTTO: one of vertical abundance profiles given a fixed temperature-pressure profile, and one of temperature given a fixed CO₂ volume mixing ratio and base pressure value. An arbitrary ILSF and linear offset value of the wavenumber grid is specified in the NEMESIS forward model itself, and then we add random Gaussian noise corresponding to a deliberately high SNR (~100,000). However, NEMESIS is not currently designed for automatic transmission baseline correction, and can only output and retrieve spectra with a flat baseline. For both sets of retrievals, we therefore compare two scenarios: one in which the transmission baseline is cali-

brated perfectly to unity at all wavenumbers, and one in which the transmission baseline is distorted in order to test the continuum subtraction model. In the latter case, we perform our own low-frequency baseline distortion using a set of random values before then attempting the retrieval with RISOTTO. This distortion model takes three separate effects into account: a) a polynomial component $P(\lambda')$ representing simple baseline distortions due to calibration errors, b) a sinusoidal component $S(\lambda')$ representing distortions in the continuum due to the presence of broad aerosol absorption features, and c) an exponential component $A(z_T)$ representing attenuation along the line of sight at a given tangent height z_T , due to an aerosol layer of fractional scale height z_{scale} present below an altitude z_{knee} :

$$T'(\lambda, z_T) = T(\lambda, z_T)A(z_T)[P(\lambda') + S(\lambda')] \quad (24)$$

Definitions are as follows:

$$P(\lambda') = 1 + a_0 + a_1\lambda' + a_2\lambda'^2 \quad (25)$$

$$S(\lambda') = A_1A_2 \sin(k_1\lambda' + \phi_1) \sin(k_2\lambda' + \phi_2) \quad (26)$$

$$A(z_T) = \begin{cases} \exp\left(\frac{z_T - z_{knee}}{z_{scale}}\right) & z_T < z_{knee} \\ 1 & z_T > z_{knee} \end{cases} \quad (27)$$

$$\lambda' = \lambda - \bar{\lambda} + \lambda_{rand} \quad (28)$$

where $\bar{\lambda}$ is the central wavenumber (in cm^{-1}) and the coefficients $\{a_0, a_1, a_2\}$, $\{A_1, A_2\}$, $\{k_1, k_2\}$, $\{\phi_1, \phi_2\}$ and λ_{rand} are all random numbers that vary from tangent height to tangent height. For both sets of retrievals we have chosen arbitrary values of $z_{knee} = 32$ km and $z_{scale} = 15$ km.

In the first set of retrievals, we chose a wavenumber range of 2932 - 2938 cm^{-1} , and injected a volume mixing ratio of 1% water vapour and 500 ppbv of formaldehyde (H_2CO) into the NEMESIS forward model, both constant with altitude. At this wavelength range, we are sensitive to three prominent absorption lines of H_2^{16}O centred on 2933.7 cm^{-1} , 2935.1 cm^{-1} and 2936.9 cm^{-1} respectively, with a smaller broad absorption feature centred on 2933.2 cm^{-1} . Several smaller $\text{H}_2^{12}\text{C}^{16}\text{O}$ absorption lines are found scattered throughout this wavelength range as well, including a line that almost directly overlaps with the 2933.7 cm^{-1} H_2^{16}O absorption feature. The cross-section values for these gases were calculated according to the HITRAN 2016 database [8]. We assumed a fixed isothermal profile at a temperature of 180 K and a reference pressure at the planetary surface, estimated by the Mars Climate Database [19] given an arbitrary set of spatio-temporal variables, to be 5.46 mbar. The pressure values were then extrapolated to higher altitudes according to equation 5. The atmosphere was assumed to have a constant molar mass of 43.34 g mol^{-1} . Since the gaseous abundances are degenerate with respect to both temperature and pressure, we chose to completely fix the temperature-pressure profile in the RISOTTO model to the aforementioned values, and only allow the instrumental variables and the molecular abundance profiles to vary in the model, starting from a prior of 1% H_2O and 100 ppbv of H_2CO at all altitudes. We chose to generate spectra with NEMESIS at tangent height values regularly spaced 1 km apart between 0 km and 20 km, and 2 km apart between 20 km up to the top of the atmosphere at 122 km. This tangent height grid spacing was chosen in order to reconcile speed and memory constraints with regards to NEMESIS on one hand, and a broad and regular vertical sampling of the atmosphere on the other hand, with the narrower spacing below 20 km chosen in order to better sample the vertical pressure variation which is taken into account differently in NEMESIS. For comparison, we also ran an additional forward

422 model using NEMESIS with tangent heights spaced apart at 2 km intervals over
423 the whole vertical range, for which we attempted to retrieve the molecular abun-
424 dance profiles using RISOTTO as in the previous cases. By contrast, the vertical
425 altitude spacing for the abundance profiles in the RISOTTO retrieval was chosen
426 to be 1km over the whole atmosphere in all cases. In addition, we attempted to re-
427 retrieve the profiles using NEMESIS itself starting from the same prior values, in
428 order to provide a visual indication of the uncertainty on the retrieved values due
429 to the finite SNR, particularly at higher altitudes where sensitivity to molecular
430 absorption is weak.

431 Figure 4a shows a comparison between the vertical water vapour and formalde-
432 hyde profiles retrieved in all the aforementioned cases, with examples of the cor-
433 responding spectral fits in figure 5. For these retrievals the correlation lengths of
434 the molecular profiles, in both the NEMESIS and RISOTTO cases, were set delib-
435 erately lower than they would in a real retrieval, in order to reduce the smoothness
436 of the profiles so that the horizontal oscillations in abundance roughly reflect the
437 *a posteriori* uncertainties on the retrieved values. In addition, there is a differ-
438 ence in the lower boundary condition between NEMESIS and RISOTTO due to
439 differences in layer splitting, which should only affect the retrieved abundance at
440 the lowest altitude gridpoint, but the difference can affect higher altitudes if the
441 profile is set to be too smooth. For altitudes above around 20 km we find that
442 the correspondence between the original forward model from NEMESIS and the
443 retrieved abundance profiles from RISOTTO is consistently accurate to within 2%
444 at most. The retrieved water vapour and formaldehyde values then start becoming
445 less precise above an altitude of around 90 km and 70 km respectively, with the
446 difference relating to the fact that the H_2CO lines are weaker and so the spectral
447 sensitivity decreases more with increasing altitude. Above these altitudes, the er-
448 rors in the retrieved values are dominated by noise, a lack of spectral sensitivity

and, for the very highest altitudes, differences in where the top of the atmosphere is defined. This is also reflected in the attempt at re-retrieval of the profiles using NEMESIS itself, with the degree of oscillation around the forward modelled value roughly equalling that of RISOTTO.

Allowing the continuum to be retrieved induces little error on the vertical profiles above z_{knee} , apart from at very high altitudes where the noise level and the decreasing sensitivity to gaseous absorption increases the uncertainty on the baseline level. Below z_{knee} , some increase in uncertainty is observed, especially with H_2CO where the attenuation of the signal results in a decrease in spectral sensitivity to the absorption lines, approximately doubling the total uncertainty at the lowest altitudes.

Below 20 km, however, there are some small systematic differences in the retrieved values between NEMESIS and RISOTTO. This is mostly due to differences in how the gas absorption cross-sections are calculated at a given pressure. In NEMESIS, these are calculated through a simple linear interpolation with respect to cross-sections at a known pressure and temperature grid. In addition, NEMESIS calculates the line of sight integral through a layer-by-layer summation, where each layer is completely homogeneous and the pressure and temperature values of each layer are calculated according to the Curtis-Godson approximation. By contrast, in RISOTTO the calculated absorption cross-sections vary continuously with respect to altitude according to equation 12. This is more clearly illustrated in Figure 4a by the fact that decreasing the spacing of spectral observations below 20 km dramatically reduces the discrepancy between the forward model and the water vapour profile retrieved by NEMESIS. Nonetheless, even in the worst case the error this pressure degeneracy induces is only of the order of around 5% at most, which in practice for a real retrieval would be substantially lower than the error due to noise and other systematics in the spectra.

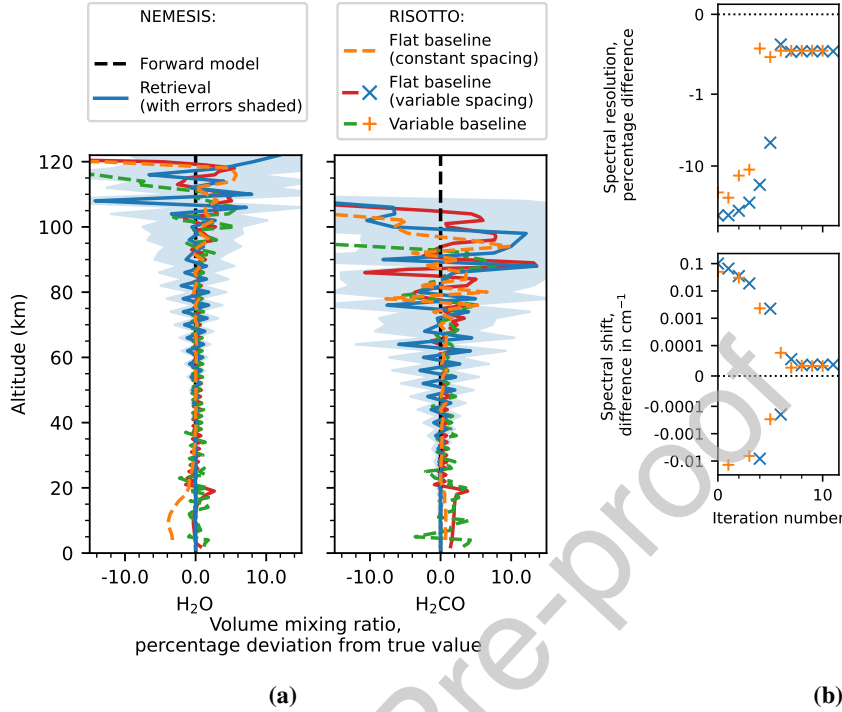


Figure 4: (a) A comparison of the percentage error on the abundances of water vapour and formaldehyde retrieved from a set of spectra generated using a NEMESIS forward model, showing the percentage deviation from the ‘true’ profiles used as an input in the NEMESIS forward model. We note that, for altitudes where there is reasonable sensitivity to the retrievals, the RISOTTO profiles are true to the forward model within around 1-2%, with some greater uncertainties possible at lower altitudes where the change in absorption cross-section with pressure starts to become substantial (the spike in the red and green profiles around 20 km is due to the discontinuity in the tangent height grid). (b) Convergence of the RISOTTO flat variable baseline retrieval cases to the NEMESIS forward modelled values of ILSF and spectral offset (black dotted lines), as a function of iteration number, where iteration number 0 is equal to the prior value. We should note that both graphs in (b) are plotted on a symmetric log-scale on the y-axis, that is to say that the values vary logarithmically except within the lowest major tick marks where they vary linearly with y. We therefore show that the ILSF converges to within around 0.5% of the ‘true’ ILSF value and within around $5 \times 10^{-5} \text{ cm}^{-1}$ of the ‘true’ wavenumber offset value.

In Figure 4b we plot the convergence of the ILSF and spectral law respectively as a function of iteration number for the RISOTTO flat and variable continuum cases respectively. Both cases converge within around 0.5% of the ‘true’ ILSF value from the NEMESIS forward model (equivalent to a Gaussian with a FWHM of 0.15 cm^{-1} as specified by NEMESIS, or a spectral resolution power of

approximately 19550 in RISOTTO terms), and to within an order of magnitude of 10^{-5} cm^{-1} of the true wavenumber offset value. In these cases the most important source of error would be the spectral sampling (equivalent to around 0.05 cm^{-1} in Figure 5).

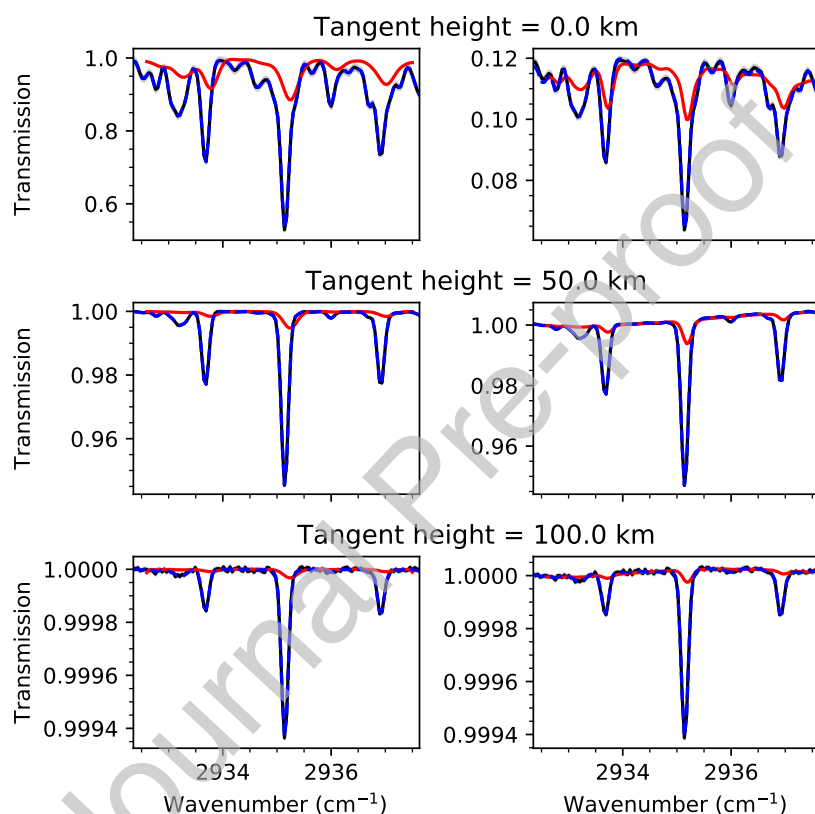


Figure 5: Diagram of convergence of the RISOTTO code to a synthetic spectrum (in black) generated by NEMESIS at a set of sample tangent heights above a surface value, for the set of retrievals shown in Figure 4a. For the spectra in the left column, the baseline was left unaltered and fixed in the RISOTTO retrieval (corresponding to the retrieval in red from Figure 4a), for the spectra in the right column, the continuum was distorted and retrieved (corresponding to the equivalent retrieval in green from Figure 4a). The prior RISOTTO forward model, in red, starts from H_2O and H_2CO volume mixing ratios a factor of 10 and 5 respectively below the ‘true’ NEMESIS forward model values, as well as a spectral resolution of $R \sim 10,000$ (vs approximately 19,550 from the NEMESIS forward model) and a constant spectral shift of 0.1 cm^{-1} to the right of the NEMESIS wavenumber grid. We can see a good convergence, in the blue dashed line, to the true spectrum in both cases, with both the true and the retrieved spectral fits barely distinguishable.

485 In order to validate the temperature retrieval, we chose to perform a second for-
 486 ward model of a set of CO₂ lines using NEMESIS between a wavenumber range of
 487 3804 - 3810 cm⁻¹ and then retrieve the temperature profile again using RISOTTO.
 488 We used CO₂ as a proxy for a gas with a known abundance that is well-mixed in
 489 the atmosphere, and so for which a temperature profile can be retrieved without
 490 worrying about degeneracies between abundance and temperature. We assumed
 491 an atmosphere with a constant volume mixing ratio of 95% CO₂ with altitude,
 492 and a fixed reference pressure value of 5.46 mbar at the planetary surface as with
 493 the previous set of retrievals. These were all made invariable in the RISOTTO
 494 retrieval model as well. Given these constraints, we modelled an isothermal at-
 495 mosphere of 180 K using NEMESIS, and then offset the wavenumber grid, added
 496 noise and distorted the transmission baseline as before. The only scientific vari-
 497 able that was therefore allowed to vary in the RISOTTO retrievals was the vertical
 498 temperature profile (with instrumental variables retrieved as before), for which we
 499 started with an isothermal prior profile of 210 K.

500 Figure 6 shows the resulting retrieved profiles from RISOTTO, in both flat and
 501 variable continuum cases. Although there is a consistent increase in error with alti-
 502 tude due to small differences in how the density scale height is calculated between
 503 RISOTTO and NEMESIS, we still find that below around 100 km the profiles re-
 504 trieved with RISOTTO are consistently within about 1% of the NEMESIS forward
 505 modelled values, with the error tending towards the prior only at higher altitudes
 506 where sensitivity to the spectral lines begins to be lost. The systematic difference
 507 in the upper atmosphere can of course be mitigated by increasing the altitude at
 508 which the reference pressure value is fixed, although this will of course come at the
 509 price of lesser accuracy at lower altitudes. The disadvantage of this method is that
 510 it does usually require a single pressure value to be known *a priori*. Nonetheless
 511 this is a common assumption made in atmospheric retrievals where there is not

512 enough information to completely disambiguate temperature and pressure (e.g.
 513 [20]). The ILSF and spectral law were observed to converge to within a similar
 514 margin of error as in the previous set of retrievals of water vapour and formalde-
 515 hyde abundance. Differences in the retrieved temperature profile between the flat
 516 and variable continuum cases were seen to be negligible below around 90 km,
 517 above which point the noise level and the decreasing sensitivity to the CO₂ lines
 518 induces greater error on the location of the baseline. In any case we find a good
 519 fit to the spectra in both cases below said altitudes as shown in figure 7.

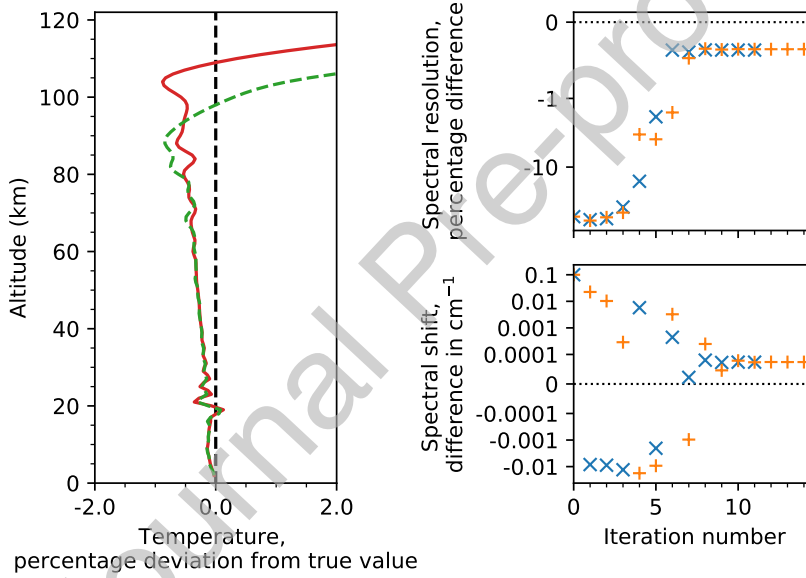


Figure 6: (left) Percentage error in the retrieved temperature profile from RISOTTO compared with the original NEMESIS forward model (black, dashed), assuming a surface pressure value of 5.46 mbar and a ‘true’ isothermal temperature profile of 180K at all altitudes. The RISOTTO retrievals in this case started from a prior isothermal temperature profile of 210 K at all altitudes. The red profile relates to the RISOTTO retrieval for a flat continuum while the green profile relates to the equivalent retrieval for a distorted baseline. We observe that the RISOTTO retrievals are within 1% error of the NEMESIS forward modelled values below 100 km, with a slight increase in error with altitude from the surface due to differences in the density scale height. On the right is shown the convergence of the RISOTTO flat (blue crosses) and variable (orange crosses) continuum retrievals to the NEMESIS forward modelled values of ILSF and spectral shift (black dotted lines, with both modelled values equivalent to those shown in figure 4b) as a function of iteration number. We find a similarly accurate retrieval of both quantities compared with the case in figure 4b.

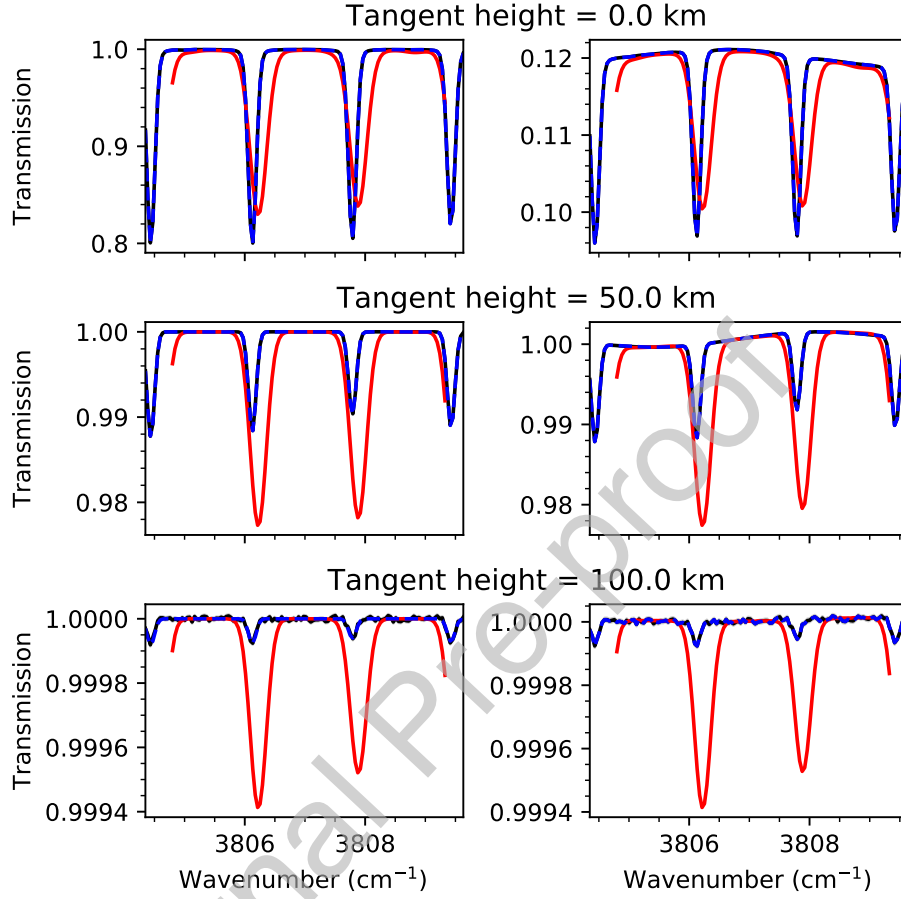


Figure 7: Fit to the NEMESIS forward modelled spectra (black) achieved by RISOTTO for the temperature retrievals shown in figure 6, (left) with a flat unity baseline and (right) with a distorted baseline, at a set of sample tangent heights. All absorption lines shown in this plot are due to the presence of $^{12}\text{C}^{16}\text{O}^{16}\text{O}$. The prior fit to the spectra is shown in red in both cases, for a prior isothermal temperature profile of 210K, a prior spectral resolution of $R \sim 10,000$ (vs approximately 19,550 from the NEMESIS forward model) and a constant spectral shift of 0.1 cm^{-1} to the right of the NEMESIS wavenumber grid. As with Figure 5 we find a barely distinguishable fit of the RISOTTO model (in blue, dashed) to the NEMESIS forward model.

520 4.2. Tests on molecules with continuum absorption

521 One major advantage in using this radiative transfer and retrieval pipeline over
 522 many existing codes, including the aforementioned NEMESIS, is that the trans-
 523 mission baseline can be retrieved iteratively as a state vector parameter in the
 524 model, without having to pre-process the spectra to estimate and fix the baseline
 525 level before retrievals of scientific information from the data can be carried out.
 526 This is important when performing retrievals in spectral regions that have multiple
 527 overlapping lines that are either very saturated, or are so dense that they cannot
 528 be resolved from each other at the given spectral resolution, and so where there is
 529 an absence of regions of the spectrum that are transparent to gaseous absorption
 530 which would allow the baseline level to be known *a priori*. This can lead to a
 531 degeneracy between the abundance of the gaseous compounds that we are aiming
 532 to retrieve and the baseline level, and hence inaccurate gas retrievals.

533 Here, we use SO₂ as an example of a gaseous compound that has substantial
 534 continuum absorption in the infrared wavenumber range, and also exhibits ab-
 535 sorption features that overlap strongly with those of CO₂. While the presence of
 536 SO₂ in the atmosphere of Venus is well-established, accurate measurements in this
 537 wavenumber region previously required a very complex procedure to fully decou-
 538 ple CO₂, SO₂ and aerosol extinction [21, 22]. In Figure 8 we show the results of a
 539 retrieval of a synthetic spectrum with a distorted continuum and with a ‘true’ SO₂
 540 volume mixing ratio of 2 ppmv at all altitudes, starting from a prior SO₂ value of
 541 0 ppmv. We can see that we can faithfully decouple the SO₂ values from varia-
 542 tions in the baseline, with only some 10% variation around the true value. This
 543 variation is due to ill-conditioning resulting from a retrieval starting from a prior
 544 that assumes no SO₂ at all, as would be the case in an atmosphere such as Mars
 545 where SO₂ remains undetected as of writing.

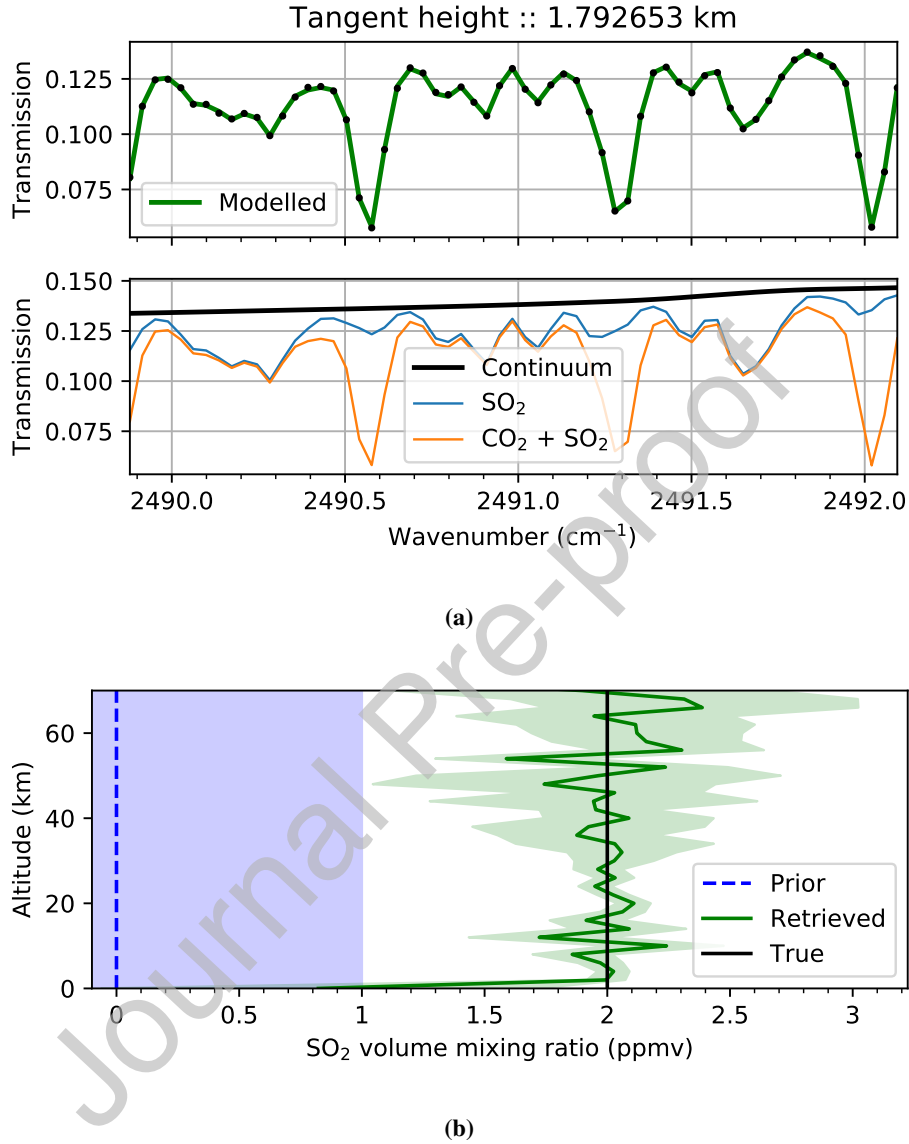


Figure 8: An example retrieval of a vertical profile of SO_2 from a synthetic set of spectra. In figure (a) we show, on the top row, the combined fit (in green) of all gaseous species to a measured spectrum (in black) at a given tangent height. On the bottom row we show the breakdown of the spectral contribution of each gaseous species to the spectrum, together with the retrieved continuum level, noting the considerable offset between both spectra and the continuum level due to the presence of continuum absorption of SO_2 . Nonetheless, as can be seen in figure (b), the retrieved SO_2 abundance profile is within error of the 'true' profile even though the prior is far from the true value.

5. Conclusion

In this paper we describe a new retrieval algorithm with an implemented forward model, that is generalisable to spectra obtained in solar occultation geometry. Using synthetic Martian spectra, we show how it could be used to retrieve sensitive vertically-resolved profiles of multiple different gaseous compounds, while also simultaneously correcting for uncertainties in instrumental calibration artefacts and the presence of broad aerosol absorption. This is particularly advantageous in retrievals of gaseous species with near-saturated lines or substantial continuum absorption at the instrumental resolution. This model is shown to be accurate to within 1-2% of an existing, well-established radiative transfer and retrieval tool, while also being faster and simpler to use.

To summarise, we note the following key features of the model:

- The model is able to retrieve several vertical gaseous abundance profiles together with temperature and pressure where applicable, including when multiple gases overlap, while correcting for uncertainties in instrumental parameters such as the transmission baseline, the line spread function and small errors in the spectral registration, all simultaneously.
- The model is suitable both for vertical gas profile retrievals where high accuracy is required, and for detection of as yet undetected trace species where no prior information is available.
- The model can automatically provide a good estimate of the signal-to-noise ratio of a given spectrum without any prior knowledge of the noise profile.

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ron, with Ashwin Braude responsible for major changes to the model in order to

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References

- [1] G. R. Smith, D. M. Hunten, Study of planetary atmospheres by absorptive occultations, *Rev. Geophys.* 28 (1990) 117–143. doi:10.1029/RG028i002p00117.
- [2] P. G. J. Irwin, N. A. Teanby, R. De Kok, L. N. Fletcher, C. J. A. Howett, C. C. C. Tsang, C. F. Wilson, S. B. Calcutt, C. A. Nixon, P. D. Parrish, The NEMESIS Planetary Atmosphere Radiative Transfer and Retrieval Tool, *J. Quant. Spec. Radiat. Transf.* 109 (6) (2008) 1136–1150. doi:10.1016/j.jqsrt.2007.11.006.
- [3] K. S. Olsen, F. Lefèvre, F. Montmessin, A. A. Fedorova, A. Trokhimovskiy, L. Baggio, O. Korablev, J. Alday, C. F. Wilson, F. Forget, D. A. Belyaev, A. Patrakeevev, A. V. Grigoriev, A. Shakun, The vertical structure of CO in the Martian atmosphere from the ExoMars Trace Gas Orbiter, *Nat. Geosci.* 14 (2021) 67–71. doi:10.1038/s41561-020-00678-w.
- [4] F. Montmessin, O. Korablev, A. Trokhimovskiy, A. Fedorova, F. Lefèvre,

- 596 J.-L. Bertaux, L. Baggio, K. Olsen, A. Shakun, A stringent upper limit of
597 20 pptv for methane on Mars and constraints on its dispersion outside Gale
598 crater, *A&A* 650 (2021) A140. doi:10.1051/0004-6361/202140389.
- 599 [5] X. Xu, J. Cisewski-Kehe, A. B. Davis, D. A. Fischer, J. M. Brewer, Model-
600 ing the Echelle Spectra Continuum with Alpha Shapes and Local Regression
601 Fitting, *AJ* 157 (6) (2019) 243. doi:10.3847/1538-3881/ab1b47.
- 602 [6] M. G. Genton, Classes of kernels for machine learning: a statistics perspec-
603 tive, *J. Mach. Learn. Res.* 2 (2001) 299–312.
- 604 [7] J. Humlíček, An efficient method for evaluation of the complex probabil-
605 ity function: The Voigt function and its derivatives, *J. Quant. Spec. Ra-
606 diat. Transf.* 21 (4) (1979) 309 – 313. doi:10.1016/0022-4073(79)90062-1.
- 607 [8] I. E. Gordon, L. S. Rothman, C. Hill, R. V. Kochanov, Y. Tan, P. F. Bernath,
608 M. Birk, V. Boudon, A. Campargue, K. V. Chance, et al., The HITRAN2016
609 molecular spectroscopic database, *J. Quant. Spec. Radiat. Transf.* 203 (2017)
610 3 – 69. doi:https://doi.org/10.1016/j.jqsrt.2017.06.038.
- 611 [9] A. Bellucci, B. Sicardy, P. Drossart, P. Rannou, P. D. Nicholson, M. Hedman,
612 K. H. Baines, B. Burrati, Titan solar occultation observed by Cassini/VIMS:
613 Gas absorption and constraints on aerosol composition, *Icarus* 201 (2009)
614 198–216. doi:10.1016/j.icarus.2008.12.024.
- 615 [10] G. Liuzzi, G. L. Villanueva, M. J. Mumma, M. D. Smith, F. Daerden, B. Ris-
616 tic, I. Thomas, A. C. Vandaele, M. R. Patel, J.-J. Lopez-Moreno, et al.,
617 Methane on Mars: New insights into the sensitivity of CH₄ with the NO-
618 MAD/ExoMars spectrometer through its first in-flight calibration, *Icarus*
619 321 (2019) 671–690. doi:10.1016/j.icarus.2018.09.021.

- [11] R. J. de Kok, D. M. Stam, The influence of forward-scattered light in transmission measurements of (exo)planetary atmospheres, *Icarus* 221 (2012) 517–524. doi:10.1016/j.icarus.2012.08.020.
- [12] R. Gorenflo, S. Vessella, Abel Integral Equations, Vol. 1461 of Lecture Notes in Mathematics, Springer, 1991.
- [13] S. Takagi, A. Mahieux, V. Wilquet, S. Robert, A.-C. Vandaele, N. Iwagami, An uppermost haze layer above 100 km found over Venus by the SOIR instrument onboard Venus Express, *Earth Planets Space* 71 (2019) 124. doi:10.1186/s40623-019-1103-x.
- [14] O. Korablev, F. Montmessin, A. Trokhimovskiy, A. A. Fedorova, A. V. Shakun, A. V. Grigoriev, B. E. Moshkin, N. I. Ignatiev, F. Forget, F. Lefèvre, et al., The Atmospheric Chemistry Suite (ACS) of Three Spectrometers for the ExoMars 2016 Trace Gas Orbiter, *Space Sci. Rev.* 214 (1) (2018) 7. doi:10.1007/s11214-017-0437-6.
- [15] B. R. Sandel, H. Gröller, R. V. Yelle, T. Koskinen, N. K. Lewis, J. L. Bertaux, F. Montmessin, E. Quémerais, Altitude profiles of O₂ on Mars from SPICAM stellar occultations, *Icarus* 252 (2015) 154–160. doi:10.1016/j.icarus.2015.01.004.
- [16] F. Montmessin, J. L. Bertaux, F. Lefèvre, E. Marcq, D. Belyaev, J. C. Gérard, O. Korablev, A. Fedorova, V. Sarago, A. C. Vandaele, A layer of ozone detected in the nightside upper atmosphere of Venus, *Icarus* 216 (2011) 82–85. doi:10.1016/j.icarus.2011.08.010.
- [17] C. D. Rodgers, Inverse Methods for Atmospheric Sounding: Theory and Practice, Vol. 2, World Scientific, 2000.

- [18] J. Alday, C. F. Wilson, P. G. J. Irwin, K. S. Olsen, L. Baggio, F. Montmessin, A. Trokhimovskiy, O. Korablev, A. A. Fedorova, D. A. Belyaev, A. Grigoriev, A. Patrakeev, A. Shakun, Oxygen isotopic ratios in Martian water vapour observed by ACS MIR on board the ExoMars Trace Gas Orbiter, *A&A* 630 (2019) A91. doi:10.1051/0004-6361/201936234.
- [19] F. Forget, F. Hourdin, R. Fournier, C. Hourdin, O. Talagrand, M. Collins, S. R. Lewis, P. L. Read, J.-P. Huot, Improved general circulation models of the Martian atmosphere from the surface to above 80 km, *J. Geophys. Res.* 104 (E10) (1999) 24155–24176. doi:10.1029/1999JE001025.
- [20] E. Quémerais, J.-L. Bertaux, O. Korablev, E. Dimarellis, C. Cot, B. R. Sandel, D. Fussen, Stellar occultations observed by SPICAM on Mars Express, *J. Geophys. Res. Planets* 111 (2006) E09S04. doi:10.1029/2005JE002604.
- [21] D. Belyaev, O. Korablev, A. Fedorova, J. L. Bertaux, A. C. Vandaele, F. Montmessin, A. Mahieux, V. Wilquet, R. Drummond, First observations of SO₂ above Venus' clouds by means of Solar Occultation in the Infrared, *J. Geophys. Res. Planets* 113 (2) (2008) E00B25. doi:10.1029/2008JE003143.
- [22] D. A. Belyaev, F. Montmessin, J.-L. Bertaux, A. Mahieux, A. A. Fedorova, O. I. Korablev, E. Marcq, Y. L. Yung, X. Zhang, Vertical profiling of SO₂ and SO above Venus' clouds by SPICAV/SOIR solar occultations, *Icarus* 217 (2) (2012) 740–751. doi:10.1016/j.icarus.2011.09.025.

666 Appendix A. Derivatives of state vector variables

667 Appendix A.1. Continuum model

668 As the corrected transmission spectrum is simply assumed to be equal to the
 669 transmission spectrum of unity baseline multiplied by the continuum model, as
 670 described in equation 1, the Jacobian for the continuum model is simply equal to
 671 the transmission spectrum of unity baseline:

$$\frac{dT}{dC} = \frac{T(\lambda_{cor}, z_T)}{C(\lambda_{cor}, z_T)} \quad (A.1)$$

672 Appendix A.2. Spectral Law Derivation

673 The Jacobians for the coefficients of the spectral law are calculated according
 674 to equation 1:

$$\frac{dT_{cor}(\lambda_{cor})_i}{da_n} = C(\lambda_{cor})_i \sum_j \frac{dK(\lambda_{cor}, \lambda_{mod})_{ij}}{da_n} T_{mod}(\lambda_{mod})_j \quad (A.2)$$

675 where the parameter $\frac{dK(\lambda_{cor}, \lambda_{mod})_{ij}}{da_n}$ is found through finite differences.

676 Appendix A.3. ILSF

677 From equation 1 and assuming a Gaussian ILSF, the derivative with respect to
 678 the spectral resolution parameter p_{gauss} can be calculated as follows:

$$\frac{dT_{cor}(\lambda_{cor})_i}{dp_x} = C(\lambda_{cor})_i \sum_j \frac{dK(\lambda_{cor}, \lambda_{mod})_{ij}}{dp_{gauss}} T_{mod}(\lambda_{mod})_j \quad (A.3)$$

679 where:

$$\frac{dK_{(ij)}}{dp_{gauss}} = \frac{K_{(ij)}(1 - \left(\frac{\lambda_{cor(j)} - \lambda_{mod(i)}}{\sigma}\right)^2)}{N_i p_{gauss}} \quad (A.4)$$

680 *Appendix A.4. Temperature*

681 From equations 11 and 15 we find that:

$$\frac{d\tau_{\lambda T}}{dT_u} = \sum_{m=1}^{N_m} \left[\frac{P_u}{Mk_B} A_{Tu} x_{mu} \left(\frac{d\sigma_{m\lambda u}}{dT_u} - \frac{\sigma_{m\lambda u}}{T_u} \right) + \sum_{v=u}^N \frac{P_v}{Mk_B T_v} A_{Tv} x_{mv} k_{m\lambda v} \frac{d \ln(P_v)}{dT_u} \right] \quad (\text{A.5})$$

682 where the term $\frac{d\sigma_{m\lambda u}}{dT_u}$ is solved through finite differences and $\frac{d \ln(P_v)}{dT_u}$ is calculated
683 according to equation 5.

684 Hence:

$$\frac{dT_{cor}(\lambda_{cor})_i}{dT_u} = -T_{cor}(\lambda_{cor})_i \frac{d\tau_{\lambda T}}{dT_u} \quad (\text{A.6})$$

685 *Appendix A.5. Gas VMR*

686 Again, from equation 15 we find that:

$$\frac{d\tau_{\lambda T}}{dx_{mu}} \approx \frac{\rho_u}{M} A_{Tu} \sigma_{m\lambda u} \quad (\text{A.7})$$

687 and so:

$$\frac{dT_{cor}(\lambda_{cor})_i}{dx_{mu}} = -T_{cor}(\lambda_{cor})_i \frac{d\tau_{\lambda T}}{dx_{mu}} \quad (\text{A.8})$$

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Declaration of interests

☒ 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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: