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## Spectroscopic requirements for ACCURATE, a microwave and infrared-laser occultation satellite mission

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### ABSTRACT

The proposed satellite mission ACCURATE consists of a small constellation of satellites in low Earth orbit, combining microwave occultation for thermodynamic state profiling with infrared-laser occultation for greenhouse gas and line-of-sight wind profiling. The mission aims to detect six greenhouse gas molecules with four additional isotopologues ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{CO}$ ,  $^{13}\text{CO}_2$ ,  $\text{OC}^{18}\text{O}$ ,  $\text{HDO}$ , and  $\text{H}_2^{18}\text{O}$ ) in the upper troposphere and lower stratosphere in the 4000–5000  $\text{cm}^{-1}$  spectral region. Greenhouse gas profiles will be retrieved to within 1–2% accuracy using a ‘differential’ method, requiring two spectral points for each species – one to sample the spectral line and the other nearby to sample the baseline.

An estimation of retrieval errors for the ACCURATE mission reveals that errors in spectroscopic line parameters dominate all other error sources. Poor knowledge of the spectroscopy introduces systematic errors into the retrieved greenhouse gas profiles. Using a simple approach, it was shown that the best line parameters currently available are too large to allow retrievals of greenhouse gases to within the stated ACCURATE mission goals of 1% accuracy for  $\text{CO}_2$  and 2% for all other species. Therefore, spectroscopic line parameters for targeted lines need to be improved before the ACCURATE mission can be launched. Requirements have been formulated in this direction, and laboratory experiments outlined that could meet these requirements.

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### 1. Introduction

Remote-sensing instruments onboard satellites allow for global and often continuous observation of the Earth’s atmosphere. In particular, instruments that measure atmospheric infrared spectra are able to determine the concentrations of trace species by utilising quantitative laboratory spectroscopy; each molecular species has its own characteristic spectral vibration–rotation signature.

The accuracy of the geophysical data derived from these instruments is largely limited by instrumental errors and/or errors in the underlying spectroscopy. Such instruments are

subject to measurement uncertainties, which are defined in terms of precision, systematic error, and accuracy. Precision is simply random measurement noise, providing a measure of the repeatability of the measurement, whereas systematic error is the bias of the measurement from the true value. Assuming that the precision and the systematic error are uncorrelated, accuracy is the square root of the sum of their squares. Using these definitions, a high accuracy implies a high degree of precision; however, a highly precise measurement does not necessarily equate with high accuracy. A reliable ‘retrieval’ requires a good characterisation of the measurement and accurate spectroscopic parameters of the target molecules, which can be found in databases such as HITRAN [1].

As an example, the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) instrument on

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SCISAT-1 [2], which utilises the solar occultation technique, has a continuum signal-to-noise ratio of greater than 300 over the 1000–3000  $\text{cm}^{-1}$  spectral range (0.02  $\text{cm}^{-1}$  resolution), implying an ideal precision of 0.3%. The original ACE mission requirement for accuracy was  $\sim 5\%$  for the volume mixing ratios (VMRs) of greenhouse gases in the most favourable cases. This limit reflects the accuracy of spectroscopic laboratory measurements in the HITRAN database, and the accuracies of the temperature (1 K) and the pressure (1%) profiles, which are retrieved from  $\text{CO}_2$  lines. The accuracies in the ACE geophysical data are also limited by pointing errors, which are quasi-random and vary from profile to profile. Taking zonal averages of the data minimises random errors, leaving the truly systematic error components that principally arise from the spectroscopy.

The next generation of satellite instruments possess higher resolution and/or better signal-to-noise ratios. This places additional burden on the quality of the spectroscopy. Inaccurate spectroscopy introduces systematic errors into the retrieval process, which offsets the benefits of a high precision instrument. For example, one of the goals of the upcoming OCO-2 mission [3] is to retrieve  $\text{CO}_2$  total columns over the globe and determine the geographic distribution of  $\text{CO}_2$  sources and sinks. Since these sources and sinks must be inferred from very small spatial variations in  $\text{CO}_2$  total columns, the OCO-2 instrument requires low measurement noise. As such it has been designed to achieve a precision of  $< 0.3\%$  (1 ppm). With such a high instrumental precision, large spectroscopic errors in the forward model will introduce systematic errors into the retrieval process, thus degrading the accuracies of the geophysical data. Therefore, the mission requires spectroscopic accuracies of 0.2% or better. Over the last few years, a concerted effort has been made to improve the laboratory spectroscopy of  $\text{CO}_2$  to achieve such accuracies, e.g. [4,5].

Even when the lines are not fully resolved, as in the case of the IASI nadir sounder [6] (0.5  $\text{cm}^{-1}$  apodised resolution) with a signal-to-noise ratio of the order of 2000 over much of the thermal IR, i.e. an implied precision of 0.05%, the underlying spectroscopy has to be accurately known. Recent technological improvements in remote-sensing instruments require improvements in laboratory spectroscopy otherwise the enhanced technological benefits of the instrument will be wasted.

Similarly, the proposed satellite mission ACCURATE—Climate Benchmark Profiling of Greenhouse Gases and Thermodynamic Variables and Wind from Space [7] puts additional demands on the accuracy of the underlying laboratory spectroscopy. The purpose of this paper is to show, using a simple approach, that the errors in HITRAN line parameters of greenhouse gases are too large to achieve the ACCURATE mission goals. The selected molecular lines need to be re-measured to high accuracy in the laboratory. The ACCURATE mission concept is discussed in more detail in the following section.

## 2. The ACCURATE mission

The ACCURATE satellite mission concept was proposed in response to the European Space Agency's (ESA) call for

Earth Explorer Core Mission proposals in 2005 and more recently as an Opportunity Mission [7]. The ACCURATE concept makes use of a new method termed LEO–LEO microwave and infrared–laser occultation (LMIO; LEO=low Earth orbit), which combines LEO–LEO microwave occultation (LMO) for thermodynamic state profiling with LEO–LEO infrared–laser occultation (LIO) for greenhouse gas and line-of-sight wind profiling (wind profiling will not be considered here) [8].

The ACCURATE mission will measure the profiles of six greenhouse gas molecules with four additional isotopologues (ten species in total) within the 4000–5000  $\text{cm}^{-1}$  spectral region:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{CO}$ ,  $^{13}\text{CO}_2$ ,  $\text{OC}^{18}\text{O}$ ,  $\text{HDO}$ , and  $\text{H}_2^{18}\text{O}$ . All of these greenhouse gases have suitable overtone vibration–rotation absorption lines in this spectral region. Of these gases,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and tropospheric  $\text{O}_3$  make major contributions to the radiative forcing of climate due to human activities (see 2007 IPCC report [9]). Generally  $\text{CO}$  is not considered a greenhouse gas due to its weak direct radiative forcing contribution; however, it has an important indirect contribution due to its reaction with OH radicals in the atmosphere, resulting in a short lifetime. This reduction in the OH abundance effectively increases the lifetime of strong greenhouse gases, such as  $\text{CH}_4$ . Ultimately, atmospheric  $\text{CO}$  leads to the production of  $\text{CO}_2$  and tropospheric  $\text{O}_3$ , which are both greenhouse gases. On the other hand,  $\text{H}_2\text{O}$  vapour, the most abundant and important greenhouse gas in the atmosphere, is a source of rapid climate feedback in response to the climate forcings of the non-condensable greenhouse gases [10].

The ACCURATE concept incorporates a small constellation of satellites, the baseline case consisting of four, with two transmitter (Tx) and two receiver (Rx) satellites. The novel aspect of this mission is to have an IR laser on each Tx satellite and a detector on each Rx satellite, with the Tx and Rx satellites in counter-rotating near-polar orbits. Each Rx satellite would measure the atmospheric transmittance of the laser beams as a function of altitude to provide height profiles of the concentrations of greenhouse gases. ACCURATE is therefore similar to solar and radio occultation but with a laser beam replacing the sun or the global navigation radio signal as a source of radiation. Typically a 2 Tx and 2 Rx constellation will produce about 240 occultation events per day (50% setting, 50% rising) and about 7200 per month. (The number of occultations increases with the square of the number of satellites.) This provides a horizontal resolution (sampling) better than 1800 km on a monthly basis for large-scale reference monitoring, consistent with the scientific needs for global climate benchmark data [7,11].

The ACCURATE proposal evaluation of 2006 recognised the potential of this novel approach, and it was recommended for further investigation and research. This led, among other studies, to the ESA-IRDAS (Differential Absorption Spectroscopy in the SWIR for Greenhouse Gas Monitoring using Coherent Sources in a Limb Sounding Geometry) study funded by ESA's Support to Science Element programme. The aim of this study was to establish the feasibility of active occultation measurements of greenhouse gases in the upper troposphere / lower stratosphere (UTLS) region using differential absorption of laser signals in the SWIR spectral region (4000–5000  $\text{cm}^{-1}$ ).

**Table 1**

The ACCURATE observational requirements [11]. The terms ‘goal’, ‘breakthrough’ (target) and ‘threshold’ [12] are explained in the text.

|                      | Goal | Breakthrough (target) | Threshold |
|----------------------|------|-----------------------|-----------|
| Temperature (K)      | 0.3  | 0.5                   | 1.0       |
| H <sub>2</sub> O (%) | 2    | 4                     | 10        |
| CO <sub>2</sub> (%)  | 1    | 2                     | 3         |
| CH <sub>4</sub> (%)  | 2    | 4                     | 10        |
| N <sub>2</sub> O (%) | 2    | 4                     | 10        |
| CO (%)               | 2    | 4                     | 10        |
| O <sub>3</sub> (%)   | 2    | 4                     | 10        |

Table 1 lists the accuracy requirements for ACCURATE as specified in the IRDAS ‘Science Objectives and Observational Requirements’ document [11]. The stated mission goals are 1% accuracy for CO<sub>2</sub> and 2% for all other species over a height range of 5–35 km (5–12 km for HDO and H<sub>2</sub><sup>18</sup>O). The terms ‘goal’, ‘breakthrough’ (target) and ‘threshold’ in Table 1 are defined by the WMO [12]. The ‘goal’ is an ideal requirement above which further improvements are not necessary, the ‘threshold’ is the minimum requirement to be met to ensure that data are useful, and the ‘breakthrough’ (target) is an intermediate level between ‘threshold’ and ‘goal’, which, if achieved, would result in a significant improvement for the targeted applications in atmospheric and climate science.

The ACCURATE concept utilises a ‘differential’ retrieval method with two channels for each species – one at the centre of the trace-gas absorption line, as far removed from the absorption of other species as possible, and one located off-line (within 0.5%), in a region of minimal absorption. A list of absorption and reference channels for the retrieval of the ten species can be found in Refs. [8,13] and a detailed description of the selection criteria and procedures in Refs. [8,14]. The LIO intensities for these two channels are corrected for effects such as defocusing loss and loss due to spherical signal spreading. The transmittance in each channel is obtained by normalising to the intensity measured at the top of the atmosphere (or a reference height where transmittance is almost unity). Taking the ratio of the transmittances (or the difference in log-space) of the two channels eliminates to high accuracy scintillations and broadband effects, which are effectively the same in each channel. However, since each channel contains slightly different contributions from the absorption of ‘foreign’ species, this differential transmittance needs to be corrected for ‘foreign’ absorption using a forward-model computation. A detailed assessment of atmospheric influences on the LIO signals is found in Ref. [15] and a detailed description of the LIO retrieval algorithm in Ref. [16].

UTLS profiles of altitude and the thermodynamic state variables temperature and pressure are obtained from the LMO measurements (to better than 0.3% accuracy) [17] and are transformed to the IR height grid, since the microwave and IR ray paths differ slightly due to refraction [15,16]. Along with the channel frequencies and spectroscopic line parameters, the thermodynamic variables are input into the forward model to calculate the appropriate absorption cross section. The differential absorption coefficient is derived from the differential transmittance of the target species

using the Abel transform [17,18], with the VMRs of the target species calculated straightforwardly. As can be seen, these VMRs crucially depend on the accuracy of the spectroscopy used to calculate the absorption cross section.

As part of the IRDAS study, the ACCURATE LIO Performance Simulator (ALPS) was developed [19] to allow the estimation of retrieval errors using limb transmittance profiles computed with the Reference Forward Model (RFM) and the HITRAN 2008 molecular spectroscopic database. Full details of the ALPS error modelling, which are beyond the scope of this paper, are given in Ref. [8]. The ALPS software considers various atmospheric losses/gains and observing system/instrumental errors, including (not an exhaustive list) loss from Rayleigh, aerosol and cloud extinction, atmospheric scintillation effects, divergence loss associated with propagation through space, laser fluctuation, loss from transmitter and receiver optics, detector (extended InGaAs) performance, pointing bias and pointing jitter errors of the satellites [19]. Assuming an amplified laser with an emitted power of 1 W and a divergence of 3 mrad, the ALPS outputs provide evidence that the greenhouse gas profiles can be retrieved within the 5–35 km height range with < 1–3% r.m.s. error (outside clouds) at ~1 km vertical resolution, although CH<sub>4</sub>, N<sub>2</sub>O and CO deteriorate above 20 km [8,16]. For climatological purposes, monthly mean profiles can be derived by averaging the profiles for a given month over a number of ‘grid boxes’, defined as the square of the horizontal sampling requirement. Assuming 36 profiles per grid box, of which there are 200 globally for a 2 Tx and 2 Rx constellation, one obtains a monthly-mean error six times smaller than the individual profile error and accuracies of within 0.15–0.5% (depending on cloudiness, tropospheric levels not reached by all profiles will receive less than 36 samples per grid box [15]). Statistical errors, arising from measurement noise, dominate the modelled individual profile errors. Such errors represent the precision or repeatability of a measurement. By binning and averaging occultations for climatological purposes, systematic errors due to, for example, uncertainty in the IR laser frequencies and spectroscopic errors begin to dominate.

Spectroscopic errors have not been incorporated into ALPS because, on the one hand, they can be viewed as time-constant errors with essentially no effect on trends and, on the other hand, they require dedicated extra study since they dominate all other error sources in absolute terms. Focusing here on the latter, it is clear that poor knowledge of the spectroscopy introduces significant systematic errors that affect the accuracy of the retrieved greenhouse gas profiles. An important part of the IRDAS study was to investigate whether the existing line parameters in the HITRAN database allow retrievals of greenhouse gases to within the stated ACCURATE mission goals of 1% accuracy for CO<sub>2</sub> and 2% for all other species. This is considered in the following section.

### 3. Errors in the spectroscopic line parameters required for ACCURATE

In order to obtain accurate geophysical parameters from active occultation measurements, one requires

**Table 2**The HITRAN 2008 line parameters and associated uncertainty ranges for the CH<sub>4</sub> and CO<sub>2</sub> lines at 4344.1635 and 4771.621441 cm<sup>-1</sup>, respectively.

| Parameter  | CH <sub>4</sub> |                    | CO <sub>2</sub> |                      |
|--|-----------------|--------------------|-----------------|----------------------|
|  | Value           | Error              | Value           | Error                |
| $\nu$ (cm <sup>-1</sup> )                                    | 4344.1635       | ≥ 0.001 and < 0.01 | 4771.62144      | ≥ 0.0001 and < 0.001 |
| $S$ (cm molecule <sup>-1</sup> )                             | 1.123E-22       | ≥ 2% and < 5%      | 1.803E-24       | ≥ 10% and < 20%,     |
| $\gamma_{\text{air}}$ (cm <sup>-1</sup> atm <sup>-1</sup> )  | 0.0614          | ≥ 20%              | 0.0680          | ≥ 5% and < 10%       |
| $\gamma_{\text{self}}$ (cm <sup>-1</sup> atm <sup>-1</sup> ) | 0.0776          | ≥ 20%              | 0.081           | ≥ 5% and < 10%       |
| $n_{\text{air}}$   | 0.70            | ≥ 20%              | 0.80            | ≥ 10% and < 20%,     |
| $\delta_{\text{air}}$ (cm <sup>-1</sup> atm <sup>-1</sup> )  | -0.008195       | ≥ 0.001 and < 0.01 | -0.006062       | ≥ 0.01 and < 0.1     |

accurate spectroscopic line parameters. The **High Resolution Transmission** (HITRAN) database [1] is the standard for calculating atmospheric molecular transmission. HITRAN is a compilation of molecular spectroscopic lines, each specified by a collection of line parameters. At a given temperature and total air pressure, each spectroscopic line is taken to have a Voigt lineshape function, which is a convolution of a Gaussian lineshape function due to Doppler broadening and a Lorentzian lineshape function due to pressure broadening. Six of these line parameters are used to determine the shape and position of each spectral line [20]:

1.  $\nu$ , the spectral line transition frequency (cm<sup>-1</sup>).
2.  $S$ , the spectral line intensity (cm/molecule) at  $T_{\text{ref}}=296$  K. The intensity is defined for a single molecule, and is weighted according to the natural terrestrial isotopic abundances (as defined by HITRAN).
3.  $\gamma_{\text{air}}$ , the air-broadened halfwidth at half maximum (HWHM) (cm<sup>-1</sup>/atm) at  $T_{\text{ref}}=296$  K and  $p_{\text{ref}}=1$  atm.
4.  $\gamma_{\text{self}}$ , the self-broadened halfwidth (cm<sup>-1</sup>/atm) at  $T_{\text{ref}}=296$  K and  $p_{\text{ref}}=1$  atm.
5.  $n_{\text{air}}$ , the coefficient of temperature dependence of  $\gamma_{\text{air}}$ , defined by

$$\gamma_{\text{air}}(p_{\text{ref}}=1 \text{ atm}, T) = \gamma_{\text{air}}(p_{\text{ref}}=1 \text{ atm}, T_{\text{ref}}=296 \text{ K}) \left( \frac{296}{T} \right)^{n_{\text{air}}}$$

6.  $\delta_{\text{air}}$ , the air-broadened pressure shift (cm<sup>-1</sup>/atm) at  $T_{\text{ref}}=296$  K,  $p_{\text{ref}}=1$  atm, of the spectral line transition frequency,  $\nu$ .

The width of the Gaussian part of the Voigt lineshape function is set by the temperature and mass of the molecule and the width of the Lorentzian part is the sum of the air-broadening and the self-broadening, calculated at the appropriate temperature and pressure from  $\gamma_{\text{air}}$ ,  $\gamma_{\text{self}}$  and  $n_{\text{air}}$ . The resulting line is calculated from the concentration of the molecule and total pressure using the  $\nu$ ,  $S$  and  $\delta_{\text{air}}$  line parameters with the normalised Voigt function.

For the purposes of the ACCURATE mission, the quality of the HITRAN 2008 line parameters for the selected lines needs to be ascertained. HITRAN employs various error codes in the form of wavenumber errors for  $\nu$  and  $\delta_{\text{air}}$ , and percentage errors for  $S$ ,  $\gamma_{\text{air}}$ ,  $\gamma_{\text{self}}$ , and  $n_{\text{air}}$ . Unfortunately, each code corresponds to an uncertainty range, and there is no information in the HITRAN database as to how

the parameters are correlated. Without this information the user must assume that there is no correlation and that the errors in the line parameters can be estimated directly from the error codes. Table 2 gives the line parameters and associated error codes for the CH<sub>4</sub> and CO<sub>2</sub> lines at 4344.1635 and 4771.621441 cm<sup>-1</sup>, respectively, two of the selected lines. These uncertainties are representative of all the lines selected for the ACCURATE mission.

Additional sources of error in HITRAN arise from the use of the Voigt lineshape, which is an approximation to the true lineshape. This induces errors into the line parameters when they are extracted from laboratory spectra; these will fold into the uncertainties of the retrieved geophysical parameters. For example, the CO<sub>2</sub> bands at 1.58 and 1.61  $\mu\text{m}$  [4,5] used by GOSAT and OCO-2, require additional parameters for line mixing and speed dependence of the collisions. Furthermore, additional parameters such as the temperature dependence of  $\delta_{\text{air}}$  are not included in HITRAN. It is not possible for us to quantify these errors without comparison to laboratory spectra, however they are not negligible.

A molecule's partition function governs the temperature dependence of its spectral line intensity, and errors in this will lead to systematic errors in the retrieval. The partition function describes the internal energy distribution between the various electronic, vibrational, rotational, torsional, nuclear spin, etc. states. Along with the lower-state energy of the transition, the partition function is required to determine the thermodynamic equilibrium populations of the lower levels for each spectroscopic line; it scales the HITRAN line strength at 296 K to the desired atmospheric temperature. HITRAN contains a comprehensive set of tabulated molecular partition functions, calculated at 25 K intervals over the temperature range 70–3000 K. The partition functions for any temperature can be rapidly calculated from these, using Lagrange 4-point interpolation [21]. Accurate partition functions require the accurate knowledge of molecular term values, which themselves require appropriate quantum mechanical expressions coupled with accurate molecular parameters. It is difficult to quantify the partition function uncertainties; however, it is likely that they are at most a fraction of a percent. Measuring line positions is relatively more straightforward than determining intensities/lineshape parameters.

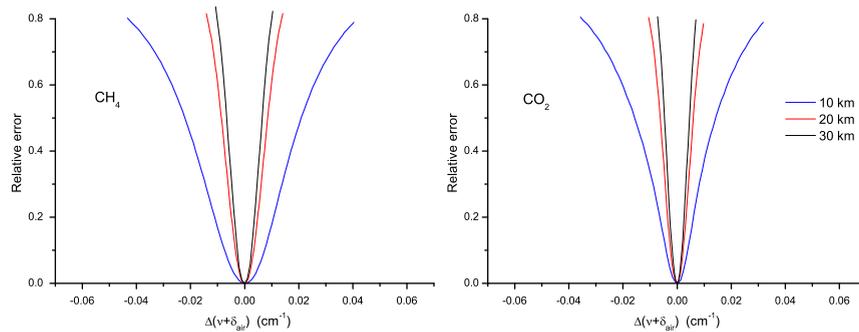
An ACCURATE retrieval involves taking the ratio of the transmittances (or the difference in log-space) of an absorption and reference channel [16]. A simple approach

to evaluate how the errors in HITRAN line parameters affect retrievals, therefore, is to investigate transmittance errors (as recently also applied for assessing atmospheric influences [15]). To this end, realistic atmospheric limb spectra were calculated in the  $4000\text{--}5000\text{ cm}^{-1}$  spectral region ( $0.002\text{ cm}^{-1}$  spectral resolution) at tangent heights between 2 and 60 km using the Reference Forward Model (RFM) [22] and the US standard atmosphere. The RFM is a ‘line-by-line’ model using spectroscopic parameters from the HITRAN 2008 database [1], and all calculations were made assuming a limb-viewing geometry at the specified refracted tangent height (i.e., the ray extends from  $-\infty$  to  $+\infty$  tangent to a spherical Earth).

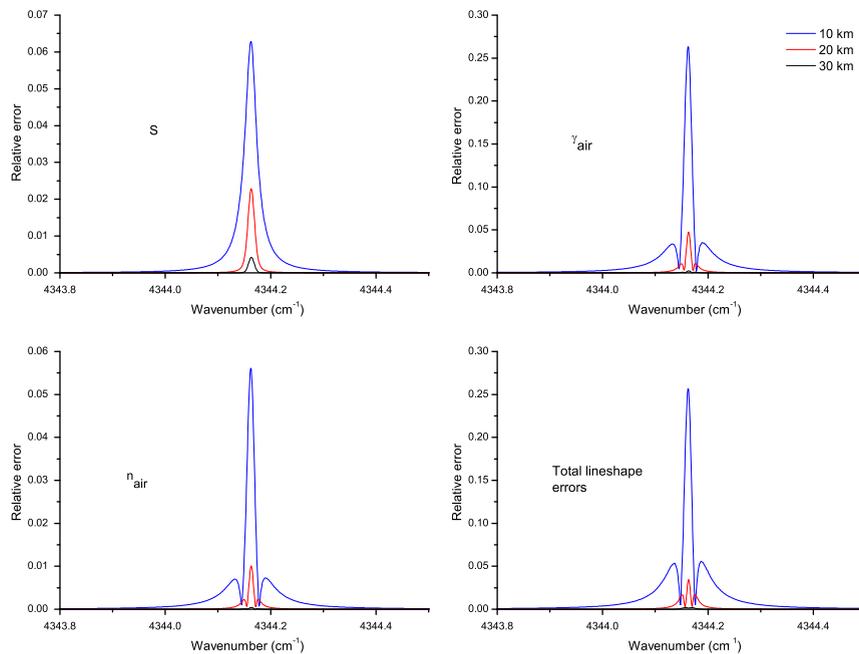
Fig. 1 shows errors in line position plotted against  $\Delta(\nu + \delta_{\text{air}})$ , the difference between the HITRAN line position (including the contribution from  $\delta_{\text{air}}$ ) and the ‘true’ line position, for the  $\text{CH}_4$  line at  $4344.1635\text{ cm}^{-1}$  and the  $\text{CO}_2$  line at  $4771.621441\text{ cm}^{-1}$ . As expected these

errors increase with  $|\Delta(\nu + \delta_{\text{air}})|$ , i.e., as the difference between the HITRAN and ‘true’ line position increases. Errors due to uncertainties in  $\nu$  and  $\delta_{\text{air}}$  can be minimised by accurately measuring the line positions. Since these errors increase more rapidly with increasing altitude (the lines are sharper at lower pressure), the line position accuracy requirement must be determined at the highest desired altitude. For the ACCURATE mission the line positions must be accurately known to within  $5 \times 10^{-5}\text{ cm}^{-1}$  [8].

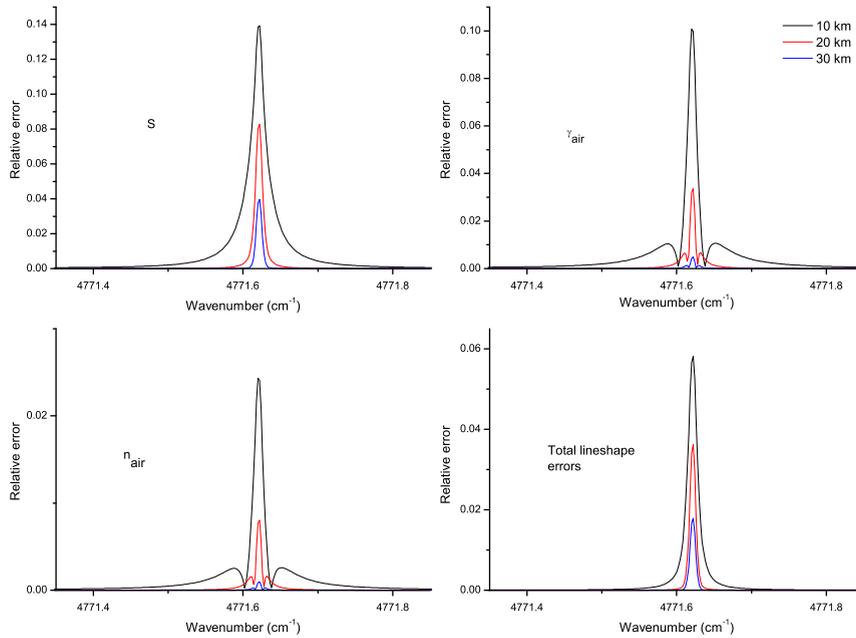
In order to investigate errors in lineshape parameters for the selected lines, RFM calculations of transmittance spectra were performed in which the HITRAN parameters were modified in turn to the maximum and minimum possible values as dictated by the error codes. In particular, for an error code range such as  $\geq 2\%$  and  $< 5\%$ , the average (i.e.,  $\pm 3.5\%$ ) was used, and for an error code with a single value (e.g.,  $\geq 20\%$ ) that value (i.e.,  $\pm 20\%$ ) was



**Fig. 1.** Relative errors in transmittance due to the HITRAN parameters  $\nu$  and  $\delta_{\text{air}}$  for the  $\text{CH}_4$  line at  $4344.1635\text{ cm}^{-1}$  and the  $\text{CO}_2$  line at  $4771.621441\text{ cm}^{-1}$ . The x-axis is the difference between the HITRAN and the ‘true’ line position,  $\Delta(\nu + \delta_{\text{air}})$ .



**Fig. 2.** Relative errors in transmittance due to the HITRAN parameters  $S$ ,  $\gamma_{\text{air}}$  and  $n_{\text{air}}$  (individually) and all combined lineshape parameters for the  $\text{CH}_4$  line at  $4344.1635\text{ cm}^{-1}$  at various tangent heights.



**Fig. 3.** Relative errors in transmittance due to the HITRAN parameters  $S$ ,  $\gamma_{\text{air}}$  and  $n_{\text{air}}$  (individually) and all combined lineshape parameters for the  $\text{CO}_2$  line at  $4771.621441 \text{ cm}^{-1}$  at various tangent heights.

used. The relative error in transmittance,  $\delta\tau$ , is defined as

$$\delta\tau = \frac{|\tau(v, P + \delta P) - \tau(v, P - \delta P)|}{2\tau(v, P)} \quad (1)$$

where  $P$  represents the HITRAN parameter(s) in question, and  $\delta P$  the associated error(s).

Figs. 2 and 3 give plots of the relative transmittance errors in the  $S$ ,  $\gamma_{\text{air}}$  and  $n_{\text{air}}$  parameters (individually) calculated for the selected  $\text{CH}_4$  line at  $4344.1635 \text{ cm}^{-1}$  and  $\text{CO}_2$  line at  $4771.621441 \text{ cm}^{-1}$  for the tangent heights 10, 20 and 30 km. As can be seen, the errors are largest at the line centres, which correspond to the ACCURATE absorption channels. For example, the error in  $\gamma_{\text{air}}$  peaks at 27% (at 10 km) for the  $\text{CH}_4$  line and for  $S$  at 14% (at 10 km) for the  $\text{CO}_2$  line. The relative error in  $S$  is constant in terms of absorbance; however, it decreases with increasing altitude as a result of the logarithmic relationship between absorbance and transmittance. Errors arising from  $\gamma_{\text{air}}$  and  $n_{\text{air}}$  decrease with altitude as the air pressure decreases. One might naively expect that only errors in  $S$  are important; however, Figs. 2 and 3 show clearly that errors in  $\gamma_{\text{air}}$  and  $n_{\text{air}}$  are not negligible. Figs. 2 and 3 also provide plots of the combined line-shape errors (associated with the parameters  $S$ ,  $\gamma_{\text{air}}$ ,  $\gamma_{\text{self}}$  and  $n_{\text{air}}$ ) for the two lines. (Note that the errors for individual parameters are not necessarily additive.) The total line-shape error peaks at 6% for the  $\text{CO}_2$  line and 26% for the  $\text{CH}_4$  line (at 10 km).

For the ACCURATE measurement scheme in which only absorption line centres are sampled, this spectroscopic error will lead to systematic errors in the retrievals larger than the mission goals of 1% accuracy for  $\text{CO}_2$  and 2% for all other species. In addition to the line position accuracy requirement of within  $5 \times 10^{-5} \text{ cm}^{-1}$ , the ACCURATE mission requires absorption cross sections accurate to  $\sim 0.1\%$  within

$\pm 0.002 \text{ cm}^{-1}$  of the channel centre [8], putting rather stringent requirements on the accuracy of the lineshape parameters. Also, the absorption at reference channel locations must be characterised with an accuracy of  $\sim 1\%$ . Furthermore, temperature and pressure knowledge comes from the LMO measurements (to better than 0.3% accuracy [17]), and introduces small errors into the LIO retrieval. This has been considered in ALPS error modelling [8] and in quasi-realistic retrievals [16].

#### 4. Future laboratory measurements of line parameters

Before the ACCURATE mission can be launched, spectroscopic line parameters for the targeted lines need to be improved. This will involve very accurate laboratory spectroscopic measurements of pure and synthetic-air-broadened samples at the pressure and temperature conditions found in the UTLS. Furthermore, line parameters for spectral interferers, particularly lines of water vapour, as well as those that interfere with reference lines, need to be improved.

Quantitative spectroscopic measurements require an accurate knowledge of the sample conditions. Since the ACCURATE lines have been selected so that they do not saturate over long limb pathlengths, the measurements will require a sample cell with a long pathlength, e.g., a White cell. Spectroscopic cells need to be free from contamination, which is best achieved by pumping with several efficient molecular turbo-pumps. Sample conditions such as pressure (and broadening pressure), temperature and cell pathlength (and its associated temperature dependence) need to be determined to better than 0.05–0.1%. Furthermore, mass-spectrometric techniques should be used to calibrate samples and verify their high chemical and isotopic purity. Extensive sets of

measurements for all species are required over a range of atmospherically relevant temperatures, absorber pressures, and synthetic-air pressures. By taking measurements for many temperature/pressure combinations, statistical errors associated with the nonlinear least-squares fitting techniques used to extract parameters will be minimised. Such an analysis will provide variance-covariance matrices which provide crucial information on the correlations between line parameters and their errors. For each ACCURATE line, the lineshape that best fits the spectral data needs to be determined, phenomenologically if necessary, and this function will have to be used in the forward model. Furthermore, accurate temperature and pressure measurements will enable the extraction of temperature-dependent line intensities, which will provide an independent check of HITRAN partition functions. Of the ten ACCURATE species, the determination of ozone concentration is most problematic since ozone decomposes. One method is to perform simultaneous UV absorption measurements at 253.7 nm [23], although this requires knowledge of the UV absorption cross section at this wavelength (0.5% uncertainty).

There are a number of ways in which these spectroscopic measurements can be performed to the required accuracy; various techniques will be outlined below. In all cases spectra need to be recorded at high resolution, determined by the Doppler or pressure broadening, to ensure that all the molecular features are fully resolved. The conventional method is to use an FTS, which can provide high-resolution spectra over wide spectral ranges, but with sensitivity limited by the use of incoherent light sources and resolution determined by the extent of a mechanical moving mirror, the speed of which determines the recording time. For the purposes of improving spectroscopic parameters, many hours of scanning (including additional background scans) are needed to achieve the required signal-to-noise ratios. The 0% and 100% transmittance levels need to be accurately known, and the instrumental lineshape well determined. Frequencies need to be calibrated by recording additional spectra of a calibrant with accurately known line positions.

The measurements could also be performed using the same technique as used in the ozone (100–000 band) study [23] made in support of the Stratospheric Wind Interferometer For Transport studies (SWIFT) satellite instrument. This work made use of an interferometrically stabilised tunable diode laser spectrometer, in which the laser beam is split into five parts; one part to control the wavenumber of the emitted radiation using a Michelson interferometer, one part is directed through the sample cell, one through a reference cell (containing N<sub>2</sub>O), one through an etalon (both these used to calibrate the wavenumber scale), and the last used as a background to enable the determination of optical depth of the sample. The shape of the diode laser emission profile also needs to be accurately known. The O<sub>3</sub> frequencies obtained were accurate to  $4 \times 10^{-5} \text{ cm}^{-1}$  and absolute intensities to about 1%; the authors were limited by the noise level of the laser. Such measurements would provide substantial improvements to the line parameters required for ACCURATE; however, further improvements could be achieved by using, for example, a quantum cascade laser in the appropriate

spectral region, which has a higher emitted power and thus an improved signal to noise ratio than a diode laser.

Recent advances in dual-comb Fourier-transform spectroscopy are making this a viable option in the coming years for accurately determining line parameters. (A mode-locked femtosecond laser emits a pulse train at a constant repetition rate, which in the frequency domain equates to a frequency ‘comb’ of evenly spaced ‘teeth’, with the spacing equivalent to the pulse repetition frequency.) This is a Fourier-transform spectroscopic technique without any moving parts, and which allows a spectrum to be recorded within a fraction of a second, providing a distinct advantage over a conventional FTS, which requires long measurement times and constant sample conditions throughout. Recently, a proof-of-principle demonstration of this technique was reported using two ceramic Cr<sup>2+</sup>:ZnSe femtosecond oscillators emitting in the 2.45 μm region, both pumped by a continuous-wave 1.61 μm erbium-doped fibre laser [24]. The first comb probes the sample and is combined with the second reference comb of slightly different spacing. The two combs beat together to produce a third comb with spacing in the radio frequency region. The time-domain signal is recorded with a fast photodetector, and Fourier transformed to produce the spectrum. The Cr:ZnSe laser, belonging to the class of ultrabroadband solid-state infrared lasers, is tunable over the 2.0–3.1 μm range with significant output power, making it ideal for trace gas measurements [25].

## 5. Conclusions

The proposed satellite mission ACCURATE combines microwave occultation for thermodynamic state profiling with infrared-laser occultation for greenhouse gas and line-of-sight wind profiling. The mission aims to detect six greenhouse gas molecules with four additional isotopologues (H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, O<sub>3</sub>, CO, <sup>13</sup>CO<sub>2</sub>, OC<sup>18</sup>O, HDO, and H<sub>2</sub><sup>18</sup>O) in the upper troposphere and lower stratosphere in the 4000–5000 cm<sup>-1</sup> spectral region. Greenhouse gas profiles will be retrieved using a ‘differential’ method, requiring two spectral points for each species – one to sample the spectral line and the other nearby to sample the baseline. An estimation of retrieval errors for the ACCURATE mission reveals that errors in spectroscopic line parameters dominate all other error sources and introduce systematic errors into the retrieved greenhouse gas profiles. Using a simple approach, it has been shown that the current line parameter errors in the HITRAN database are too large to allow retrievals of greenhouse gases to within the stated ACCURATE mission goals of 1% accuracy for CO<sub>2</sub> and 2% for all other species. Before the ACCURATE mission can be launched, spectroscopic line parameters for targeted lines need to be improved; future laboratory experiments that could meet these requirements have been discussed. Line positions must be accurately known to within  $5 \times 10^{-5} \text{ cm}^{-1}$ , and absorption cross sections accurate to  $\sim 0.1\%$  within  $\pm 0.002 \text{ cm}^{-1}$  of the channel centre. Also, absorption at the spectral locations of reference channels must be accurately characterised to  $\sim 1\%$ . A ground-based demonstration experiment of LIO sounding (of CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O) is currently being prepared

for implementation in the Canary Islands, using a laser link along a 144 km pathlength at  $\sim 2.4$  km altitude. Amongst other objectives, this will provide further valuable information on the utility and limitations of current spectroscopic knowledge of the relevant lines.

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## References

- [1] Rothman LS, Gordon IE, et al. The HITRAN 2008 molecular spectroscopic database. *J Quant Spectrosc Radiat Transfer* 2009;110:533–72.
- [2] Bernath PF, McElroy CT, et al. Atmospheric chemistry experiment (ACE): mission overview. *Geophys Res Lett* 2005;32:L15S01, doi:10.1029/2005GL022386.
- [3] <http://oco.jpl.nasa.gov/>. Accessed April 2011.
- [4] Devi VM, Benner DC, Brown LR, Miller CE, Toth RA. Line mixing and speed dependence in CO<sub>2</sub> at 6348 cm<sup>-1</sup>: positions, intensities, and air- and self-broadening derived with constrained multispectrum analysis. *J Mol Spectrosc* 2007;242:90–117.
- [5] Devi VM, Benner DC, Brown LR, Miller CE, Toth RA. Line mixing and speed dependence in CO<sub>2</sub> at 6227.9 cm<sup>-1</sup>: constrained multispectrum analysis of intensities and line shapes in the 30013–00001 band. *J Mol Spectrosc* 2007;245:52–80.
- [6] Razavi A, Clerbaux C, Wespes C, Clarisse L, Hurtmans D, Payan S, et al. Characterization of methane retrievals from the IASI spaceborne sounder. *Atmos Chem Phys* 2009;9:7889–99, doi:10.5194/acp-9-7889-2009.
- [7] Kirchengast G, et al. ACCURATE—climate benchmark profiling of greenhouse gases and thermodynamic variables and wind from space (ESA Earth Explorer opportunity mission EE-8 proposal). *Sci Rep* 2010;36 Wegener Center Verlag <w?w?w?.wegcenter.at/wcv>, Graz, Austria.
- [8] Kirchengast G, Schweitzer S. Climate benchmark profiling of greenhouse gases and thermodynamic structure and wind from space. *Geophys Res Lett* 2011;38:L13701, doi:10.1029/2011GL047617.
- [9] Forster P, Ramanathan V, et al. Changes in Atmospheric constituents and in radiative forcing. In: *Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2007. Also see <http://www.ipcc.ch/>.
- [10] Lacis AA, Schmidt GA, Rind D, Ruedy RA. Atmospheric CO<sub>2</sub>: principal control knob governing Earth's temperature. *Science* 2010;330:356–9.
- [11] Larsen GB, Kirchengast G, Bernath PF. ESA-IRDAS study: science objectives and observational requirements of the ACCURATE mission concept. Doc-ID: DMI/ESA-IRDAS/ObsReq/Oct2009; 2009.
- [12] <http://www.wmo.int/pages/prog/sat/Databases.html#UserRequirements> [accessed April 2011].
- [13] Harrison JJ, Bernath PF. ESA-IRDAS study: spectroscopic properties of greenhouse gases from 2.0 to 2.5  $\mu\text{m}$ . Doc-ID: UoY/ESA-IRDAS/Greenhouse/27 January 2010.
- [14] Schweitzer S. The ACCURATE concept and the infrared laser occultation technique: mission design and assessment of retrieval performance (Ph.D. thesis). *Sci Rep* 2010;34 Wegener Center Verlag <w?w?w?.wegcenter.at/wcv>, Graz, Austria.
- [15] Schweitzer S, Kirchengast G, Proschek V. Atmospheric influences on infrared-laser signals used for occultation measurements between Low Earth Orbit satellites. *Atmos Meas Tech Discuss* 2011;4:2689–747, doi:10.5194/amtd-4-2689-2011.
- [16] Proschek V, Kirchengast G, Schweitzer S. Greenhouse gas profiling by infrared-laser and microwave occultation: Retrieval algorithm and demonstration results from end-to-end simulations. *Atmos Meas Tech Discuss* 2011;4:2273–328, doi:10.5194/amtd-4-2273-2011.
- [17] Schweitzer S, Kirchengast G, Schwärz M, Fritzer J, Gorbunov ME. Thermodynamic state retrieval from microwave occultation data and performance analysis based on end-to-end simulations. *J Geophys Res* 2011;116:D10301, doi:10.1029/2010JD014850.
- [18] Kursinski ER, et al. A microwave occultation observing system optimized to characterize atmospheric water, temperature and geopotential via absorption. *J Atmos Oceanic Tech* 2002;19:1897–914.
- [19] Kirchengast G., Schweitzer S., Proschek V., Bernath P.F., Thomas B., Harrison J.J., et al. ALPS—ACCURATE LIO performance simulator—user guide and documentation. Technical Report. ESA-ESTEC 3/2010. Graz: Wegener Center, University of Graz.
- [20] Rothman LS, Rinsland CP, Goldman A, et al. The Hitran molecular spectroscopic database and hawks (Hitran atmospheric workstation): 1996 edition. *J Quant Spectrosc Radiat Transfer* 1998;60:665–710.
- [21] Fischer J., Gamache R.R., Goldman A., Rothman L.S., Perrin A. Total internal partition sums for molecular species in the 2000 edition of the HITRAN database. *J Quant Spectrosc Radiat Transfer* 2003;82:401–412.
- [22] <http://www.atm.ox.ac.uk/RFM/>. Accessed April 2011.
- [23] Guinet M, Mondelain D, Janssen C, Camy-Peyret C. Laser spectroscopic study of ozone in the 100–000 band for the SWIFT instrument. *J Quant Spectrosc Radiat Transfer* 2010;111:961–72, doi:10.1016/j.jqsrt.2010.01.011.
- [24] Bernhardt B, Sorokin E, Jacquet P, Thon R, Becker T, Sorokina IT, et al. Mid-infrared dual-comb spectroscopy with 2.4  $\mu\text{m}$  Cr<sup>2+</sup>:ZnSe femtosecond lasers. *Appl Phys B* 2010;100:3–8, doi:10.1007/s00340-010-4080-0.
- [25] Sorokin E, Naumov S, Sorokina IT. Ultrabroadband Infrared Solid-State Lasers. *IEEE Journal of Selected Topics in Quantum Electronics* 2005;11:690–712.