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N_2O and O_3 arctic column amounts from PARIS-IR observations: Retrievals, characterization and error analysis

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Abstract

Ground-based solar absorption infrared spectra were recorded in the Canadian Arctic during the early spring of 2004 using a moderate-resolution Fourier transform spectrometer, the Portable Atmospheric Research Interferometric Spectrometer for the Infrared (PARIS-IR). As part of the Canadian Arctic Atmospheric Chemistry Experiment (ACE) validation campaign, the PARIS-IR instrument recorded solar absorption spectra of the atmosphere from February to March 2004 as the Sun returned to the Arctic Stratospheric Ozone Observatory (AStrO) near Eureka, Nunavut, Canada (80.05°N, 86.42°W). In this paper, we briefly outline the PARIS-IR instrument configuration and data acquisition in the high Arctic. We discuss the retrieval methodology, characterization and error analysis associated with total and partial column retrievals. We compare the PARIS-IR measurements of N_2O and O_3 column amounts with those from the Fourier transform spectrometer (ACE-FTS) onboard the Canadian SCISAT-1 satellite and the ozonesonde data obtained at Eureka during the validation campaign.

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1. Introduction

The portable atmospheric research interferometric spectrometer for the infrared (PARIS-IR) is a terrestrial version of the Fourier-transform spectrometer (ACE-FTS) onboard the Canadian satellite SCISAT-1 [1]. Both spectrometers operate in the spectral region between 750 and 4400 cm^{-1} and are therefore capable of observing many atmospheric trace molecules simultaneously in one single scan. As part of the Canadian Arctic Atmospheric Chemistry Experiment (ACE) validation campaign in 2004 [2,3], ground-based measurements were made with PARIS-IR at the arctic stratospheric ozone observatory (AStrO) near Eureka, Nunavut, Canada (80.05°N, 86.42°W, 0.61 km elevation). AStrO (now called the Polar Environment Atmospheric Research Laboratory, PEARL) was built by Environment Canada in 1993 and is located on

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a ridge about 15 km northwest of the Eureka weather station. Column amounts were retrieved using the SFIT2 package (version 3.81) which is a state-of-art computer program capable of retrieving volume mixing ratio (VMR) profiles of trace gases. SFIT2 is the successor of SFIT1. SFIT1 retrieves total column densities of trace gases by performing a point-by-point fitting of observed atmospheric spectra using a nonlinear least-squares method for the inverse model [4–6]. The nonlinear least-squares method in SFIT1 was replaced by the Optimal Estimation Method in SFIT2. SFIT2 was developed by C.P. Rinsland of NASA Langley Research Center and B. Connor of the National Institute of Water and Atmospheric Research Lauder, NZ. SFIT2 retrieves vertical VMR profiles of atmospheric gases as well as their total column densities from ground-based spectroscopic observations [7–10].

Very high resolution ($\sim 0.004 \text{ cm}^{-1}$) ground-based measurements were conducted for the validation of ACE-FTS measurements. Among them is a preliminary comparison of stratospheric columns of HCl and ClONO₂ at selected northern latitudes [11]. In comparing profiles derived from ground-based measurements with those obtained from ACE-FTS, it is important to note the geometric differences between the observations. In particular, in ground-based observations an atmospheric column or low vertical resolution profile is retrieved from a single spectrum (or a co-added spectrum with improved signal-to-noise ratio (SNR)) whereas, being a limb sounder, an ACE-FTS profile is derived from inverting a series of spectra measured at different tangent heights. As a result, the retrieval approach is quite different and a careful assessment of the error budget is required. Despite having a lower spectral resolution (0.02 cm^{-1}) than other ground-based spectrometers widely used in the satellite validation, PARIS-IR [12] has advantages for the validation of ACE-FTS measurements. Firstly, the PARIS-IR has wide spectral coverage, like ACE-FTS, so that information on many atmospheric species can be retrieved from each spectrum. Secondly, the integration time required to record spectra is relatively short (400 s to produce one co-added measurement). Compared with 15 northern hemisphere ACE-FTS measurements (per day), which are spread in longitude, PARIS-IR measurements allow for very fine time resolution for sampling the atmosphere. Finally, PARIS-IR is transportable and can be used for field campaigns in remote locations (such as the Canadian Arctic) or mounted on a balloon gondola to make measurements from high altitudes ($\sim 35 \text{ km}$) [12].

In this paper, we discuss the data acquisition and subsequent analysis of vertical column density measurements made with PARIS-IR. A brief description of the PARIS-IR instrumental configuration is followed by sections describing the low-level processing of our recorded spectra: wavenumber calibration, the derived instrumental line shape function, and the choice of spectral fitting intervals (microwindows—MWs). The remainder of our work focuses on the characterization and error analysis of the retrieved N₂O and O₃ columns amounts, which are taken as representative species for the troposphere and stratosphere, respectively. Examples of column comparisons with ACE-FTS and ozonesonde measurements are also presented.

2. Instrument and data acquisition

2.1. PARIS-IR

PARIS-IR was constructed by ABB-Bomem using the flight spare components of the ACE-FTS [1] instrument. The spectrometer is based on a double pendulum interferometer with two cube corner reflectors. It records a double-sided interferogram using liquid nitrogen cooled mercury cadmium telluride (MCT) and indium antimonide detectors in a sandwich arrangement. By recombining the signals from each detector, continuous spectral coverage from 750 to 4400 cm^{-1} is achieved in every single sweep of the moving mirrors. The instrument has a flexible design, offering variable maximum optical path differences (MOPDs) from 1.25 to 25 cm with an independent gain adjustment for each detector. For the measurements discussed herein, the MOPD was 25 cm with a scanning speed of 2.5 cm/s, yielding a spectral resolution ($0.5/\text{MOPD}$) of 0.02 cm^{-1} . Further specifications can be found in the paper of Fu et al. [12].

2.2. Data acquisition

AStrO has been a primary Arctic station in the Network for the Detection of Stratospheric Change (NDSC, <http://www.ndsc.ws>, now called the Network for the Detection of Atmospheric Composition Change,

NDACC) since 1993 [13,14]. The observatory has sun-tracking mirrors specially designed for the low solar elevation angles and a Bomem DA8 FTS (from here on called DA8) operated by Environment Canada on a campaign basis. During the intensive phase of the Canadian Arctic ACE Validation Campaign (February 21–March 9, 2004), the sun tracker was alternately shared between PARIS-IR and the DA8 by means of a movable mirror that could be repeatedly placed in exactly the same position in the solar beam. PARIS-IR records a double-sided interferogram and it takes 20 s to sweep the distance from -25 to $+25$ cm. Raw PARIS-IR measurements consist of 20 double-sided interferograms. These interferograms were individually Fourier transformed into spectra and co-added resulting in a total integration time of 400 s for each spectrum used in the column amount determinations. The signal-to-noise ratio (SNR) of each co-added measurement was typically between 150 and 200.

While the MCT detector installed in the ACE-FTS is a photovoltaic detector, PARIS-IR uses a photoconductive MCT detector. When exposed to high solar radiation fluxes, the response of photoconductive MCT detectors can be quite nonlinear [15]. This nonlinear response appears in the spectra as out-of-band artifacts and a positive zero offset within the spectral band (i.e. the absorption spectra do not go to zero even for saturated absorption lines). A zero-level offset, when not corrected, was previously observed to produce artificially high column densities [15,16]. To minimize nonlinear effects, the gain setting of the detectors was monitored such that the intensity level of the interferogram at zero path difference was less than 50% of the detector analog-to-digital converter range. Finally, a nonlinearity correction was performed during the Fourier transformation using the data processing software supplied by ABB-Bomem.

When PARIS-IR was first delivered, noise bursts were present in each interferogram at about ± 12.5 cm optical path difference. These features gave rise to substantial channeling throughout the spectrum. To reduce this, the noise bursts were removed by zeroing these regions of the interferogram as first suggested by Mertz [17]. Any residual channeling was removed during the fitting of the observed spectra by introducing a sine wave with adjustable parameters into the calculation of each spectrum in the forward model (Section 3.2.3). Following the validation campaign in 2004, the mechanical problem giving rise to the noise bursts was eliminated during a retrofit by ABB-Bomem.

The calibration was performed in two steps. The metrology laser in PARIS-IR is a single mode, distributed feedback diode laser operating at 1.55 microns. Although the laser frequency is stable for the duration of a 400 s (20 scans) spectral measurement, its frequency exhibits some daily variability due to changes in the instrument temperature. To ensure absolute calibration of the atmospheric spectra, N_2O gas cell spectra were recorded at the beginning and end of each day of the Arctic campaign. Thus, by comparing the molecular line positions (ν_{obs}) in the N_2O gas cell spectra with the reference line positions (ν_{ref}) from the HITRAN 2004 database [18], a set of relative wavenumber errors was derived to provide absolute wavenumber calibration. The relative wavenumber errors, defined as $10^6(\nu_{\text{ref}} - \nu_{\text{obs}})/\nu_{\text{obs}}$ in units of parts per million, were compared against various instrument housekeeping parameters. As shown in Fig. 1, a linear correlation was observed between the relative wavenumber errors and the laser thermoelectric cooler current. For individual atmospheric spectra, the relative wavenumber error computed by using the correlation in Fig. 1 was adequate for estimating the wavenumber shift parameter required by the ABB-Bomem PARIS-IR processing software. Finally each spectrum in the 20 spectra measurement set was independently calibrated against reference lines of N_2O from the HITRAN 2004 database [18] and then co-added after resampling to a common wavenumber grid. We have observed that the accuracy of the PARIS-IR wavenumber calibration factor is approximately 10^{-6} (about 0.003 cm^{-1} at 3000 cm^{-1}).

In order to obtain accurate column densities from spectral lines, it is important to have detailed knowledge regarding the instrument line shape (ILS). In the case of a FTS, instrumental effects, such as the finite optical path difference, finite size of the entrance aperture and modulation efficiency of the interferometer, influence the line shape function. The Fourier transform of the line shape function gives rise to a peaked function in the interferogram domain that has a value of 1 near zero optical path difference and decreases as the optical path difference increases. In an ideal FTS, the spectral line shape is a *sinc* function in the spectral domain, which corresponds to a “boxcar” in the interferogram domain because of the finite optical path difference. The line shape function of a real FTS can thus be viewed as an apodization of the boxcar function or as an effective modulation efficiency which is a function of optical path difference in the interferogram domain. We therefore represent the line shape as an Empirical Apodization Parameter (EAP) function in the interferogram domain.

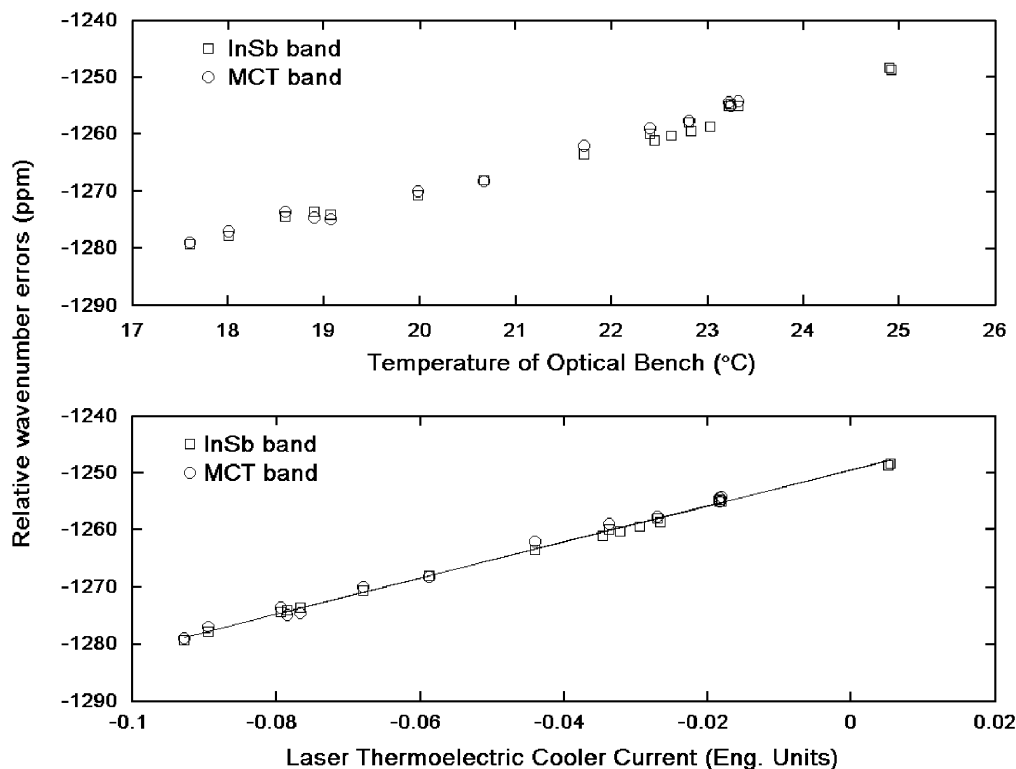


Fig. 1. A linear correlation is observed between the relative wavenumber errors, defined as $10^6(v_{\text{ref}} - v_{\text{obs}})/v_{\text{obs}}$, and temperature of the optical bench (upper panel) and the laser thermoelectric cooler current (lower panel).

The EAP parameters were determined in two steps. From the N_2O gas cell measurements, preliminary values of the EAP function near 2550 cm^{-1} were determined in a fourth-order polynomial form using a customized nonlinear least-squares fitting program. SFIT2 can be used to retrieve an EAP function in a polynomial form as part of the fitting procedure. A series of EAP functions for various spectral fitting intervals, called MWs, were subsequently retrieved from the atmospheric spectra by adopting the EAP function retrieved at 2550 cm^{-1} as an initial value in a preliminary SFIT2 fit. Mean EAP functions for each MW were obtained by averaging the EAPs retrieved from the preliminary fits. The spectra used to derive the mean EAP function were recorded throughout one of the good observing days (March 3, 2004) during the campaign. As an example, the mean EAP function retrieved for a MW near 2775 cm^{-1} is presented in Fig. 2, which shows substantial apodization. The mean EAP function for each MW was then held fixed in the final fit, unless stated otherwise.

3. Retrieval method

The method used in the determination of atmospheric constituent concentration from a 400 s co-added PARIS-IR spectrum is based on fitting of an observed spectrum to a calculated spectrum by adjusting the atmospheric profile and a few instrument-related parameters. Given a parameterized model of the instrument, the forward equation of radiative transfer and the unknown retrieval parameters, the forward problem can be written as

$$\mathbf{y} = \mathbf{F}(\mathbf{q}, \mathbf{b}) + \boldsymbol{\varepsilon}_y, \quad (1)$$

where $\mathbf{y}$ is a vector of measured spectral intensity (consisting of m datapoints), $\mathbf{F}(\mathbf{q}, \mathbf{b})$ is the forward model, $\mathbf{q}$ is a composite or *full* state vector (having n fitting variables) consisting of a collection of variables to be retrieved from the measurement, $\mathbf{b}$ is a set of non-retrieved parameters that are additional inputs to the forward model, and $\boldsymbol{\varepsilon}_y$ is the measurement noise. Eq. (1) is commonly linearized to yield,

$$\mathbf{y} = \mathbf{K}\mathbf{q} + \boldsymbol{\varepsilon}_y, \quad (2)$$

where $\mathbf{K} = \partial\mathbf{F}/\partial\mathbf{q}$ gives a $m \times n$ weighting function matrix (also called Jacobian matrix) [19,20].

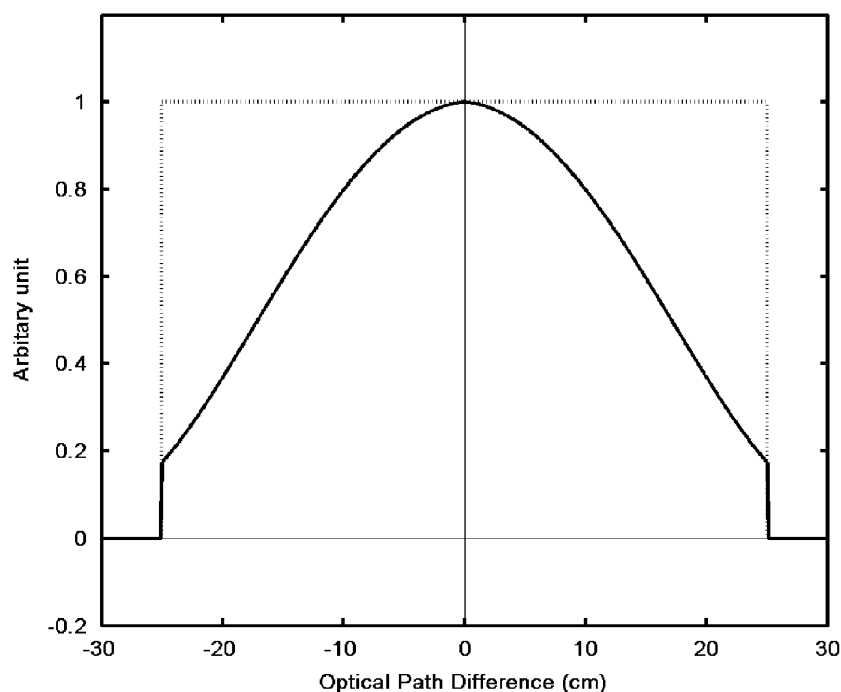


Fig. 2. The PARIS-IR modulation efficiency (or Empirical Apodization Parameter, EAP) function determined for the 2775 cm^{-1} region. Observed shown with solid line and ideal (boxcar) shown with dashed line. See text for details.

For this study, we are primarily interested in characterizing the independent retrieval of atmospheric N_2O and O_3 from Arctic PARIS-IR measurements. Accordingly, the measurement vector, $\mathbf{y}$, consists of a spectral MW, typically $1\text{--}5\text{ cm}^{-1}$ in width, chosen to contain well-isolated absorption features of the species of interest with a minimal number of interfering molecular lines. In the cases for a given gas, when there are several spectral regions separated by less than 60 cm^{-1} , a multi-MW approach is taken where $\mathbf{y}$ consists of a concatenated set of MWs. Additional inputs to the forward model, $\mathbf{b}$, include a set of instrument and forward model parameters that are known to some accuracy. Included in this vector are spectroscopic line parameters, an assumed temperature profile, the observed solar zenith angle, MOPD and so forth. Finally, the composite state vector, $\mathbf{q}$, includes the relative VMR profile, for either N_2O or O_3 , scaled by the *a priori* mixing ratio, and extra retrieval parameters that include a background level, wavenumber shift, and uniform VMR profile scaling factors for interfering molecules, etc. Adopting the notation of Rodgers and Connor [20], we take the composite state vector, $\mathbf{q}^T = (\mathbf{x} \mathbf{e})^T$, to include the atmospheric VMR profile of interest, $\mathbf{x}$, and the *extra* parameters, $\mathbf{e}$, that are not related to the VMR profile of a target gas.

3.1. Forward model

As given in Eq. (1), the forward model relates the true atmosphere to the measured spectrum. Atmospheric spectra are simulated using a multi-layer, multi-species, line-by-line radiative transfer model originally developed at the NASA Langley Research Center for the analysis of infrared solar spectra recorded with FTSS [6,21,22]. The model assumes the atmosphere is well represented as homogeneous layers in local thermodynamic equilibrium and that the modeled spectral lines have a Voigt profile. Similarly, refractive ray-tracing calculations are assumed to be separate and iterative [6,23,24].

The synthetic atmospheric spectra output by the forward model are simulated based on a 29-layer atmosphere that is widely used to retrieve column densities and VMR profiles [7,21,22]. Formulated on an altitude scale, the lower boundary of the height coordinate is 0.61 km. Subsequent layers are defined with 1 km thickness up to 10 km, and with increasing thickness between 10 and 40 km. Between 40 and 80 km, layers have thicknesses of 10 km and the upper boundary occurs at 100 km. This layering scheme is similar to the High Resolution Troposphere (HRT) scheme described by Meier [25], but constructed with slightly increasing layer

thickness for the stratosphere to minimize the possible occurrence of artifacts in the retrieved VMR profiles such as an oscillation [24].

Three sources of spectroscopic line parameters are used for the line-by-line calculation of the monochromatic atmospheric transmission. For molecular line parameters, the HITRAN 2004 database [18] was adopted. For molecules that have spectra with unresolved rotational structures, HITRAN only reports their absorption cross-sections. Under these circumstances, we have used the ‘pseudo-lines’ generated by Toon et al. [26] which are included in the SFIT2 package. For solar lines, we adopted the parameter set from Meier et al. [27].

As part of the forward model, the FSCATM [23] program was used to calculate column densities along the atmospheric absorption path in each layer. These column densities are used directly in Beer’s law to compute the monochromatic transmission. Based on the ephemeris and simple non-refracting geometry, the “astronomical solar zenith angle” for each co-added measurement was computed at the arithmetic mean between the start and end time of recording the 20 individual spectra. This is acceptable because each spectral scan is completed in 20 s and therefore the difference in astronomical solar zenith angle between the one computed at the arithmetic mean time and the average value of solar zenith angles corresponding to the 20 individual spectra is $\sim 0.001^\circ$. The astronomical solar zenith angle is then supplied as an initial value for the iterative ray-tracing calculation that accounts for atmospheric refraction. The astronomical solar zenith angles are typically greater than 85° for the measurements at Eureka during the intensive phase of the Arctic campaign even at solar noon so the airmass values for the measurements are very large (< 10). Since the airmass influences the total column retrieved, errors in the computation of the solar zenith angle and airmass need to be considered. It was found that the solar zenith angle varies less than 0.1° over 200 s (i.e., half of the integration time of a PARIS-IR co-added measurement) and that the variation in airmass during a full PARIS-IR measurement (20 co-added scans) at a solar zenith angle of 89° is less than $\pm 3\%$. Since most of the atmospheric spectra used in this work were recorded at astronomical solar zenith angles less than 89° , the errors introduced into the airmass calculation by the change in solar zenith angle during a PARIS-IR measurement have a minor effect on the retrieved column. The typical PARIS-IR integration time of 400 s therefore is acceptable for co-adding. More specific error estimates associated with solar zenith angles will be discussed in Section 5.

3.2. Inverse model parameters

In determining the total column from infrared spectra, we use SFIT2 (version 3.81) to first estimate the VMR profile and then proceed to determine the column amount. In contrast to SFIT1 [6], which adopts nonlinear least-squares method to determine a single multiplicative scale factor that is applied to an *a priori* profile, SFIT2 uses optimal estimation [19,20,28] to retrieve the profile directly. Wood et al. [10] have pointed out that SFIT2 generally provides more reliable column densities than SFIT1 because SFIT2 produces a more realistic representation of the atmospheric VMR profiles.

In optimal estimation, the *a priori* state, $\mathbf{q}_a$, and the measurement, $\mathbf{y}$, are statistically combined to yield the most probable estimate of the state, $\hat{\mathbf{q}}$, given an estimate of the *a priori* error covariance, $\mathbf{S}_a$, and the measurement noise covariance, $\mathbf{S}_e$. The problem of retrieving a VMR profile from measurements is moderately nonlinear in that the linearization given in Eq. (2) is adequate for characterization and error analysis, but not for finding a solution. Thus, SFIT2 performs a Gauss–Newton iteration of the optimal estimation,

$$\mathbf{q}_{i+1} = \mathbf{q}_a + (\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_e^{-1} \mathbf{K}_i)^{-1} \mathbf{K}_i^T \mathbf{S}_e^{-1} [(\mathbf{y} - \mathbf{y}_i) - \mathbf{K}_i(\mathbf{q}_a - \mathbf{q}_i)] \quad (3)$$

in which $\mathbf{q}_i$ is the full state vector for the *i*th iteration, and $\mathbf{K}_i$ and $\mathbf{y}_i$ are the weighting function and a synthetic spectrum evaluated and simulated at $\mathbf{q}_i$, respectively. Throughout our work, the measurement noise covariance matrix, $\mathbf{S}_e$, is taken to be diagonal, with the elements being equal to the square of the reciprocal of the observed SNR. The $\mathbf{S}_{ax}$, the VMR profile part of the full *a priori* error covariance, was chosen to be diagonal with the elements corresponding to an *ad hoc* relative standard deviation of 20% for all of the 29 layers. The additional elements of the *a priori* error covariance corresponding to the extra parameters, $\mathbf{S}_{ae}$, were also taken to have uncorrelated errors of values between 20 and 100%, depending on the fitting variables.

3.2.1. First guess and *a priori* information

Daily temperature and pressure profiles were constructed by combining multiple sources of meteorological data. The measurements of a radiosonde launched from the Eureka weather station, 15 km away from the AStrO site [3], were adopted from the surface to the maximum height reached by the balloon (typically ~38 km). Above this, National Centers for Environmental Prediction (NCEP) data (obtained from the Goddard Automailer science@hyperion.gsfc.nasa.gov) [29,30] was generated for the observing day to extend our profiles to ~50 km. Finally, for high altitudes, the winter sub-arctic profile from the US standard atmosphere [31] was used.

The *a priori* trace gas profiles used in this work were provided by Environment Canada [32]. The VMR profiles are based on a model mid-latitude atmosphere with daily VMR adjustments for the high latitude atmosphere over AStrO [33,34]. For O₃ and H₂O, the lower portions of the *a priori* profiles were taken from daily ozonesonde and radiosonde measurements, respectively, obtained from balloons launched at the Eureka weather station. While the ozonesonde measurements were used from surface to the maximum balloon flight altitude, the radiosonde data was used only up to the tropopause (usually ~8 km during the validation campaign), above which the relative humidity data recorded by the radiosonde are less reliable due to very low water concentration.

Daily adjustments to the *a priori* profiles include tropopause and subsidence corrections. The tropopause height, which varies daily depending on the activity of the polar vortex, was obtained from the radiosonde measurements. Cold air in the Arctic vortex sinks, so subsidence corrections are needed for the Arctic winter stratosphere [25,26]. The degree of the stratospheric subsidence is parameterized as the Degree of Subsidence and Ascent (DOSA) [25] and was derived from DA8 measurements [32]. Attempts to obtain the reliable daily DOSA values from the PARIS-IR spectra were unsuccessful because of the residual channeling and the relatively low resolution (0.02 cm⁻¹ for PARIS-IR versus 0.004 cm⁻¹ for the DA8).

3.2.2. Spectral MWs

For the PARIS-IR Arctic spectra acquired at solar zenith angles greater than 85°, it proved challenging to find MWs having unsaturated, well isolated spectral line features. For example, O₃ lines in the 10 μm region are nearly saturated in our spectra due to the long atmospheric absorption path length associated with such high solar zenith angles. In selecting MWs, a forward model simulation and linear error characterization were performed to determine spectral fitting intervals that contribute to the atmospheric information content while minimizing the influence of interfering molecules. The MWs selected for O₃ and N₂O are listed in Table 1. One should recall that PARIS-IR usually records multiple spectra each day, and that each single spectrum contains various fitting MWs. Therefore, an independent SFIT2 column estimate was derived for each listed MW in each spectrum with the final reported results being a statistical mean for the day.

It is important to emphasize that, unlike many other ground-based FTSs which observe at very high spectral resolution (~0.004 cm⁻¹), PARIS-IR has significantly lower spectral resolution (0.02 cm⁻¹). Both measurements rely on the different transmission characteristics of a spectral line to derive information on the concentration from different optical depths in the atmosphere. Thus, an instrument with very high spectral

Table 1
List of the microwindows used for N₂O and O₃ column retrievals^a

Species	Microwindow	Spectral range	Interfering species
N ₂ O	MW2523	2520.50–2524.09	CO ₂ , CH ₄ , HDO
	MW2806	2806.10–2808.10	HDO, CH ₄ , H ₂ CO, solar lines
O ₃	MW2775 ^b	2775.68–2776.30	CH ₄ , CO ₂ , HCl, N ₂ O,
		2778.90–2779.50	HDO, solar lines
		2781.54–2782.09	
	MW3040	3039.80–3041.70	CH ₄ , H ₂ O, CH ₃ D

^aSpecies, spectral fitting interval labels (MW followed by four digits representing the spectral location of the microwindow), spectral ranges, and interfering molecules are presented.

^bNote that “MW2775” describes a multiple microwindow fit.

resolution (i.e., capable of fully resolving an individual spectral line) is able to estimate the species concentration as a function of altitude by measuring 1–2 spectral lines in a narrow spectral interval within which interfering lines can be avoided. Measuring at a lower spectral resolution, PARIS-IR samples each ro-vibrational line with only 3–4 independent points, which makes it difficult to estimate an atmospheric profile from a single line. This is particularly problematic when observing stratospheric species as the spectral lines are not subject to substantial pressure broadening. To overcome this limitation, wider MWs and multiple MW are used to increase the atmospheric information content of the target species.

Examples of our spectral fits and their residuals, computed as measured minus calculated spectrum, are shown in Figs. 3–6 for a series of spectra recorded on March 3, 2004. As shown in Fig. 3, the residuals in the MW2523 for N_2O are observed to be less than 1% in most of the spectral region of the MW. Similarly, Fig. 4 shows that residuals of MW2806 for N_2O are less than 2% over most of the spectral region with systematic residual features near the CH_4 lines present in the MW. For O_3 , fitting results from the O_3 MW2775 multiple MW consisting of three MWs near 2775, 2779, and 2781 cm^{-1} are presented in Fig. 5(a–c). The unfit feature near 2776 cm^{-1} in Fig. 5(a) is due to absorption by an unidentified species whose spectroscopic parameters are either missing or underestimated in the HITRAN 2004 database [18]. However, the unfit feature is well localized and the effect on the O_3 column density retrieval is minimal. The residuals from MW3040 presented in Fig. 6 are within 2% over most of the spectral range.

3.2.3. Spectral channeling

As noted in Section 2.2, raw PARIS-IR spectra are corrected for channeling by a manipulation of the recorded interferogram. Despite this correction, residual channeling at the high and low wavenumber extremes of our spectral bandpass were noticeable in our preliminary analysis. Accordingly, SFIT2 (ver.3.81) was modified to use the channeling fit sub-routines from SFIT1 (ver. 1.09e). Spectral channeling was therefore taken into account in our forward model by including a sine function with 4 parameters (amplitude, period, zero-phase wavenumber and variation in the amplitude with wavenumber) for each MW. Although these channeling parameters were determined during our preliminary analysis, the MWs used in this study show no significant residual channeling effects therefore the channeling parameters were not included in the final fitting.

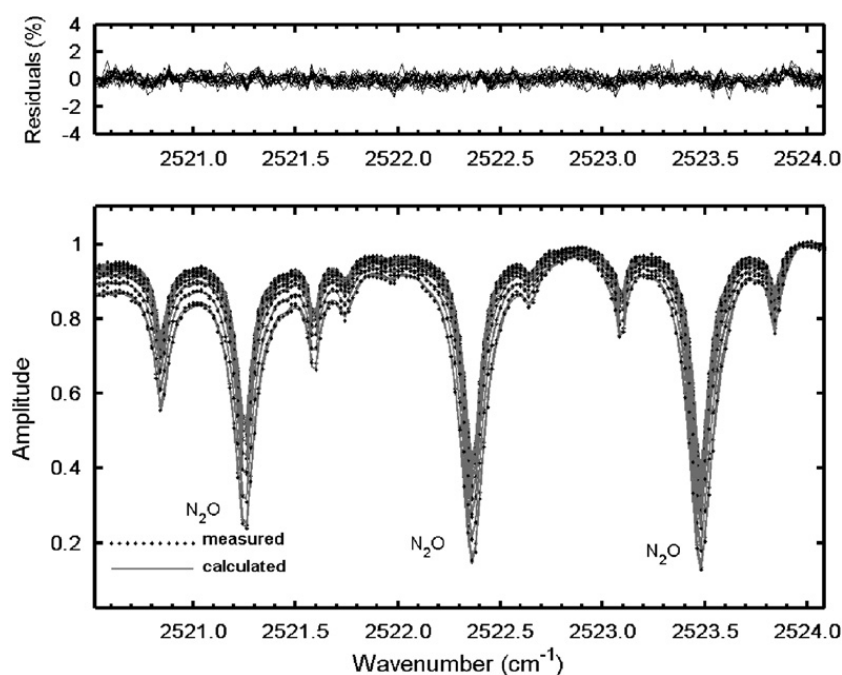


Fig. 3. An example of the spectral fitting residuals (measured minus calculated given in percent) from MW2523 for a series of spectra recorded on March 3, 2004 during the observation period between 9:48 am and 4:11 pm (Local Time).

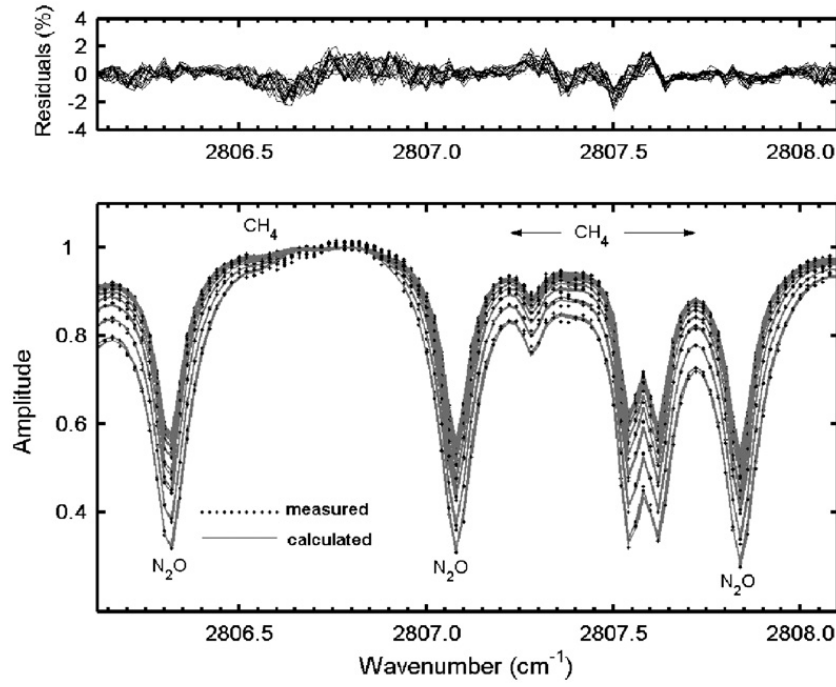


Fig. 4. An example of the spectral fitting residuals (measured minus calculated given in percent) from MW2806 for a series of spectra recorded on March 3, 2004 during the observation period between 9:48 am and 4:11 pm (Local Time).

4. Averaging kernels and characterization of the retrievals

When using optimal estimation, the accuracy of the retrieval is influenced by the complete observing system, which is defined by Rodgers [28] as the combination of the observing instrument and the retrieval method. Thus, retrieval accuracy is limited not only by the performance of the instrument and the forward model, but also by errors in the ancillary data and our implicit discretization of the problem. Uncertainty in spectroscopic parameters, temperature, pressure and the assumed *a priori* profile for other trace species all contribute to the overall accuracy of the retrieval. Following the approach of Rodgers [19,20], we characterize the retrieval by relating the retrieved composite state vector, $\hat{\mathbf{q}}$, to the true quantity, $\mathbf{q}$, and any *a priori* $\mathbf{q}_a$ used in its retrieval by

$$\hat{\mathbf{q}} - \mathbf{q}_a = \mathbf{A}(\mathbf{q} - \mathbf{q}_a) + \text{errors}, \quad (4)$$

where $\mathbf{A}$ is the averaging kernel matrix and the errors comprise random and systematic uncertainties that contribute to the retrieval. Recall that the full state vector, $\mathbf{q}$, is partitioned into elements corresponding to the atmospheric VMR profile of interest, $\mathbf{x}$, and extra parameters, $\mathbf{e}$, that are simultaneously retrieved but not directly related to the VMR profile. Accordingly, Eq. (4) can be expanded to

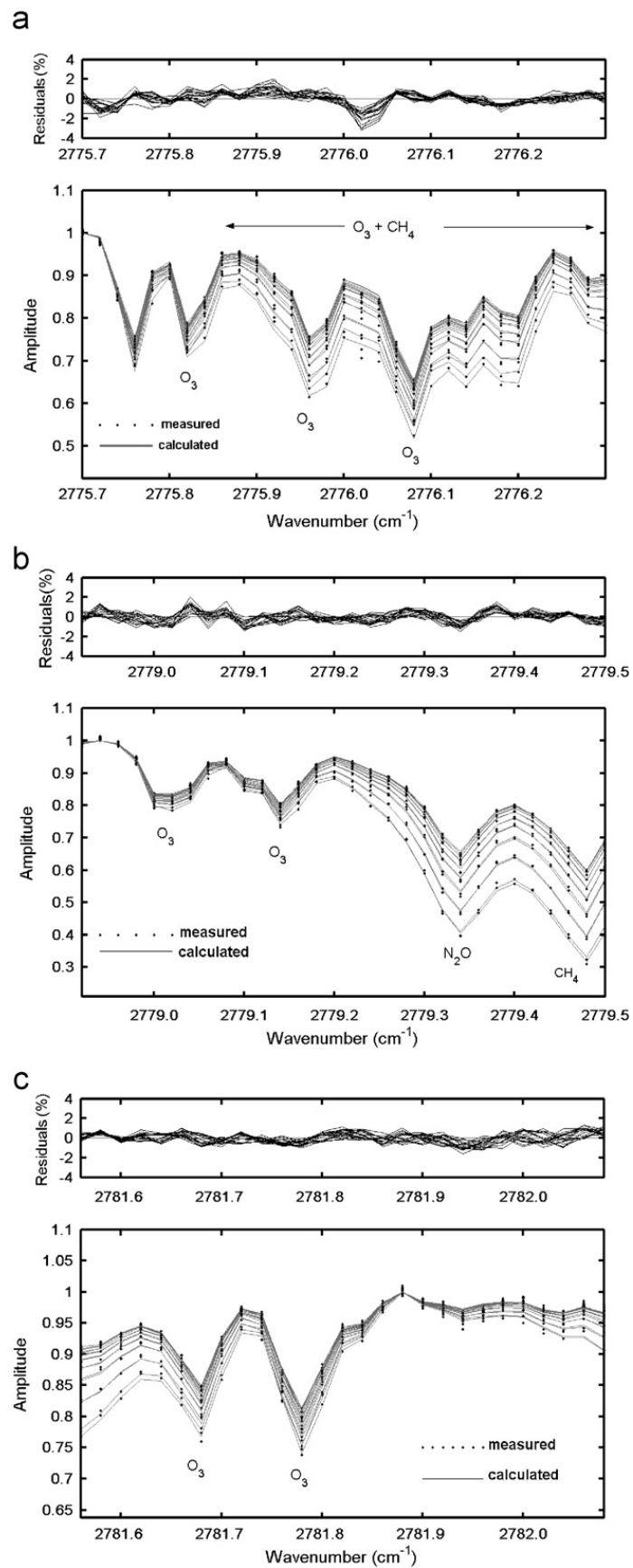
$$\begin{pmatrix} \hat{\mathbf{x}} - \mathbf{x}_a \\ \hat{\mathbf{e}} - \mathbf{e}_a \end{pmatrix} = \begin{pmatrix} \mathbf{A}_{xx} & \mathbf{A}_{xe} \\ \mathbf{A}_{ex} & \mathbf{A}_{ee} \end{pmatrix} \begin{pmatrix} \mathbf{x} - \mathbf{x}_a \\ \mathbf{e} - \mathbf{e}_a \end{pmatrix} + \text{errors}, \quad (5)$$

where $\mathbf{A}_{xx}$ is the averaging kernel for the atmospheric VMR profile. Conceptually, rows of $\mathbf{A}_{xx}$ represent smoothing functions, called averaging kernels, for each of our 29 atmospheric layers and are generally peaked functions with a width describing the vertical resolution of the profile retrieval. The area of each averaging kernel for the profile is approximately unity in layers where the retrieval is accurate. Outside this range, the area tends towards zero and the retrieved profile tends to $\mathbf{x}_a$ plus measurement error.

Rearranging Eq. (5), the error in $\hat{\mathbf{x}}$ is

$$\hat{\mathbf{x}} - \mathbf{x} = (\mathbf{A}_{xx} - \mathbf{I})(\mathbf{x} - \mathbf{x}_a) + \mathbf{A}_{xe}(\mathbf{e} - \mathbf{e}_a) + \text{errors}, \quad (6)$$

where $\mathbf{I}$ is a unit matrix, $(\mathbf{A}_{xx} - \mathbf{I})(\mathbf{x} - \mathbf{x}_a)$ is the usual smoothing error and $\mathbf{A}_{xe}(\mathbf{e} - \mathbf{e}_a)$ represents the interference error that arises when considering the different parts of the state vector. Taking $\mathbf{x}$ and $\mathbf{e}$ to be



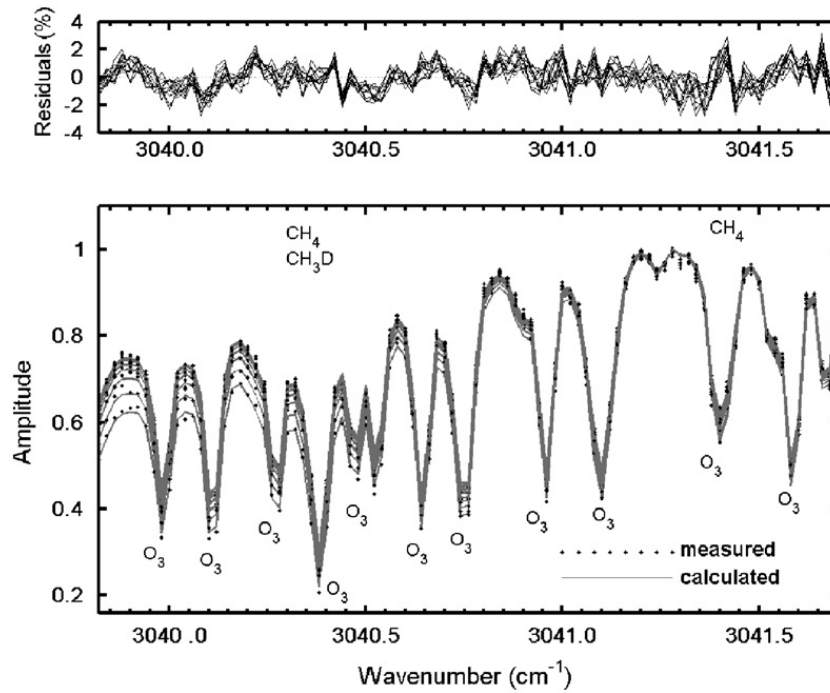


Fig. 6. An example of the spectral fitting residuals (measured minus calculated given in percent) from MW3040 for a series of spectra recorded on March 3, 2004 during the observation period between 9:48 am and 4:11 pm (Local Time).

uncorrelated, we group the interference error with the retrieval error ('errors' in Eqs. (4–6)) and consider these in Section 5.2.2.

Total and partial vertical columns can be obtained by integrating the retrieved column contributions $\hat{c}_i$ computed as $\hat{c}_i = \hat{x}_i N_i$, where N_i is the air column density at the i th layer (in molecules/cm²). Analogous to Eq. (4), the retrieved columns per layer can be written as

$$\hat{\mathbf{c}} - \mathbf{c}_a = \mathbf{A}^c (\mathbf{c} - \mathbf{c}_a) + \text{errors}, \quad (7)$$

where the rows of $\mathbf{A}^c$ are the column averaging kernels referenced to layer amounts obtained by

$$A_{ij}^c = A_{ij} (N_i / N_j). \quad (8)$$

The sensitivity of the retrieved column to the true state can be monitored by checking the column averaging kernels. Partial columns for merged layers are computed by summing the retrieved column contributions for each layer in a specified altitude range.

Following Rodgers [19], the degrees of freedom for signal (DOFS) are estimated to be in the range of 1.9–2 for the MWs of N₂O and 1.3–1.9 for the MWs of O₃. Accordingly, partial columns can be independently determined for up to two merged layers for N₂O and less than two merged layers for O₃ for the MWs used. Representative averaging kernels for total columns and partial columns associated with specified altitude ranges are presented in Figs. 7 and 8 for N₂O and O₃, respectively. The total column averaging kernels for N₂O (Fig. 7), whose values are close to one below ~12 km, demonstrate that the retrievals are most sensitive to the troposphere, as expected. For both N₂O MWs, two partial columns can be determined. The peak altitude of the partial column averaging kernel in the 0.61 to 6 km range for MW2523 is lower than that for MW2806 (~2 km versus ~3 km, respectively). The averaging kernel for the merged layers from 6 to 100 km has

Fig. 5. An example of the fitting results for O₃ with the residuals (measured minus calculated given in percent) from the multiple microwindow (MW) fit during the observation period on March 3, 2004 between 9:48 am and 4:11 pm (Local Time): (a) 2775 cm⁻¹ region (b) 2779 cm⁻¹ region and (c) 2782 cm⁻¹ region. The three MWs were fit simultaneously with SFIT2 and termed MW2775 in Table 1. Note that the unfit feature near 2776 cm⁻¹ in Fig. 5(a) is due to absorption by an unidentified species whose spectroscopic parameters are either missing or underestimated in the HITRAN 2004 database [18].

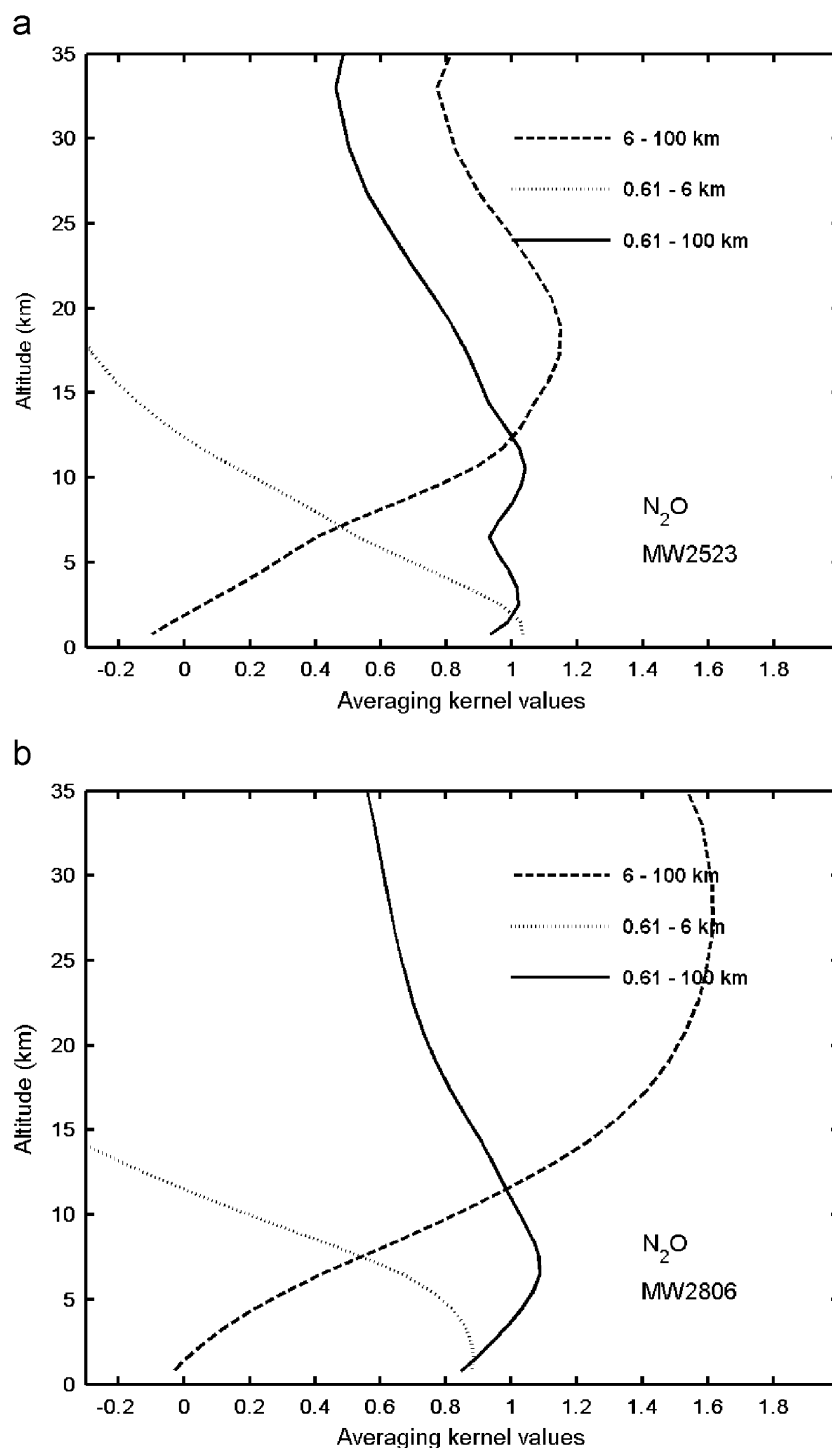


Fig. 7. Representative column averaging kernels from a single microwindow fit of (a) MW2523 and (b) MW2806 for N₂O. The degrees of freedom for signal (DOFS) are 2.0 and 1.9, respectively.

a maximum near 17 km for MW2523 and near 25 km for MW2806. A secondary peak near 45 km (not shown) in the total column averaging kernel for MW2523 of N₂O is seen, which is an artifact introduced by Eq. (8) in the averaging kernel rescaling process. For O₃, the total column averaging kernels are peaked in the lower-to-mid-stratosphere and the retrievals in the two MWs are most sensitive to the atmosphere over different altitude ranges: the averaging kernel for MW2775 in Fig. 8(a) has a broad peak between approximately 15 and 30 km and the one for MW3040 in Fig. 8(b) has a sharper peak near 15 km with a width of ~20 km (FWHM). The ozone partial column averaging kernels in the 0.61–6 km range show that the

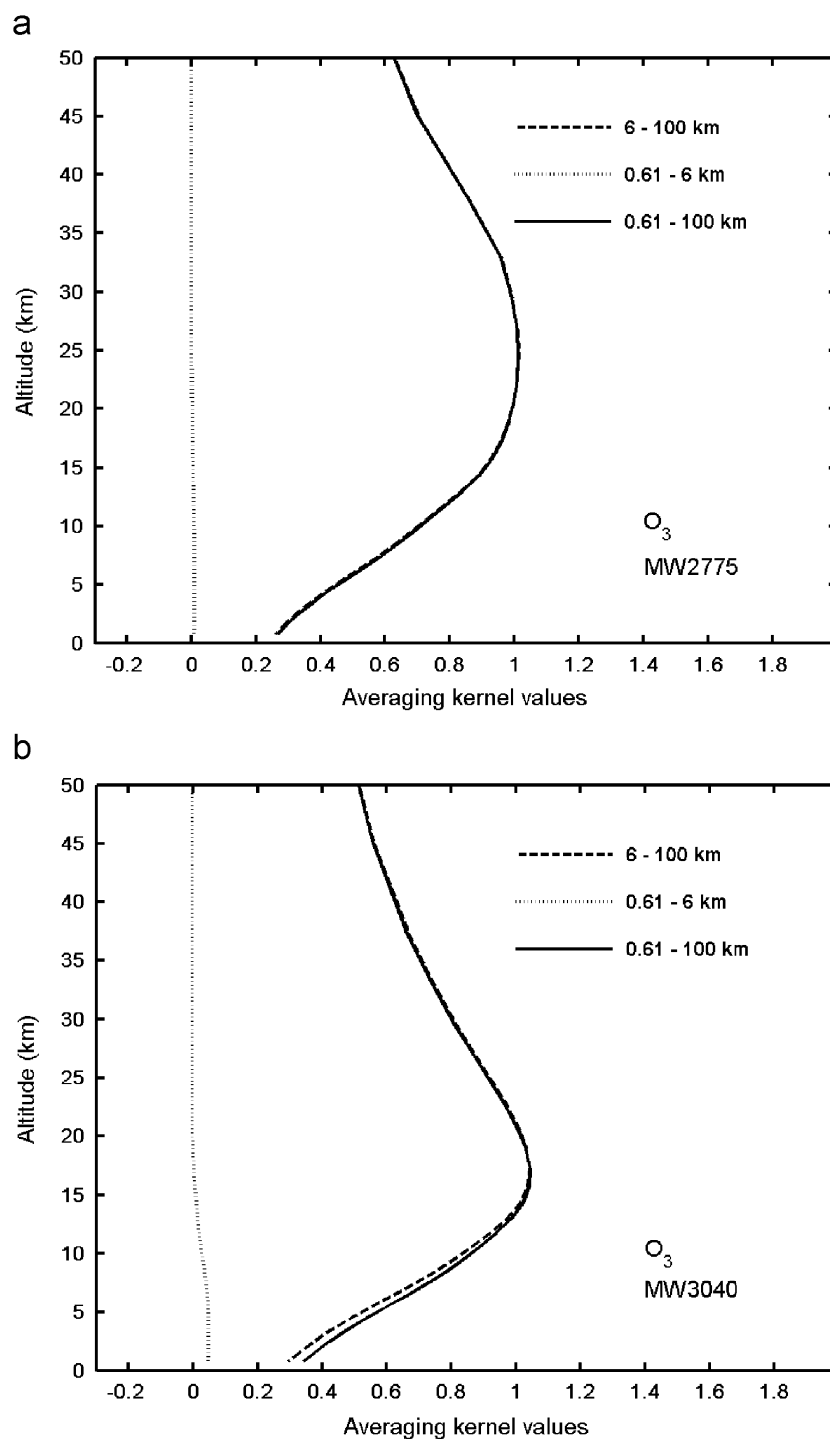


Fig. 8. Representative column averaging kernels for O_3 (a) from a multiple microwindow (MW) fit of MW2775 (2775, 2779 and 2782 cm^{-1} regions), (b) from a single MW fit of MW3040. The DOFS values are 1.3 and 1.9 for these MWs, respectively.

retrievals for both MWs have virtually no sensitivity to ozone in the troposphere. Therefore, we report only total column density for O_3 .

5. Error analysis

In this section we attempt to quantify the various uncertainties in the PARIS-IR observing system and estimate the accuracy of the inferred columns. Assuming the fundamental physics described by the SFIT2

Table 2

List of the error sources in the retrieved total columns for N₂O and O₃ (see text for details)

Sources		Errors (%)			
		N ₂ O		O ₃	
		MW2523	MW2806	MW2775	MW3040
Random errors	Retrieval error ^a	2.0	1.1	1.9	1.1
	SZA ^b	2.7	2.7	1.7	1.0
	Temperature	~1	~1	~1	~1
	Sub-total	3.5	3.1	2.7	1.8
Systematic errors	Line parameters	~2	~2	~5	~5
	EAP ^c	1.6	1.1	3.8	5.0
	<i>A priori</i>	6.7	5.7	10.5	7.2
	Sub-total	7.2	6.1	12.2	10.1
Total error		8.0	6.8	12.5	10.3
Total mean error ^d			7.4		12.8

^aInterference plus retrieval noise. See text for further details.

^bSolar Zenith Angle.

^cEmpirical Apodization Parameter function.

^dComputed by using total errors, based on column densities calculated for each species on March 3, 2004.

radiative transfer model is a negligible contributor, the error in our VMR profile estimate given in Eq. (5) expands to

$$\begin{aligned}
 \hat{\mathbf{x}} - \mathbf{x} = & (\mathbf{A}_{xx} - \mathbf{I})(\mathbf{x} - \mathbf{x}_a) && \text{smoothing} \\
 & + \mathbf{A}_{xe}(\mathbf{e} - \mathbf{e}_a) && \text{interference} \\
 & + \mathbf{G}_y \mathbf{K}_b(\mathbf{b} - \hat{\mathbf{b}}) && \text{model parameter} \\
 & + \mathbf{G}_y \varepsilon && \text{retrieval noise}
 \end{aligned} \tag{9}$$

where $\mathbf{G}_y$ is the retrieval gain matrix showing the sensitivity of the retrieval to the measurement and $\mathbf{K}_b = \partial \mathbf{F} / \partial \mathbf{b}$ gives the sensitivity of the forward model to the non-retrieved parameters [19]. It is customary to consider smoothing error separately and group the remaining as either systematic or random errors. We follow the approach taken by Wood et al. [35] where random uncertainties give rise to daily variability while systematic ones tend to bias the retrieved profile and subsequent column amounts in a more consistent way. Hence, random errors arise from instrument noise, the atmospheric temperature profile used, uncertainties associated with the solar zenith angle and interfering species present in our MWs. In contrast, uncertainties in spectroscopic line parameters and the ILS tend to give rise to systematic errors.

Where meaningful statistics, in the form of a covariance matrix, are available, we explicitly compute the propagated uncertainties. When this information is not available, uncertainties are estimated by computing the column corresponding to a perturbed input parameter and then comparing with the original, unperturbed result. Using the definitions of Rodgers and Connor [19,20], uncertainties due to the interferences, model parameters and retrieval noise are grouped and collectively termed the *measurement error*. The *total error* includes all the terms given in Eq. (9). Complete error budgets for the retrieved N₂O and O₃ columns are summarized in Table 2.

5.1. Smoothing error

As noted in Section 3.2, the VMR profile retrieved using SFIT2 statistically incorporates atmospheric information from both our spectroscopic measurements and an *a priori* profile. Accordingly, uncertainty in the *a priori* profile in a discretized layering scheme will contribute to the uncertainty in the retrieved profile and, depending on the exact *a priori* profile used in the retrieval, the resulting error is called smoothing error

$\mathbf{S}_s$, which tends to have both systematic and random components. The smoothing error quantifies how strongly fine structures of the true atmospheric state are smoothed by the observing system due to the limited altitude resolution captured in the measured transmittances [19,28]. In practice, however, this is difficult to estimate, as it requires independent knowledge about variability in the fine structure being smoothed. Assuming the actual statistics are expressed in the *a priori* covariance matrix, $\mathbf{S}_a$, the smoothing error covariance, $\mathbf{S}_s$, is computed as

$$\mathbf{S}_s = (\mathbf{I} - \mathbf{A}_{xx})\mathbf{S}_a(\mathbf{I} - \mathbf{A}_{xx})^T. \quad (10)$$

We consider the PARIS-IR retrieved profile as an estimate of a smoothed version of the true atmospheric state, where the smoothing function is defined by the averaging kernel and the *a priori* information. Because of the difficulties in accurately estimating the smoothing error, an alternate approach was used to estimate errors associated with the *a priori* profile contribution, which is discussed in Section 5.3.3.

5.2. Random errors

5.2.1. Spectral noise

To correctly account for the influence of spectral noise, ε in Eq. (9), on the retrieval it is prudent to consider the statistical impacts of the algorithms used to compute spectra from the recorded interferograms. These algorithms can introduce off-diagonal elements into the large measurement noise covariance matrix, $\mathbf{S}_e$, and therefore introduce computational difficulties into the retrieval. In particular, we note that PARIS-IR spectra are neither interpolated nor zero-filled as these actions would most certainly correlate the spectral noise. With regards to the algorithms used to correct for detector nonlinearity, primary channeling and spectral re-sampling, a preliminary study indicates these do not add significant correlations to the spectral noise. Accordingly, $\mathbf{S}_e$ is taken to be diagonal with elements defined as the square of the reciprocal of the SNR given in Section 2.2. Uncertainty arising from the random measurement noise in the PARIS-IR spectra is included in our analysis by transforming the measurement covariance with the gain matrix,

$$\mathbf{S}_m = \mathbf{G}_y \mathbf{S}_e \mathbf{G}_y^T. \quad (11)$$

Spectral noise was found to introduce an uncertainty of less than 1% for both N_2O and O_3 .

5.2.2. Interference

As given in Eq. (6), the partitioning of errors in the full state vector, $\mathbf{q}$, introduces an additional term in the error analysis, $\mathbf{A}_{xe}(\mathbf{e} - \mathbf{e}_a)$, due to the interference between the VMR profile component, $\mathbf{x}$, and the rest of the full state vector, $\mathbf{e}$. In our case, these additional parameters include a background slope for the measurement vector, a wavenumber scaling factor, a residual phase correction parameter, solar line parameters (when present), and multiplicative scaling factors for VMR profiles of interfering molecules. Their corresponding error covariance, $\mathbf{S}_e$, is computed as

$$\mathbf{S}_e = \mathbf{A}_{xe} \mathbf{S}_{ea} \mathbf{A}_{xe}^T \quad (12)$$

where $\mathbf{S}_{ea}$ is the *a priori* error covariance for the extra parameters. The contribution to the total column uncertainty is 0.2–1.2% for N_2O and 0.5–1.2% for O_3 , depending on their respective MWs.

5.2.3. Viewing geometry

The uncertainty arising from errors in the solar zenith angle was estimated by perturbing the solar zenith angle input to the ray trace calculation by FSCATM [23]. Since the sun tracker mirror could track the sun when up to half of the solar disk was blocked by clouds, the field of view of the instrument could be offset from the center of the Sun by up to one quarter of the solar angular diameter (i.e. $\sim 0.125^\circ$). Therefore, we took the uncertainty associated with the pointing of the sun tracker mirror to be 0.125° . The resulting variation in the retrieved columns was found to be 2.7% for N_2O and 1.0–1.7% for O_3 . The effect of a solar zenith angle perturbation on the retrieved N_2O column was observed to be greater than that for O_3 , which is consistent with the fact that N_2O is more prevalent in the troposphere, where the bending of solar rays is larger. One should note that these uncertainty estimates arise from the uncertainty in the viewing geometry,

while the $\pm 3\%$ variation in airmass during a measurement estimated in Section 3.1 is related to the change in solar zenith angle over the duration of one co-added measurement.

5.2.4. Atmospheric temperature

Since molecular line parameters are temperature dependent, an SFIT2 profile retrieval is influenced by uncertainty in the temperature profile. Typical uncertainties in the temperature data are known to be ± 0.5 K for radiosonde measurements and ± 5 K for NCEP data. By perturbing the temperature profile input to the forward model, errors of $\sim 1\%$ were observed for both N_2O and O_3 total columns. This observation is consistent with the results obtained by other experiments [35–37].

5.3. Systematic errors

5.3.1. Line parameter errors

Spectroscopic line parameters and uncertainties were taken from the HITRAN 2004 database [18]. The uncertainties in the line intensity and broadening coefficients were reported to have an accuracy range of 2–5% for the lines in the N_2O MWs and 5–10% for those in the O_3 MWs in HITRAN 2004 database [18]. As noted in Schneider et al. [36], the total column amount of O_3 remains nearly unaffected by the errors in line broadening coefficients because the concentration profile responds in a compensating way at altitudes above and below its peak. However, errors in the line intensity parameters propagate directly into the retrieved column. We took the less conservative value of the errors for our analysis, which are $\sim 2\%$ and $\sim 5\%$ for N_2O and O_3 , respectively.

5.3.2. Instrument line shape parameters

The effect of the uncertainty associated with the EAP on the retrieved columns was investigated by using the perturbation approach given by Zhao et al. [38]. The errors in the retrieved columns were estimated to be in the range of 1.1–1.6% for N_2O and 3.8–5.0% for O_3 , depending on the MW. In general, we observed that the column of a pressure-broadened tropospheric species such as N_2O is less sensitive to the errors in the EAP than that of a stratospheric species such as O_3 .

5.3.3. A priori

Errors resulting from possible fine-scale structures in the VMR profile were investigated by comparing the column amounts retrieved when localized perturbations are applied to individual layers in the *a priori* profile, which may reflect a more realistic atmosphere. Following the work of Pougatchev et al. [7] and Zhao et al. [38], perturbed *a priori* profiles were constructed by doubling the VMR of a single layer at a time for each of the 29 layers for both N_2O and O_3 . Using these perturbed *a priori* profiles, 29 synthetic spectra for each molecule were generated and analyzed by using the unperturbed original *a priori* profile with all fitting conditions and parameters held unchanged. The differences between the column retrieved from the synthetic spectra and the “true” columns computed from the perturbed *a priori* profiles give an estimate of the errors arising solely from fine-scale structures unaccounted for in the *a priori* VMR profile and is thus related to the smoothing error given in Section 5.1. The errors were estimated to be in the range of 5.7–6.7% for N_2O and 7.2–10.5% for O_3 , respectively, depending on MW, by summing the individual differences from all the layers. These values are used in the total error budget estimates.

5.4. Summary of error estimates

The retrieval error was obtained by $\sqrt{S_m + S_e}$, which was computed to be 1.1–2.0% for N_2O total column and 1.1–1.9% for O_3 total column. The total RMS errors are summarized in Table 2 and are estimated for the given spectral intervals to be 7.4% and 12.8% for N_2O and O_3 , respectively. Considering the difficult observing conditions, including very high solar zenith angles, scarcity of measurement data points sampling over each molecular line, and the limitations of the retrieval approach used, the total column uncertainties are reasonable when compared to the reported uncertainty (5.3%) of total ozone column measured by a much higher resolution (0.004 cm^{-1}) FTS at Poker Flat, Alaska [39]. The column amounts are more suitable than

the VMR profile for comparisons with results from other ground-based and space-borne instruments participating in the Canadian Arctic ACE Validation Campaign.

6. Results and discussion

As mentioned earlier, one of the advantages of PARIS-IR is the high time resolution of its measurements. For each day of PARIS-IR measurements, a series of co-added spectra (up to 18 on a clear day) were obtained. Total column densities have been derived using the profiles retrieved from the individual spectra as discussed in Section 4. In addition, for N_2O , partial column densities were computed for the altitude range between 6 and 100 km. The maximum altitude for the ACE-FTS N_2O retrievals is about 60 km and the contribution to the retrieved column from the altitudes higher than the maximum retrieved heights is negligible ($<0.1\%$). The time series of total column density for N_2O and for O_3 are presented in Figs. 9 and 10, respectively. Total errors for the N_2O MWs are shown for the results near local noon on March 3, 2004. These errors are 8.0% for MW2523 (the error bar on the left) and 6.8% for MW2806 (the error bar on the right). Since the length of each day at Eureka increases by about 30 min per day through late February and early March, the number of spectra recorded per day increases accordingly throughout the campaign. There appears to be no systematic difference in the retrieved total column densities for the N_2O MWs. However, the agreement is noticeably worse for some days which can be attributed to poor weather conditions such as thin hazy clouds. In Fig. 10, the time series of total O_3 column densities retrieved from MW2775 and MW3040 show persistent systematic discrepancies of about 10% throughout the campaign. These discrepancies are mostly within the combined uncertainties, 12.5% for MW2775 (shown on the March 3 plot with the error bar on the left) and 10.3% for MW3040 (shown by the error bar on the right).

The total and partial columns retrieved from the individual spectra were statistically combined to obtain daily mean values for each species. In doing so, the fitting residuals were used as weights. From this point on, all comparisons are made using the daily mean columns measured with PARIS-IR, so we omit the “daily mean” label for brevity. These column amounts were compared with ACE-FTS measurements that occurred within 500 km of AStrO during the campaign and with ozonesondes launched daily from the Eureka weather

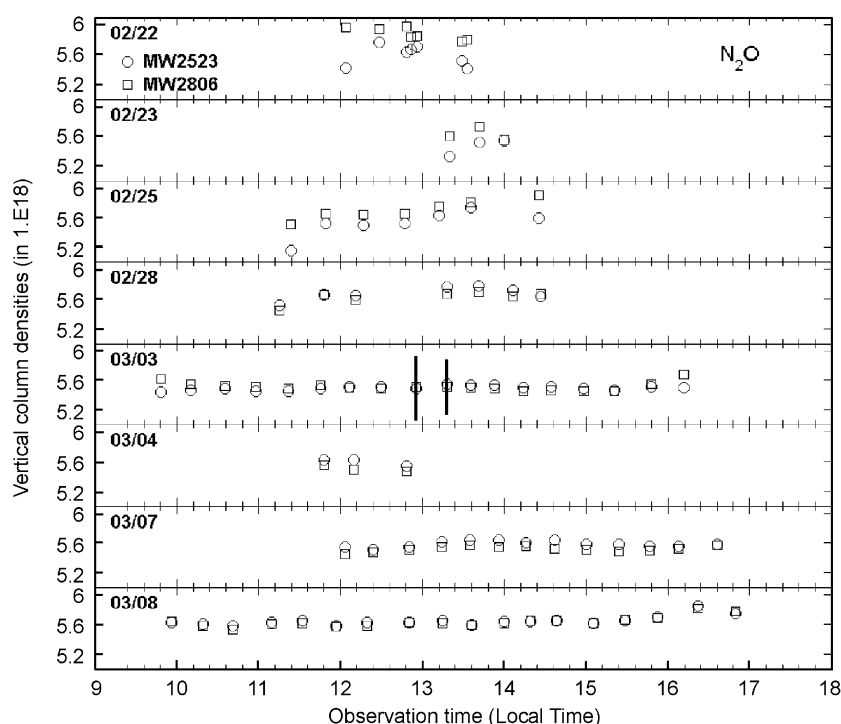


Fig. 9. Time series of measurements of total column density of N_2O during the intensive phase of the campaign (February 21–March 9, 2004). Results from MW2523 and MW2806 are shown with circles and squares, respectively, with their representative total errors given on March 3, 2004. The error bar on the left is for MW2523 and the one on the right is for MW2806.

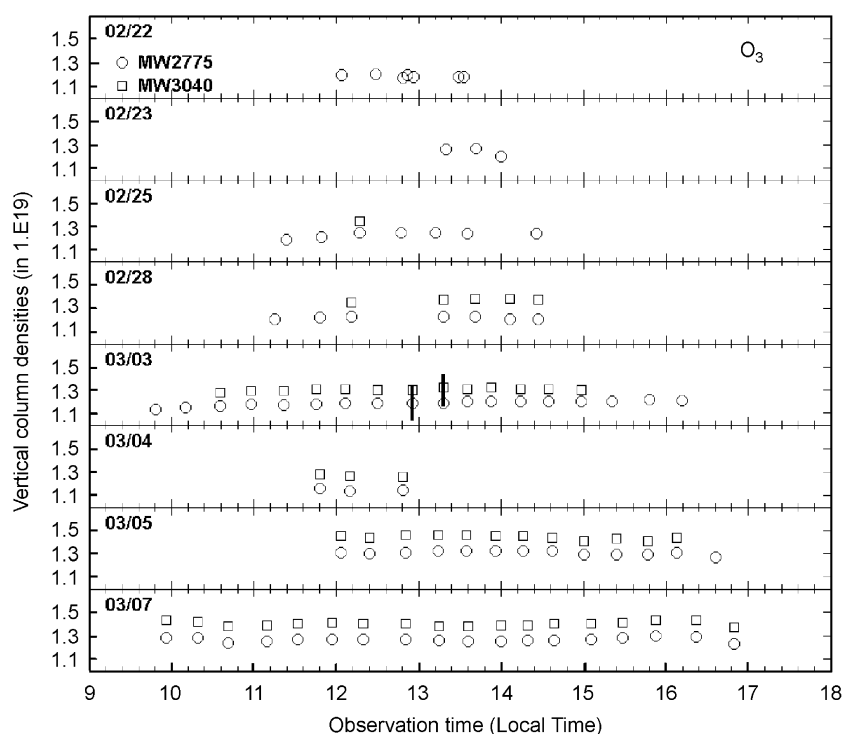


Fig. 10. Time series of measurements of total column density of O_3 during the intensive phase of the campaign (February 21–March 9, 2004). Results from MW2775 and MW3040 are shown as circles and squares, respectively, with their representative total errors given on March 3, 2004. The error bar on the left is for MW2775 and the one on the right is for MW3040.

station (15 km southeast of the AStrO site). The ACE-FTS results used for these comparisons were version 2.2 including ozone updates. The retrieval technique used to determine trace gas profiles from the ACE-FTS observations is described in Boone et al. [40]. N_2O is retrieved between approximately 5 and 60 km using 14 MWs in the $1171\text{--}1279\text{ cm}^{-1}$ range and 50 MWs between 1861 and 2668 cm^{-1} . Results for O_3 are obtained between 5 and 95 km in altitude from 37 MWs in the range from 922 to 1129 cm^{-1} . For both species, these ranges include MWs that are used to improve the results for interfering species (e.g. CCl_2F_2 in O_3 fits and CH_4 in N_2O fits). The HITRAN 2004 linelist [18] is used in the ACE-FTS retrievals. Partial column amounts are calculated by integrating the ACE-FTS profiles from 6 to 100 km. For each ACE-FTS profile, the VMR values provided for the region above the highest retrieved altitude are a constant times the input guess profile. This method provides a reasonable estimate of the profile to allow the upper altitude part of the column to be calculated. To obtain total O_3 column densities from the ACE-FTS profiles, a composite profile was produced for each occultation using the ACE-FTS results above 6 km and the daily ozonesonde result below 6 km. Then this profile was integrated to produce the total column density. The contribution from the ozonesonde was usually smaller than 5%. For the ozonesonde total columns, the residual O_3 (i.e. the column density above the highest measured altitude) was determined by assuming a constant mixing ratio [41]. The ozonesonde launches occurred at 23:15 UT (6:15 pm Local Time) each day during the intensive phase of the campaign. Typically, the midpoint of the PARIS-IR measurements was 4–6 h prior to the sonde launch.

The N_2O total column densities from PARIS-IR measurements, shown in the lower panel of Fig. 11, show little daily variation, as is expected for long-lived species. In the upper panel of Fig. 11, the partial columns (6–100 km) of N_2O are compared with measurements from ACE-FTS which occurred within 200 km of AStrO. In this figure, the total error for the PARIS-IR partial column amounts was adopted from that for the total column (7.4%). For ACE-FTS partial columns, the error bars are derived from the fitting error of the profiles since there is no complete error budget available for the ACE-FTS retrievals. Good agreement was observed for the partial columns of N_2O from ACE-FTS and PARIS-IR. Although the total error for PARIS-IR partial columns could be slightly underestimated, the differences in the partial column measurements made with the two FTSs are within 5%, which is already less than the adopted total error for the partial columns.

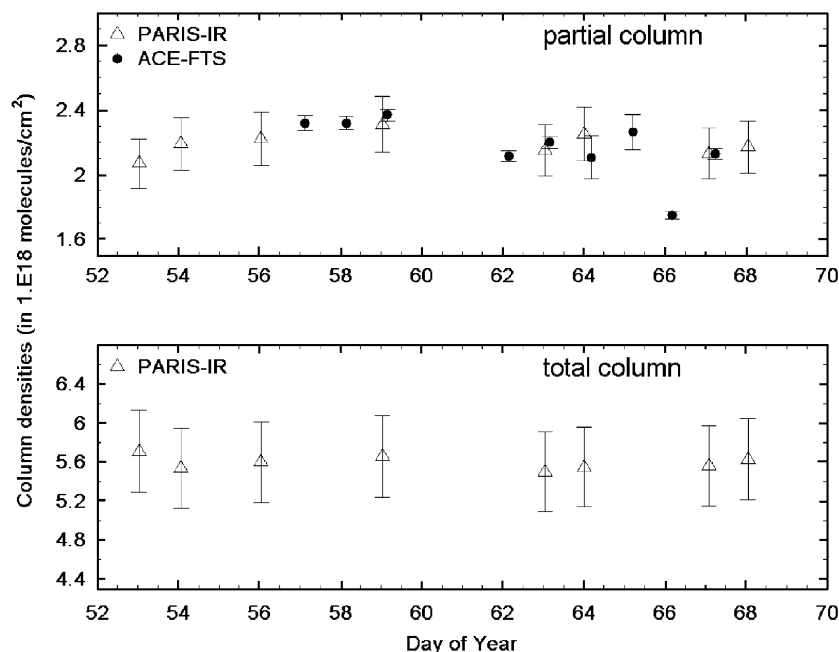


Fig. 11. Comparison of PARIS-IR partial (6–100 km) and total column measurements of N_2O . The x-axis tickmark for each day indicates local noon (12:00 pm Local Time).

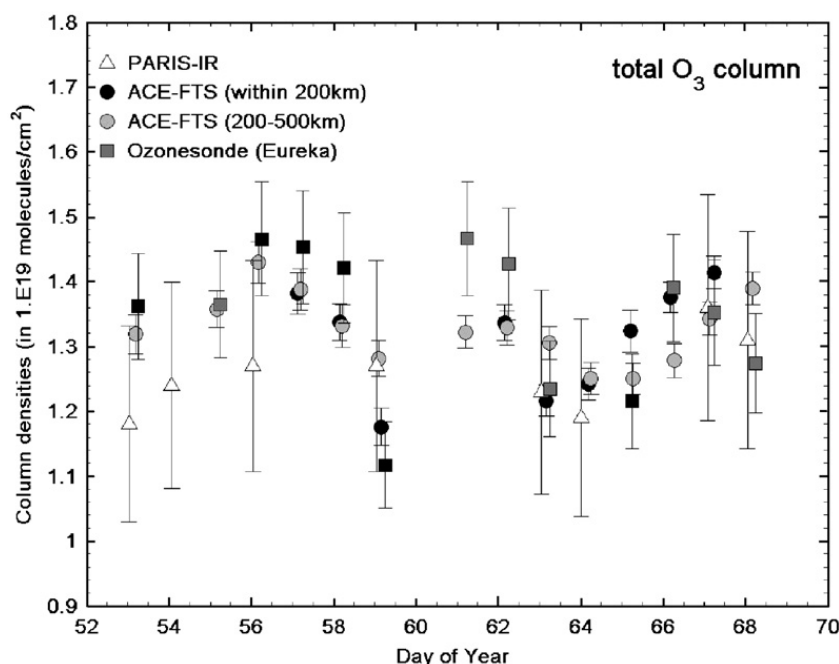


Fig. 12. Comparison of PARIS-IR total column measurements by day of year with those from ozonesondes launched from Eureka at 6:15 pm (Local Time) and measurements from ACE-FTS within 500 km of AStrO. See text for details. The x-axis tickmark for each day indicates local noon (12:00 pm Local Time).

In Fig. 12, total ozone column densities obtained from the PARIS-IR measurements were compared with ACE-FTS measurements that occurred within 500 km of AStrO during the campaign and with measurements from ozonesondes launched daily from the Eureka weather station. Error bars on the O_3 total columns correspond to the total errors listed in Table 2 (12.8%) for PARIS-IR and the average error of 6% for the ozonesondes (taken from Tarasick et al. [41]). As was done for N_2O , the ACE-FTS O_3 error bars are derived

from the fitting error of the profiles. In general, the total columns from PARIS-IR, ACE-FTS, and the ozonesondes agree within the given uncertainties. The agreement in the O₃ total columns tends to improve towards the end of the campaign, as the period of daylight increased and the weather conditions improved. The total uncertainty for the PARIS-IR measurements is less than the daily variation in the ozone columns.

Since the solar zenith angles were greater than 85° during the intensive phase of campaign, the region of stratosphere observed by PARIS-IR was 400–800 km away from the observation site. Therefore, the ACE-FTS measurements from occultations that were between 200 and 500 km away from AStrO have been included in the comparison. It is interesting to observe that, out of four PARIS-IR measurement days when there were ACE-FTS measurements both within 200 km and between 200 and 500 km from AStrO (Day of year: 59, 63, 64 and, 67), PARIS-IR shows better agreement on Day 59 and 67 with the ACE-FTS occultations that occurred between 200 and 500 km than those within 200 km. In fact, the occultations within 200–50 km on Days 59 and 67 occurred to the south east of the observation site, while those on Day 63 and 64 occurred into the west south west of the observation site. On the whole, no significant depletion in O₃ total columns was seen in the Arctic stratosphere over AStrO and Eureka in the spring of 2004, and the day-to-day variations were less than 14%. These measurements are consistent with the anomalously warm winter observed in 2003/2004 [42] and the location of the polar vortex. Based on visual inspection of maps of potential vorticity on the 475 K potential temperature surface, Eureka and AStrO were outside of the polar vortex for the duration of the intensive phase of the campaign.

7. Conclusions

This paper presented the retrieval methodology, characterization and error analysis for the PARIS-IR total and partial column retrievals. The PARIS-IR measurements of N₂O and O₃ column amounts were compared with those from the ACE-FTS onboard the Canadian SCISAT-1 satellite and the ozonesondes flown from Eureka during the validation campaign. PARIS-IR was able to observe statistically meaningful daily variation in the ozone columns. The advantage of the PARIS-IR measurements is their high temporal resolution so they can be used to observe atmospheric changes that occur throughout each observing day. Work is underway to extend these retrievals to further species including HCl, CH₄, HF and HNO₃ and compare the results with ACE-FTS and the other instruments that participated in the Canadian Arctic ACE Validation Campaign in 2004.

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