TEN YEARS OF MEASURING THE COMPOSITION OF THE EARTH'S ATMOSPHERE FROM SPACE USING ACE-FTS

BY KALEY A. WALKER

Kaley A. Walker, <kaley.walker@utoronto.ca>, Department of Physics, University of Toronto, 60 St. George Street Toronto, ON. M5S 1A7

SUMMARY

The Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) on board Canada's SCISAT is described including the instrument and measurement technique and the utilization of results from the past decade.

The trace gases in the Earth's atmosphere, those with concentrations less than 1%, have a strong impact on life on the planet. The stratospheric ozone layer that shields the Earth from ultraviolet radiation typically contains ozone concentrations of the order of several parts per million (ppm) [1]. Chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) species contribute to anthropogenic ozone depletion when they break down and release chlorine into the stratosphere. These CFCs and HCFCs have concentrations of the order of tens to hundreds of parts per trillion (ppt) in the lower atmosphere [1]. Greenhouse gases, which absorb and emit thermal infrared radiation but not shorter visible and ultraviolet wavelengths, trap heat in the atmosphere and thereby regulate the surface temperature of the planet. Carbon dioxide and methane, two of the most important of these greenhouse gases, currently have tropospheric concentrations of $\sim$400 ppm and $\sim$1850 ppb (parts per billion), respectively [2]. In Ontario, the pollutants sulfur dioxide and nitrogen dioxide are deemed to contribute to poor air quality when their daily average concentrations exceed $\sim$200 ppb [3].

While the relative concentrations of these trace gases are very low (compared to the bulk of the atmosphere that is made up of nitrogen, oxygen and argon), their concentrations are not constant. They vary due to both natural processes and those that are caused by human activities. These variations can occur on time scales that range from daily or seasonal to yearly or multi-yearly. Also, trace gas concentrations vary with altitude and geographical location. Thus to understand the composition of the atmosphere along with its processes and its changes, accurate measurements are needed that can quantify these variations in time, space and height.

Remote sensing using infrared spectroscopy provides an excellent method to determine the profiles of trace gases from space. Remote sensing in this context utilizes measurements of atmospheric spectra to infer the concentrations of the molecules of interest. In the infrared region, rotation-vibration transitions of a wide range of molecules can be measured thus allowing chemical processes in the atmosphere to be better understood and modeled. From a satellite platform, an instrument can measure atmospheric spectra originating from different altitudes thereby providing height resolved (or profile) measurements. By looking at the limb of the Earth, the instrument measures through a long path in the atmosphere (typically several hundred km) and this provides very high sensitivity to molecules with low abundances. Also, this view from space can allow a global dataset to be collected throughout the time period that the instrument is in orbit.

Fourier transform infrared spectrometry has been used very successfully for remote sensing of the atmosphere [4]. In a Fourier transform spectrometer (FTS) using a Michelson interferometer, the input radiation is divided into two beams by a semi-transparent mirror. A varying optical path difference is introduced between the reflected and transmitted beams before they are recombined. This results in an interference pattern as a function of optical path difference, or an interferogram, that is recorded at the detector. The frequency calibration is accomplished by recording the signal of a laser, which is also modulated by the interferometer. Using a Fourier transform of the interferogram, the spectrum of the input radiation beam is obtained. The maximum optical path difference of the FTS determines the spectral resolution of the measurements, with a longer path difference providing higher resolution. For a satellite FTS, a balance must be struck between the spectral resolution necessary and the limited mass and volume available for the instrument. A well-designed FTS can provide a compact instrument with the high spectral resolution required for atmospheric composition measurements.

Profile measurements of the atmosphere have been made by space-borne FTSs recording either absorption or emission spectra. The first profile measurements were made, between 1985 and 1994, by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment [5] during four flights on board the Space Shuttle By viewing the Sun through the atmosphere during sunrise or sunset, solar absorption spectra were measured and used to derive trace gas profiles. More recently, the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) was deployed on the European Environmental Satellite (Envisat) from March 2002 to April 2012 [6]. MIPAS measured atmospheric emission spectra by scanning in altitude throughout its orbit. By using emitted thermal infrared radiation, these profile measurements could be made during both day and night.

The solar occultation technique, employed by ATMOS, typically produces a maximum of 15 sunrises and 15 sunsets per day, which is far fewer measurements than the emission observations made by MIPAS (more than 500 [6]). However, solar occultation provides a number of advantages. The ~5800 K Sun provides infrared radiation over a wider spectral range than the thermal infrared emission from the Earth's much cooler atmosphere. This enables an infrared solar occultation FTS to measure the spectral signatures of more species than an infrared emission instrument. Also, the solar absorption spectra have much higher signal-to-noise ratios than atmospheric emission spectra and thus provide enhanced measurements of low abundance species.

Currently, the only FTS making atmospheric profile measurements from space is the Canadian-led Atmospheric Chemistry Experiment (ACE) mission [7]. Carried by the SCISAT satellite, ACE was developed to investigate the composition of the Earth's atmosphere with a primary focus on the chemical and dynamical processes that determine the distribution of ozone over Canada and the Arctic. The ACE mission builds on Canada's strong heritage in ozone science [8]. The ACE-FTS, which operates in the mid-infrared region, is the main instrument [9] and a second instrument, named MAESTRO (Measurement of Aerosol Extinction in the Stratosphere and Troposphere Retrieved by Occultation), was added during the development of the mission to provide an ultraviolet-visible measurement capability [10]. SCISAT was launched by the U.S. National Aeronautics and Space Administration (NASA) in August 2003 and has been providing profiles from atmospheric solar occultation measurements routinely since February 2004. This has resulted in a ten-year-long data record (as of 21 February 2014) that is on-going. In the following sections, the discussion will focus on the ACE-FTS and its measurements, highlights of its scientific results and the potential for new missions using this technique.

INSTRUMENTATION AND MEASUREMENTS

The ACE-FTS is a modified Michelson interferometer that was custom built for SCISAT by ABB Bomem [9]. Briefly, it utilizes two cube corner reflectors mounted on a pivoting arm mechanism and a folded optical path to provide a maximum optical path difference of +25 cm to −25 cm within a compact instrument. The flight instrument is shown in Fig. 1. The resulting spectral resolution (0.02 cm^{-1}) is sufficient to resolve transitions for the molecules of interest to the mission. Two co-aligned photovoltaic detectors (mercury cadmium telluride and indium antimonide) are used to cover the 750–4400 cm^{-1} (13.3–2.2 μm) spectral range. To operate, these detectors are cooled using a passive radiator directed towards deep space. On orbit, this cooler provides detector operating temperatures of 80–100 K. A suntracking mirror system is located within the ACE-FTS. It uses a four-quadrant detector to provide feedback to the pointing mirror and keep instrument field-of-view pointed at the centre of the Sun throughout each sunrise and sunset.

The SCISAT satellite is in a circular orbit (altitude ~650 km and an inclination angle 74° with respect to the equator) that

Fig. 1 Picture of the ACE-FTS instrument showing the interferometer arm and beam splitter configuration (from ABB Bomem). The cone located at the "top" of the instrument provides the passive cooler with protection from stray radiation from the Earth and the Sun.

was optimized to yield global coverage with a focus on measurements over Canada and the Arctic [7]. For each day, the 15 sunrises and 15 sunsets are evenly spaced in longitude around the Earth within a narrow range of latitudes. Over a period of three months all latitudes from 82°N to 82°S are measured by ACE. During each sunrise or sunset occultation, ACE-FTS produces a series of spectra extending from the cloud tops to $\sim$150 km in altitude with a typical measurement spacing of 3–4 km. In addition, calibration observations of deep space and of the Sun above the atmosphere (e.g. exo-atmospheric) are recorded with each occultation. From these, atmospheric transmission spectra are calculated. This measurement method provides a "self-calibration" for the ACE-FTS that can account for small changes in instrument performance that may occur over time.

The process to retrieve atmospheric profiles from the ACE-FTS measurements is undertaken in two steps [11]. First, since carbon dioxide is well mixed throughout much of the atmosphere, its concentration can be fixed and the relative line intensities provide information about temperature and the amount of absorption provides information about pressure. Second, this temperature/pressure profile is used to retrieve volume mixing ratio (VMR) profiles for each of the trace gases by a nonlinear least squares fitting of all of the transmission spectra for a single occultation. Narrow regions of the spectra, called microwindows, are selected to isolate (as much as possible) the pertinent spectral features of each molecule to be retrieved from those of other species. The signal-to-noise ratio for a single ACE-FTS spectrum is greater than 300:1 over most of the spectral range. This allows molecules with abundances of the order of tens of parts per trillion (ppt) to be detected without averaging spectra.

In total, profiles of more than 35 molecules and 20 minor isotopologues (molecules containing less abundant isotopes of certain atoms) are retrieved in the current data version (v3.0/3.5) [11]. These include ozone, halogen- and nitrogen-containing species involved in ozone depletion (e.g. CFCs, HCFCs, HCl, NO, NO_2), greenhouse gases (e.g. H_2O, CH_4, N_2O), tracers of atmospheric motion (e.g. CO, HF), and carbon-containing species related to biomass burning and pollution (e.g. HCN, C_2H_6). This is the largest number of atmospheric constituents that has been measured by a single satellite instrument to date. These data are verified through comparisons with measurements taken by satellite-based, balloon-borne and ground-based instruments [12]. This validation process is continued throughout the mission to ensure the ongoing data quality of the ACE-FTS profiles [13].

UTILIZATION OF ACE-FTS RESULTS

When ACE on SCISAT was proposed to the Canadian Space Agency, the most pressing scientific questions were focused on understanding the stratospheric ozone layer and its recovery. This is because the Montreal Protocol on Substances that Deplete the Ozone Layer had been brought into force a decade earlier to control the use of CFCs. Thus, the ACE primary objective focused on understanding the processes that control the distribution of ozone [7]. Over the mission development and operations phases for ACE, the scientific focus has broadened to also include monitoring of greenhouse gas distributions and investigations of pollutant species and how they are transported in the upper troposphere.

Over the mission, more than 300 peer-reviewed papers have been produced using ACE results. The majority are scientific studies with the rest comprising validation results, measurements using ground-based versions of the ACE instruments, and works relating to testing, calibration and retrievals. In 2013, a book was published to celebrate the 10th Anniversary of ACE (*The Atmospheric Chemistry Experiment ACE at 10: A Solar Occultation Anthology (edited by Peter F. Bernath)*, A. Deepak Publishing, 2013). A listing of these papers and book chapters is provided on the ACE mission website (http://www.ace.uwaterloo.ca).

The long measurement record and large number of molecules measured by ACE-FTS have enabled the SCISAT mission to contribute significantly to several international projects and programs. For example, every four years the World Meteorological Organization coordinates an assessment of the effectiveness of the Montreal Protocol in reducing the concentrations of ozone depleting substances and publishes a report on the "Scientific Assessment of Ozone Depletion" (e.g. [1]). This regular assessment is mandated in the Montreal Protocol. ACE has contributed prominently to both the 2006 and 2010 reports, and now to the 2014 report, through our measurements of ozone, ozone depleting substances (such as CFCs and HCFCs) and their breakdown products. With the loss of the MIPAS instrument on Envisat in 2012, there are no other satellite instruments providing profiles of many of the species that are needed to identify and to understand the causes of changes observed in stratospheric ozone. For many of the CFC and HCFC species, the only other measurements are made at ground level. Through this, ACE contributes to monitoring the effectiveness of the Montreal Protocol and the initial stages of the recovery of the stratospheric ozone layer.

One of the strengths of ACE-FTS is the diverse set of molecules that are measured simultaneously during each occultation. In the area of ozone depletion chemistry, these have been used to examine how chlorine is distributed between different species (e.g. HCl, $ClONO_2$) in the Arctic and Antarctic stratosphere and how this changes with time during polar spring [14]. ACE-FTS measurements have demonstrated how pollutants can be moved rapidly from the troposphere into the lower stratosphere over the Asian summer monsoon region, by showing this effect for several species [15]. Also, the chemical changes that occur in gas/smoke plumes as they are transported away from boreal forest fire regions have been investigated using measurements from ACE-FTS [16].

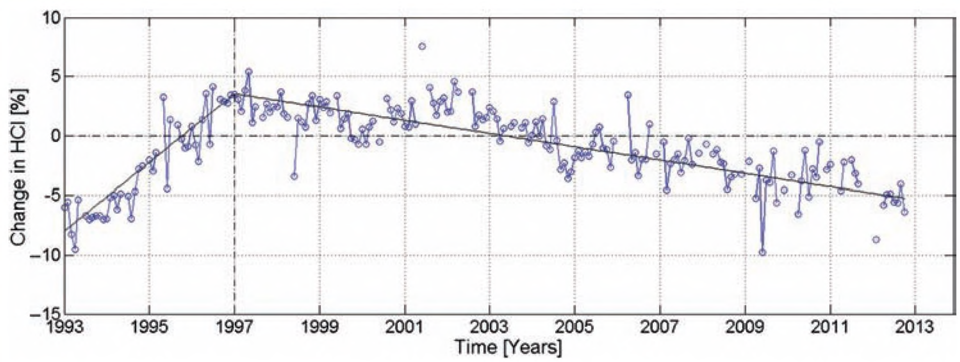

Fig. 2 Plot showing the change in HCl concentration at 35–45 km in altitude and between 30°N and 50°N, derived from ACE-FTS (2004–2013) and HALOE (1993–2005). The calculated change is relative to the average value for this time period, seasonal variations have been removed and the trend lines have been calculated for the periods before and after January 1997 [17].

Global and regional models that can simulate both chemical and dynamical processes are required to predict the possible evolution of the Earth's atmosphere. To have confidence in the results from these models and to evaluate their uncertainties, the model output must be assessed using high quality datasets such as those from ACE-FTS. For example, multi-year climatological datasets have been generated from the ACE-FTS results to allow average profiles for a particular latitude range, time period and species to be compared easily to the same quantity from global chemistry-climate models [18]. These data have been used in model evaluation projects such as the Chemistry-Climate Model Validation Activity of the World Climate Research Program [19]. ACE is also being included in international initiatives to generate long-term datasets that extend over many years by merging profiles from different satellite instruments [20]. Because of the long-term stability of the ACE-FTS occultation measurements, they are of particular value for inclusion in "merged" datasets or for on-going validation of the resulting time series. Fig. 2 shows how the ACE-FTS measurements of HCl in the upper stratosphere (35–45 km) have continued those from the Halogen Occultation Experiment (HALOE) to produce a "merged" time series of concentration changes extending from 1993 to 2012 [17]. This data set shows the decrease in chlorine in the upper atmosphere that has resulted from the Montreal Protocol. Finally, Environment Canada uses ACE data to assess the quality of their model predictions of stratospheric ozone and to identify where improvements can be made. The output from this model is used for the UV (ultraviolet) index forecast so SCISAT results are being utilized to the benefits of Canadians.

CONCLUSION

On 12 August 2014, ACE on SCISAT celebrated 11 years in orbit. This is a tremendous achievement for a Canadian satellite and payload that were designed to operate for only two years. The development of ACE has significantly increased the scientific and industrial capacity for atmospheric remote sensing within Canada. Nationally, nearly 120 graduate and undergraduate students, postdoctoral fellows and research associates have been trained through ACE and a further 110 have been involved internationally. Due to the success of ACE-FTS, ABB has developed new business partnerships to provide interferometers and components for international satellite and airborne remote sensing missions such as the TANSO-FTS on the Japanese Greenhouse gases Observing Satellite (GOSAT).

Since 2009, several concept and mission definition (phase 0) studies have been undertaken to develop a new mission with a next-generation solar occultation FTS instrument on either the International Space Station or a satellite. These have included the Solar Occultation for Atmospheric Research (SOAR) mission and the Chemical and Aerosol Sounding Satellite (CASS) [21]. However, to date, no new missions have been approved for development in Canada or internationally to continue the observation record from ACE-FTS. As of the time of this writing, the instruments and spacecraft continue to operate nominally and there are no known or predictable conditions that will limit further years of measurements. To support the extension of this valuable atmospheric composition time series, it is hoped that the Canadian Space Agency will fund the continuation of ACE operations until a new mission is developed and launched.

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REFERENCES

1. WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project–Report No. 52, 516 pp., Geneva, Switzerland, 2011.
2. ESRL (Earth System Research Laboratory) Global Monitoring Division, Interactive Data Visualization Tool, http://www.esrl.noaa.gov/gmd/dv/iadv/; accessed on 14 June 2014.
3. Ontario Ministry of the Environment, Standards Development Branch, "Ontario's Ambient Air Quality Criteria (sorted by contaminant name)", April 2012, http://www.airqualityontario.com/downloads/AmbientAirQualityCriteria.pdf; accessed on 14 June 2014.
4. S.P. Davis, M.C. Abrams, and J.W. Brault, *Fourier Transform Spectrometry*, Academic Press, 2001.
5. M.R. Gunson, M.M. Abbas, M.C. Abrams, M. Allen, L.R. Brown, T.L. Brown, A.Y. Chang, A. Goldman, F.W. Irion, L.L. Lowes, E. Mahieu, G.L. Manney, 1 H.A. Michelsen, M.J. Newchurch, C.P. Rinsland, R.J. Salawitch, G.P. Stiller, G.C. Toon, Y.L. Yung, and R. Zander, "The Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment: Deployment on the ATLAS Space Shuttle missions", *Geophys. Res. Lett.*, **23**, 2333–2336 (1996).
6. H. Fischer, M. Birk, C. Blom, B. Carli, M. Carlotti, T. von Clarmann, L. Delbouille, A. Dudhia, D. Ehhalt, M. Endemann, J. M. Flaud, R. Gessner, A. Kleinert, R. Koopman, J. Langen, M. López-Puertas, P. Mosner, H. Nett, H. Oelhaf, G. Perron, J. Remedios, M. Ridolfi, G. Stiller, and R. Zander, "MIPAS: an instrument for atmospheric and climate research", *Atmos. Chem. Phys.*, **8**, 2151–2188 (2008).
7. P.F. Bernath, C.T. McElroy, M.C. Abrams, C.D. Boone, M. Butler, C. Camy-Peyret, M. Carleer, C. Clerbaux, P.-F. Coheur, R. Colin, P. DeCola, M. DeMazière, J.R. Drummond, D. Dufour, W.F.J. Evans, H. Fast, D. Fussen, K. Gilbert, D.E. Jennings, E.J. Llewellyn, R.P. Lowe, E. Mahieu, J.C. McConnell, M. McHugh, S.D. McLeod, R. Michaud, C. Midwinter, R. Nassar, F. Nichitiu, C. Nowlan, C.P. Rinsland, Y.J. Rochon, N. Rowlands, K. Semeniuk, P. Simon, R. Skelton, J.J. Sloan, M.-A. Soucy, K. Strong, P. Tremblay, D. Turnbull, K.A. Walker, I. Walkty, D.A. Wardle, V. Wehrle, R. Zander, and J. Zou "Atmospheric Chemistry Experiment (ACE): Mission overview", *Geophys. Res. Lett.* **32**, L15S01 (2005).
8. C.T. McElroy, "The Canadian Ozone Story", *Physics in Canada*, **61**, 261–268 (2005).
9. H.L. Buijs, M.-A. Soucy, and R.L. Lachance, "ACE-FTS Hardware and Level 1 Processing", in *The Atmospheric Chemistry Experiment ACE at 10: A Solar Occultation Anthology (Peter F. Bernath, editor)*, p. 53–80, A. Deepak Publishing, 2013.
10. C.T. McElroy, C.R. Nowlan, J.R. Drummond, P.F. Bernath, D.V. Barton, D.G. Dufour, C. Midwinter, R.B. Hall, A. Ogyu, A. Ullberg, D.I. Wardle, J. Kar, J. Zou, F. Nichitiu, C.D. Boone, K.A. Walker, and N. Rowlands, "The ACE-MAESTRO Instrument on SCISAT: description, performance and preliminary results", *Appl. Opt.* **46**, 4341–4356 (2007).
11. C.D. Boone, K.A. Walker, and P.F. Bernath, "Version 3 Retrievals for the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS)" in *The Atmospheric Chemistry Experiment ACE at 10: A Solar Occultation Anthology (Peter F. Bernath, editor)*, p. 103–127, A. Deepak Publishing, 2013.
12. K.A. Walker, "Calibration and Validation Program for the Atmospheric Chemistry Experiment (ACE) on SCISAT" in *The Atmospheric Chemistry Experiment ACE at 10: A Solar Occultation Anthology (Peter F. Bernath, editor)*, p. 149–162, A. Deepak Publishing, 2013.
13. C. Waymark, K.A. Walker, C.D. Boone, and P.F. Bernath, "ACE-FTS version 3.0 data set: validation and data processing update", *Ann. Geophys.* **56**, Fast Track-1 (2013).
14. M.L. Santee, I.A. MacKenzie, G.L. Manney, M.P. Chipperfield, P.F. Bernath, K.A. Walker, C.D. Boone, L. Froidevaux, N.J. Livesey, J.W. Waters, "A study of stratospheric chlorine partitioning based on new satellite measurements and modeling", *J. Geophys. Res.* **113**, D12307 (2008).
15. M. Park, W.J. Randel, L.K. Emmons, P.F. Bernath, K.A. Walker and C.D. Boone, "Chemical isolation in the Asian monsoon anticyclone observed in Atmospheric Chemistry Experiment (ACE-FTS) data", *Atmos. Chem. Phys.* **8**, 757–764 (2008).
16. K.A. Tereszchuk, G. González Abad, C. Clerbaux, J. Hadji-Lazaro, D. Hurtmans, P.-F. Coheur, P.F. Bernath, "ACE-FTS observations of pyrogenic trace species in boreal biomass burning plumes during BORTAS", *Atmos. Chem. Phys.* **13**, 4529–4541 (2013).
17. A. Jones, J. Urban, D.P. Murtagh, C. Sanchez, K.A. Walker, N.J. Livesey, L. Froidevaux, M.L. Santee, "Analysis of HCl and ClO time series in the upper stratosphere using satellite data sets", *Atmos. Chem. Phys.* **11**, 5321–5333 (2011).
18. A. Jones, K.A. Walker, J.J. Jin, J.R. Taylor, C.D. Boone, P.F. Bernath, S. Brohede, G.L. Manney, S. McLeod, R. Hughes, and W.H. Daffer, "Technical Note: A trace gas climatology derived from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) dataset", *Atmos. Chem. Phys.* **12**, 5207–5220 (2012).
19. Stratospheric Processes And their Role in Climate, 2010, *SPARC Report on the Evaluation of Chemistry-Climate Models*, V. Eyring, T.G. Shepherd, D.W. Waugh (eds.), SPARC Report No. 5, WCRP-132, WMO/TD-No. 1526, 2010.
20. V.F. Sofieva, N. Rahpoe, J. Tamminen, E. Kyrölä, N. Kalakoski, M. Weber, A. Rozanov, C. von Savigny, A. Laeng, T. von Clarmann, G. Stiller, S. Lossow, D. Degenstein, A. Bourassa, C. Adams, C. Roth, N. Lloyd, P. Bernath, R.J. Hargreaves, J. Urban, D. Murtagh, A. Hauchecorne, F. Dalaudier, M. van Roozendael, N. Kalb, and C. Zehner, "Harmonized dataset of ozone profiles from satellite limb and occultation measurements", *Earth Syst. Sci. Data* **5**, 349–363 (2013).
21. S.M.L. Melo, K.A. Walker, and D. Degenstein, "The Chemical and Aerosol Sounding Satellite (CASS) Mission as a Solution for Global Climate Quality Atmospheric Composition Measurements" in *The Atmospheric Chemistry Experiment ACE at 10: A Solar Occultation Anthology (Peter F. Bernath, editor)*, p. 323–330, A. Deepak Publishing, 2013.