

NEW ORGANIC MOLECULES FROM ACE-FTS OBSERVATIONS

Jeremy J. Harrison¹, Christopher D. Boone² and Peter F. Bernath³

¹University of York, Heslington, York YO10 5DD, United Kingdom

²University of Waterloo, Department of Chemistry, Ontario N2L 3G1, Canada

³Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, Virginia 23529, USA

Abstract

The primary aim of the Atmospheric Chemistry Experiment (ACE), an ESA third-party mission, is the study of ozone chemistry in the stratosphere. In addition to this, ACE is capable of measuring the vertical distributions of over 30 trace gases in the atmosphere, more than any other satellite instrument. Profiles of new organic molecules continue to be retrieved from ACE spectra recorded over the last ten years, often with the aid of new quantitative laboratory spectroscopic measurements. ACE version 3.0 research products are now available for acetonitrile (CH₃CN), acetone (CH₃COCH₃), and trifluoromethane (HFC-23; CHF₃).

INTRODUCTION

The emission of volatile organic molecules (VOCs), from both natural and anthropogenic sources, along with NO_x (=NO+NO₂) is responsible for air pollution. NO_x catalyses the oxidation of VOCs, leading to the formation of tropospheric ozone, a toxic and potent greenhouse gas. Air pollution is one of the most important issues in atmospheric science because of the potential negative effects on human health and ecosystems. Satellite missions such as the Atmospheric Chemistry Experiment (ACE) can contribute to the research on air quality on a regional and global scale.

On the other hand, the success of the Montreal Protocol in phasing out ozone-depleting substances (ODSs), principally the chlorofluorocarbons (CFCs), has resulted in the development and commercialisation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as replacement refrigerants. HFCs do not deplete the ozone layer, and so are not restricted by the Montreal Protocol, but they are powerful greenhouse gases (along with CFCs and HCFCs) with global warming potentials (GWPs) many times greater than CO₂.

The primary ACE instrument is a high-resolution (0.02 cm⁻¹) Fourier Transform Spectrometer (FTS) that operates between 750 and 4400 cm⁻¹. The ACE-FTS uses the sun as a light source to record atmospheric limb transmittance spectra during sunrise and sunset ('solar occultation'). A sun-tracking mirror is used to keep the instrument pointed at the sun centre during sunrise and sunset. A passive cooler, radiating to deep space, is used to cool the photovoltaic MCT and InSb detectors. The resulting transmittance spectra, with high signal-to-noise ratios, are recorded through long atmospheric limb paths (~300 km effective length), thus providing a low detection threshold for trace species. In fact, the ACE-FTS is able to detect more organic molecules in the atmosphere than any other satellite instrument. ACE has an excellent vertical resolution of about 2-3 km in the troposphere and can measure up to 30 occultations per day, with each occultation sampling the atmosphere from 150 km down to the cloud tops (or 5 km in the absence of clouds). The locations of ACE occultations are dictated by the 650 km altitude, 74° inclination circular orbit of the SCISAT-1 satellite and the relative position of the sun. Over the course of a year, the ACE-FTS records atmospheric spectra over a large portion of the globe [1].

ACETONITRILE

Acetonitrile (CH_3CN) is a minor constituent of the Earth's atmosphere, with the majority of emissions arising from biomass burning. A major sink for acetonitrile is wet removal in the troposphere and deposition into the ocean, with chemical loss primarily through the reaction with the hydroxyl radical (OH), which is rather slow. The lifetime of acetonitrile is of the order of 6 months, making this molecule a useful tracer for biomass burning and other atmospheric transport processes. *In situ* observations of tropospheric acetonitrile have indicated typical background levels of 50–200 ppt (parts per trillion). In regions of forest fire activity, tropospheric volume mixing ratios (VMRs) are significantly enhanced.

A new set of high-resolution infrared absorption cross sections for acetonitrile / synthetic air [2] has been used to retrieve CH_3CN VMR profiles from ACE-FTS spectra. The strongest CH_3CN spectral feature, and the only one appropriate for quantitative analysis, is on the wing of a strong water line. In order to minimise the impact of bad residuals from this water line, the retrieval employs a narrow microwindow (1462.96 to 1463.60 cm^{-1}) and allows for a quadratic variation of the baseline. Saturation of this water line limits the lower altitude of the retrieval to ~11 km; this is essentially a stratospheric retrieval. A Version 3.0 research product, consisting of retrieved CH_3CN VMR profiles for all ACE occultations until 2010, is now available [3].

For a single ACE profile, the 1σ statistical fitting errors at each altitude are comparable to the magnitude of the retrieved CH_3CN VMRs. This large random error contribution coupled with the limited global coverage of the ACE-FTS instrument (a maximum of 30 measurements per day, and most of these at high latitudes) make it very difficult to quantify the CH_3CN variability due to biomass burning.

Median 'background' CH_3CN profiles have been determined in 20 latitude bins for all available ACE data (see Fig. 1). Plots for individual years indicate that any inter-annual variability is well within the error bars. Therefore all data were plotted together, thereby reducing the random noise contribution to the profiles. Errors at each altitude are taken as one median absolute deviation (MAD) of the VMR distribution for the filtered dataset. All the profiles show median VMRs between 110 and 160 ppt at the lowest altitudes, which decrease as altitude increases. This drop-off with altitude occurs more rapidly in the high-latitude/polar regions, with acetonitrile VMRs dropping to zero by ~ 25 km. In the mid-latitude/tropical regions, acetonitrile still persists in small quantities (~ 50 ppt) at the top of the retrieval range (30 km). This reflects the larger acetonitrile concentrations near the equator, where biomass burning activity is most prevalent, and the large scale circulation of air around the globe, in which tropospheric air ascends into the stratosphere over the tropics and descends into the troposphere towards the poles. Full details of this study can be found in [3].

ACETONE

Acetone (CH_3COCH_3), sometimes known as propanone, is one of the most abundant VOCs in the free troposphere, with a lifetime of between two and four weeks. The largest source is the oxidation of organic precursors, mainly propane, isobutene and isobutene. Other sources include biomass burning, direct biogenic emissions (including plant growth and decay), and a minor contribution from anthropogenic emissions. Acetone sinks include the reaction with hydroxyl radicals (OH) and photolysis in the troposphere, in which the molecule dissociates into acetyl (CH_3CO) and methyl (CH_3) radicals. The acetyl radical in the free troposphere is a major source of peroxyacetyl nitrate (PAN), a reservoir for NO_x . Due to PAN's thermal stability at lower temperatures, it can be transported over long distances in the middle and upper troposphere. The consequence of this long-distance transport of NO_x is that the sources of pollutant emission may be long distances from the regions of resulting elevated tropospheric ozone. Additionally, acetone photolysis in the upper troposphere, where conditions are dry and the usual $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ pathway to HO_x formation is slow, is an important additional source of HO_x ($=\text{HO}+\text{HO}_2$).

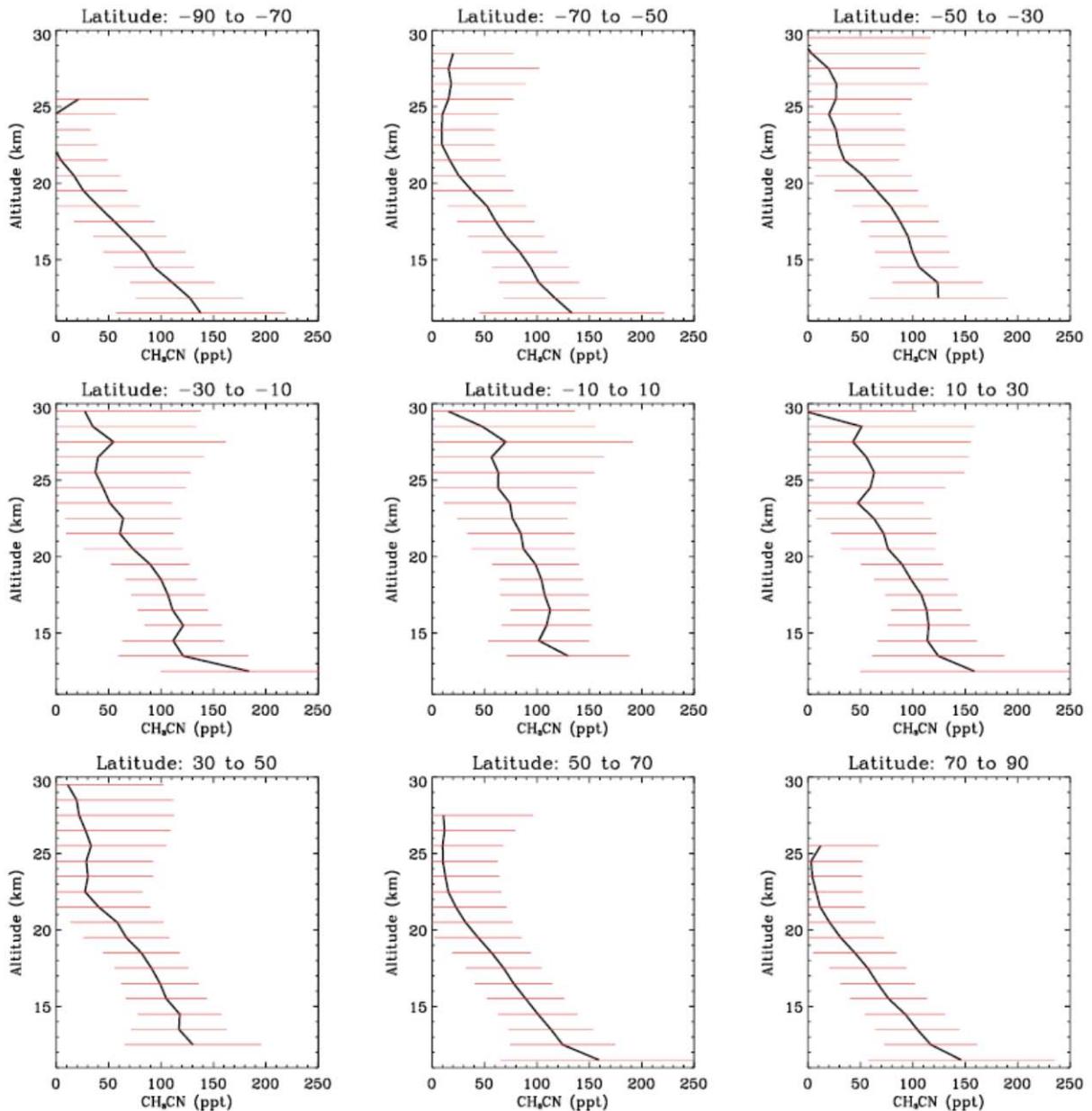


Figure 1: Median 'background' ACE CH₃CN VMR profiles in 20° latitude bins.

A recently derived set of high-resolution infrared absorption cross sections for acetone / synthetic air [4] has been used to retrieve acetone VMR profiles from ACE-FTS spectra. In order to avoid CH₄ line mixing effects, the microwindow set consists of 16 'slices' between CH₄ lines (1184.54 - 1241.66 cm⁻¹) across the acetone spectral feature, with a common set of baseline parameters.

A Version 3.0 research product, consisting of retrieved acetone VMR profiles for all ACE occultations until 2010, is now available. This will be described in the peer-reviewed literature in the near future.

TRIFLUOROMETHANE

The primary emissions of trifluoromethane (HFC-23) do not arise through its use as an ODS replacement, but as a byproduct (over-fluorination of chloroform) during the production of HCFC-22 (CHClF₂). HFC-23 is the second most abundant HFC in the atmosphere, and its abundance continues to increase. It possesses a long atmospheric lifetime of 222 years and a 100-yr GWP of 14,200, meaning that continued HFC-23 emissions will significantly contribute to climate forcing.

A set of HFC-23 pseudo-lines were derived from available quantitative infrared spectra and incorporated into the ACE forward model. Version 3.0 of the ACE-FTS retrieval software was used to retrieve HFC-23 VMRs for 8809 ACE occultations. These are the first satellite remote-sensing measurements of HFC-23. The trend in the growth of HFC-23 between 2004 and 2009 (4.0 ± 1.6 % per year) agrees well with surface observations from Cape Grim Air Archive samples over the same time period (4.7 ± 0.3 % per year). The absolute HFC-23 VMRs measured by ACE in the UTLS are in good agreement with each other, but are ~30% larger than the ground-based measurements. Full details of this study can be found in [5]. It has since been recognised that this 30% high bias is caused by problems with the pseudo-lines and the poor quality of the original spectra. New spectroscopic measurements have recently been taken [6]; these will lead to an improved VMR retrieval for the upcoming ACE Version 4.0 data product.

ACKNOWLEDGEMENTS

We thank the UK Natural Environment Research Council (NERC) for supporting J.J.H. through grant NE/I022663/1. The ACE satellite mission is funded primarily by the Canadian Space Agency (CSA).

REFERENCES

1. Bernath, P.F., et al. (2005). Atmospheric Chemistry Experiment (ACE): Mission overview. *Geophys. Res. Lett.* **32**, L15S01.
2. Harrison, J.J. & Bernath, P.F. (2012). Mid- and long-wave infrared absorption cross sections for acetonitrile. *J. Quant. Spectrosc. Rad. Trans.* **113**, pp 221-225.
3. Harrison, J.J. & Bernath, P.F. (2013). ACE-FTS observations of acetonitrile in the lower stratosphere. *Atmos. Chem. Phys.* **13**, pp 7405-7413.
4. Harrison, J.J., et al. (2011). Mid-infrared absorption cross sections for acetone (propanone). *J. Quant. Spectrosc. Rad. Trans.* **112**, pp 457-464.
5. Harrison, J.J., et al. (2012). First remote-sensing observations of trifluoromethane (HFC-23) in the upper troposphere and lower stratosphere. *J. Geophys. Res.* **117**, D05308.
6. Harrison, J.J. (2013). Infrared absorption cross sections for trifluoromethane. *J. Quant. Spectrosc. Rad. Trans.* **130**, pp 457-464.