INFRA-RED REMOTE SENSING OF ORGANIC COMPOUNDS IN THE UPPER TROPOSPHERE

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ABSTRACT

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument measures the intensity of atmospheric radiation emitted in the infra-red spectral region at high spectral resolution in five bands ranging from 685 cm\(^{-1}\) to 2410 cm\(^{-1}\). The instrument has an excellent radiometric calibration, allowing the determination of weak features of organic compounds which are present and rather important in the upper troposphere. We have recorded spectral data for peroxyacetyl nitrate (PAN) and acetone in the laboratory with a typical accuracy of better than 10%. These data have allowed us to analyse spectral data from the MIPAS instrument and to detect the spectral signatures of these gases for the first time. For PAN, the detection has been possible in two bands with consistent concentrations giving excellent confidence in the observations. In addition, the signatures of formic acid and ethane have been observed in the MIPAS spectra, although that for ethane is rather better known and not a surprise. The quality of formic acid and ethane retrievals from the MIPAS data will be limited by current uncertainties in the quality of the spectral databases. For PAN, acetone and formic acid, it is shown that the concentrations of these gases can be retrieved both in the Western Mediterranean, a region close to the balloon validation site at Aire-sur-l’adour, and in the polluted region of the East China Sea in April 2003. Typical detection limits for PAN are close to background limits in the Northern hemisphere upper troposphere (60 pptv) whilst those for acetone are somewhat larger and are of the order of 150-250 pptv. Tentatively we assign a detection limit to formic acid of 120 pptv, an estimate limited by uncertainties in spectroscopic data.

1 INTRODUCTION

The upper troposphere (UT) is a key region in the atmosphere which is of significant importance for climate studies, in addition to weather forecasting and transport of pollutants. Key aspects include the radiative forcing effects of anthropogenic and natural greenhouse gases with impacts on surface temperature and potentially circulation, long-range advection of pollutants with its direct influence on the UT and effects on the lower troposphere through subsidence, and control of the injection of source gases into the stratosphere. The composition of the UT is of significance, therefore, for climate through both physical and chemical processes (climate-chemistry interactions), and it is essential for modelling of past and future climate scenarios that we test our understanding, on global and regional scales, of key markers of UT composition. Given the role of organic compounds in the chemistry of the troposphere, it is clear we should target, if at all possible, some of the primary molecules of this type. However, although limited aircraft campaigns have been able to provide focussed process studies in targeted regions, satellite estimates for organic species have not previously been derivable prior to MIPAS (formaldehyde has been derived from GOME but is weighted towards the near-surface).

Acetone is believed to be important in the upper tropospheric budget of HO\(_x\). However, based on standard (IUPAC) kinetics there is uncertainty in its global budget. Sources of acetone include oxidation of isoprenes, vegetation, biomass burning with sinks through photolysis, oxidation by OH and dry deposition. Reference [1] performed a detailed study of acetone and, in order to reconcile models with remote observations of acetone in the Pacific, e.g. during PEM-tropics B, they had to infer a large oceanic source of acetone (14 Tg yr\(^{-1}\)). They also had to adjust other terms such as vegetation sources.

PAN is produced through the reaction of peroxyacetyl radicals and NO\(_2\). Peroxyacetyl radicals are produced through the decomposition of organic precursors, in particular oxygenated VOCs and biogenics such as isoprene. Hence PAN is a marker of the coupling between NO\(_x\) and VOC chemistry, where a significant source of VOCs can be biogenic emissions. PAN is stable at cold temperatures in the UT and can transport NO\(_x\) to remote areas before release by
thermal decomposition. Tropospheric ozone production can result with significant enhancements in remote regions (e.g. [2]).

Formic acid is noted to be one of the most abundant organic compounds in the troposphere but is expected to be highly variable due to its solubility [3].

Recent aircraft campaigns to study UT chemistry have revealed, using gas chromatography measurements, that acetone and PAN are ubiquitous in the mid- to upper troposphere with high concentrations apparently observed in some regions of up to 4500 pptv for acetone and 660 pptv for PAN (e.g.;[4] Observed UT concentrations of formic acid range from as little as 10 pptv to nearly 600 pptv [5. The variability of these compounds and the regional/temporal nature of enhancements in concentrations suggest strongly that more extensive and regular measurements of VOC concentrations would provide considerable new information.

2 THE MIPAS INSTRUMENT

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument[6,7] is a Fourier transform spectrometer (FTS) providing limb sounding spectra of atmospheric infra-red emission between 685 cm\(^{-1}\) (14.60 µm) and 2410 cm\(^{-1}\) (4.15 µm) at a spectral resolution of 0.025 cm\(^{-1}\) (unapodized). The data are recorded in five spectral channels but near-continuous coverage is available in the spectral domain albeit with narrow gaps between channels. Vertical profiles are scanned from 6 km to 68 km with a vertical spacing of 3 km in the UT and lower stratosphere commensurate with the vertical resolution of the instrument. Each profile requires approximately 75 s corresponding to an along-track distance of 500 km between vertical scans. Calibration of the spectra to produce geo-located, radiometrically corrected spectra (level 1b) incorporates data from views of an on-board blackbody near 240 K and views of “space” at greater than 200 km altitude above the Earth’s surface. The quality of the level 1b spectra are excellent with offsets in the calibrated spectra believed to be less than 2 nW/cm\(^2\) sr cm\(^{-1}\) [8]. Typical noise values for a single spectrum vary between 40 nW/cm\(^2\) sr cm\(^{-1}\) at 800 cm\(^{-1}\) to less than half that value at 1200 cm\(^{-1}\).

3 INTRODUCTION

The organic compound features to be examined are relatively weak (typically less than 5% of the total measured spectrum) and in fact cannot be observed directly in measured atmospheric spectra. Therefore, rather than matching the observed spectra, we instead seek to match residuals in the spectra. Hence we match a measured residual spectrum, \(\Delta Y\), with a simulated residual spectrum, \(\Delta F\). \(\Delta Y\) is defined as:

\[
\Delta Y(\tilde{\nu}) = R_F(\tilde{\nu}) - R_{F-GAS}(\tilde{\nu})
\]

(5.1)

where \(\Delta Y\) is the measured residual spectrum as a function of wavenumber, \(\tilde{\nu}\), and \(R_F\) and \(R_{F-GAS}\) are the measured and simulated spectra respectively. The \(R_{F-GAS}\) term describes a simulated spectrum with the target gas (GAS) excluded from the simulated atmosphere. \(\Delta F\) is defined here as:

\[
\Delta F(\tilde{\nu}) = R_F(\tilde{\nu}) - R_{F-GAS}(\tilde{\nu})
\]

(5.2)

Iteration is employed to adjust \(\Delta F\) to match \(\Delta Y\) by adjusting concentration profiles of the principal atmospheric gases contributing to the spectrum and aerosol extinction using Jacobian perturbation spectra. The spectral baseline close to each target spectral feature was a particular indicator of the quality of the fit and minimised principally using aerosol extinction.; there is also a contribution from also heavy molecules such as CFC-12 and HCFC-22 for which the band shape can be fitted (not shown). At each iteration step, i.e. after adjustment of the expected profile values, a full recalculation of the model spectrum and Jacobians was performed using a forward model (see below) to ensure accuracy in the calculated residuals. The process was performed at tangent altitudes from 15 km to 8.5 km, fitting sequentially
in an onion peeling type approach from higher to lower tangent altitudes with only the lowest two altitudes considered for detection.

3.1.1. The Oxford RFM

For the forward model, the Oxford Reference Forward Model (RFM) is employed in order to model the observed spectra measured by MIPAS-B2. The RFM is an infra-red, line-by-line radiative transfer model, derived from the Genln2 model with the ability to simulate spectra given the instrument lineshape and field of view (See www.atm.ox.ac.uk/RFM/ for further details). Where available, the RFM uses spectroscopic parameters for specified gases, for example from the HITRAN 2000 reference database described by [9]. For many other heavy cross-sectional molecules, where line parameters are not available, reference data for such molecules can be input as a special supplement to HITRAN in the form of the absorption cross-section per molecule as a function of wavenumber.

3.1.2. Laboratory spectral data.

Since even for ethane, there are considerable uncertainties, a laboratory programme has been instituted at the University of Leicester to examine the spectral signatures of compound such as acetone and PAN. In recent studies, the spectroscopy of acetone [10] and peroxyacetyl nitrate or PAN [12,13] have been investigated and cross-sectional data obtained under conditions appropriate to the upper troposphere; temperatures down to 220 K for acetone and 250 K for PAN. Typically, the accuracy of these laboratory cross-sections is of the order of 10%. The laboratory data have therefore been applied to atmospheric spectra obtained by MIPAS type instruments, producing substantial evidence, as will be seen below, that the spectral signatures of acetone and PAN can be observed ([10] and [11] respectively). These provide encouragement for future studies of these compounds and for exploitation of MIPAS spectra of the atmosphere.

4 RESULTS

The new laboratory spectral data recorded for PAN and acetone have been used to simulate, detect and retrieve the atmospheric signatures of acetone and PAN in infrared MIPAS spectra, a significant challenge but one which provides confidence for our retrieval studies for the future. Figure 1 shows detections for a case of pollutant outflow from China observed by MIPAS where we have observed close to 500 pptv of PAN and well over 1 ppbv of acetone; we have also performed detections for mid-latitude concentrations in the Western Mediterranean near Aire-sur-l’adour (500 pptv acetone, 140 pptv PAN). These detections, performed for the first time for the upper troposphere, verify two crucial aspects: a) our ability to perform radiative transfer modelling to levels close to the instrument noise level; b) the high radiometric accuracy of MIPAS. It is these factors which permit the retrieval of weak species with some confidence (e.g. SO2 and H2O2 retrievals at other MIPAS institutes). Figure 1 shows the detection of PAN in one spectral region but in fact we have detected the PAN signature between 1135 and 1185 cm^-1 (not shown) with very consistent mixing ratios for the PAN values determined independently from the two bands. Figure 2 shows the corresponding result for formic acid between 9 and 11 km over the China Sea.

In our work, we have found that retrievals of acetone or PAN jointly with aerosol, from cloud-cleared spectra, work well because broad spectral uncertainties such as gain, offset, and a large component of temperature error are subsumed into the retrieved “aerosol” and affect the target PAN/acetone much less. For line contaminant species, problematic features can be identified by residual structure in the detections of Figure 1 and can be reduced by use of microwindows which do not include the worst affected regions; this process will be optimised in the future when we hope to apply our methods to global retrievals of PAN, acetone and formic acid.

5 CONCLUSIONS

New PAN and acetone spectral reference data have been used to detect clear and characteristic spectral signatures of these gases in the upper troposphere for the first time. The results clearly demonstrate the potential of the MIPAS instrument to obtain important measurements of trace gases in the upper troposphere which are of considerable importance for local ozone chemistry, determination of the concentrations of greenhouse gases concentrations, and transport of pollutants.
Fig. 1 Detection of acetone and PAN by residual analysis for 1450 pptv acetone at 9 km and 450 pptv PAN at 11 km over the China Sea in April 2003. (a) Residual of MIPAS spectrum minus a forward model simulation not including acetone (residual=dark line); b) the same for PAN; c) difference between forward model calculations with and without acetone; d) the same for PAN. The difference spectra c) and d) are actually overplotted in grey (red in colour plots) in figures a) and b) respectively but are shown separately because they are difficult to see in black/white printing. Colour figures can be found at http://www.leos.le.ac.uk/mipas/spectroscopy/fits.html. Good agreement between measured residuals and forward model differences indicate positive detection. The noise in the acetone and PAN spectral regions are 15 nW/(cm² sr cm⁻¹) and 30 nW/(cm² sr cm⁻¹) respectively.

Fig. 2 Detection of formic acid by residual analysis for 1.2 ppbv formic acid between 9 and 11 km over the China Sea in April 2003. Residual of MIPAS spectrum minus a forward model simulation not including formic acid (dark line) compared to the difference between forward model calculations with and without formic acid. Good agreement between measured residuals and forward model differences indicate positive detection. The noise in the formic acid spectral region is less than 30 nW/(cm² sr cm⁻¹) respectively.
The PAN spectral signature was detected simultaneously for two separate PAN bands in the mid-IR in two independent MIPAS spectral channel. PAN concentrations in the UT (8-15 km) have been retrieved from the best-fit to MIPAS spectral residuals with consistent concentrations inferred for both PAN band. Clear signatures were also observed for acetone and formic acid. Although acetone is less observable than that for PAN, its characteristic shape is clear at the high concentrations which may be found in the East China Sea in April 2000. Limits of detection by MIPAS, using the method described here (whole band analysis) are estimated to be:

a. PAN. 60 pptv (9-15 km) = Detectable at NH background concentrations
b. Acetone: Less than 250 pptv and perhaps as low as 125 pptv (9-12 km) = Detectable near background concentrations and in polluted airmasses
c. Formic acid: 120 pptv (9-15 km) = Detectable near source regions (high rainout)

For formic acid, there is considerable concern that the spectroscopy needs to be revised and thus the concentrations quoted must be treated with caution. Typically, formic acid can be detected at levels an order of magnitude less than those in the East China Sea in April 2003.

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7 References

5. Reiner et al., T., O. Mohler and F. Arnold, Measurements of acetone, acetic acid and formic acid in the northern mid-latitude upper troposphere and lower stratosphere, J.G.R., 13943-13952,1999