

SPARC²⁰⁰² newsletter n° 19 July

STRATOSPHERIC PROCESSES AND THEIR ROLE IN CLIMATE
A Project of the World Climate Research Programme

Report on the 23rd Session of the Joint Scientific Committee (JSC) for the World Climate Research Programme (WCRP)

Hobart, Australia, March 18-22, 2002

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The SPARC co-chairs, Marv Geller and Alan O'Neill, attended the 23rd meeting of the Joint Scientific Committee (JSC) of the WCRP in Hobart, Australia, March 18-22, 2002. At the meeting, they presented a review of SPARC progress in its present projects and its plans for the future. The point was made that while SPARC has made great progress in its present configuration of examining Stratospheric Indicators, Stratospheric Processes, and Modelling, its future efforts will be taking a more wholistic approach to Documenting and Understanding Stratospheric Change. Examining Stratospheric Processes will remain an important part of SPARC's activities since some processes remain to be sufficiently understood to be incorporated reliably in models. It was also stressed that study of the stratosphere has changed from being an exotic branch of atmospheric science to one being squarely in the middle of the climate agenda, being

pivotal in such topics as attributing observed climate changes and in recent research on the Arctic Oscillation. Plans for holding the SPARC 2004 Assembly in Victoria, British Columbia, Canada, during the period July 19-23, 2004 were presented. Finally, some information on the status of the SPARC Office in Paris and the SPARC Data Center in Stony Brook was given. Members of the JSC were happy with the progress of SPARC and with its future plans.

Two topics that were discussed extensively at the meeting were for the JSC to emphasize its goal of improving climate forecasts on many time scales. SPARC's future plans fit in nicely with this. Another theme was to seek better integration with the IGBP, and particularly with IGAC in the area of Chemistry-Climate. Toward this end, a SPARC/IGAC workshop is planned to formulate how to proceed in this area.

One specific item that arose from the JSC meeting was a task force to develop an overarching WCRP activity, "Predictability Assessment of the Climate System." This task force will be chaired by B. Hoskins and include J. Shukla and J. Church from the JSC, as well as nominees from GEWEX, CLIVAR, SPARC, ACSYS/CLIC, WGNE, and WGCN. This task force will bring implementation proposals to the JSC at its next meeting in March 2003.

Another item was a call for increased dialogue among the WCRP projects on data management. The SPARC co-chairs were charged with developing studies and cooperation between IGAC and SPARC with the goal of launching an "Atmospheric Chemistry and Climate" initiative. This summer's SPARC/IGAC workshop is meant to make progress on this.

The 24th meeting of the JSC is planned for Reading, UK in March 2003.

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Climate-Chemistry Initiative Discussions

Zurich, Switzerland, June 29-30, 2002

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A small group of SPARC associated scientists got together in Zurich on June 29-30, 2002 to briefly discuss the most pertinent issues that should be considered for inclusion in the joint SPARC-IGAC initiative. Prof. **Th. Peter** of ETH, Zurich and member of the SSG hosted the discussion session. Thanks to **Th. Peter** and **P. Forney** for making all the local arrangements in Zurich.

I. Bey (EPFL, Lausanne), **P. Forster** (University of Reading), **C. Johnson** (Hadley Center, Met Office), **D. Kley** (KFA, Juelich), **K. Law** (University of Cambridge), **A. O'Neill** (University of Reading), **S. Pawson** (NASA-Goddard), **Th. Peter** (ETH, Zurich), **J. Pyle** (University of Cambridge), **V. Ramaswamy** (GFDL, NOAA), **A. R. Ravishankara** (AL, NOAA), **M. Schultz** (Max-Planck-Institute, Hamburg), **T. Shepherd** (University of Toronto), and **M. Takahashi** (University of Tokyo) attended the discussions.

A.R. Ravishankara presented an overview of the aims of the SPARC interest in the Climate-Chemistry initiative and discussed what is being planned in starting the joint initiative. Each attendee presented a few discussion points that were assigned to them from the following list of topics.

- Ozone in the Upper Troposphere (UT) and Lower Stratosphere (LS),
- Condensed matter in UT/LS: Aerosol and Radiation; Cirrus; Chemistry in/on condensed matter,
- Impact of regional emissions on global state,
- Tropical Tropopause Layer (TTL),
- Dynamical Influences,
- Water Vapour,
- Current State of GCMs,
- Tropospheric chemistry.

Following the presentations and vigorous discussions, it was concluded that crosscutting process related issues and modelling issues should be addressed. These include issues and topics such as:

- The extent and role of stratosphere-troposphere exchange in controlling the abundances of ozone and other species in the UT and LS. Specifically, an accurate quantification of the STE contribution to tropospheric and upper-tropospheric ozone budget (which is likely to be a function of time and location).

- The role of convection (both deep and warm) in controlling the water vapour abundance and redistribution of chemical constituents.
- The state of radiative transfer codes in calculating heating rates and photolysis rates.
- The use of variability in observations and in models to identify and diagnose roles and contributions of processes. An assessment of the role of inter-annual variability in the circulation patterns affecting the distribution of chemical constituents in the stratosphere and troposphere.

Understanding of microphysics and their incorporation in numerical models.

- Determination of the fundamental parameters in kinetics, heterogeneous chemistry (specifically aerosols and ice in UT), photolytic processes, spectroscopy, and optical properties via laboratory studies.

It was concluded that these are a very large number of issues and topics to be jointly studied by the SPARC-IGAC community. Furthermore, these issues were not prioritised at this meeting. Once the IGAC community can look at



First row left to right: S. Pawson, P. Forster, A.R. Ravishankara

Second row left to right: Th. Peter, T. Shepherd, K. Law, I. Bey, M. Schultz, A. O'Neill, C. Johnson, M. Takahashi

- The role of Tropical Tropopause Layer (TTL) in climate-chemistry interactions.
- The role of lightning in the production and distribution of nitrogen oxides.
- The role of aerosols in chemistry, climate, and their interactions. The processing of aerosol in the atmosphere and their impact on chemistry and climate. Understanding and representing microphysical processes in numerical models.
- The age of air in the UT - its definition, determination, and use.
- The use of numerical models to analyse the feasibility of process studies and quantification of key processes.

these issues and topics and decide on their interests, the top priorities for the joint initiative should be very apparent. In facilitating this process, the conclusions of this discussion group will be shared with the IGAC co-chairs, then **A.R. Ravishankara** and **A. O'Neill** will make a presentation to the IGAC community at the IGAC symposium in Crete in September. Before the meeting, a venue and date for a joint workshop with IGAC will be decided in consultations with the IGAC co-chairs.

Report on the First SPARC Data Assimilation Workshop

University of Maryland Baltimore County, USA, 10-12 June, 2002

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Organizing committee: I. Stajner (USA), W. Lahoz (UK), R. Swinbank (UK),
and S. Pawson (USA)

The first SPARC Data Assimilation (DA) workshop was held on June 10-12, 2002. It was hosted by the NASA/Goddard Data Assimilation Office, through the Goddard Earth Sciences and Technology Center (GEST) at the excellent facilities of the University of Maryland Baltimore County (UMBC). The workshop was well attended, with representatives of 16 groups that work on meteorological and constituent assimilation in the stratosphere or use these products. The programme was divided into five sessions: Introduction, Stratospheric assimilation, PV reconstruction and satellite data, Ozone assimilation, and Chemical assimilation.

The workshop began by a welcome given by **T. Low** from GEST. **A. O'Neill**, SPARC co-chair, presented his view on the rationale and priorities of the SPARC data assimilation project. He started by describing existing SPARC projects. He advocated a formation of a SPARC DA working group with a purpose of coordinating and promoting data assimilation relevant to SPARC. He suggested a list of priorities for the working group, and encouraged workshop participants to attend the Third SPARC General Assembly in July 2004.

An overview of ESA's missions collecting constituent data was given by **C. Zehner**. He described data assimilation as a key tool for exploitation of ESA's atmospheric measurements. Data assimilation is one of the techniques that will be used in calibration and validation of Envisat products.

G. Manney presented an example of inter-comparisons of assimilated fields that this SPARC initiative is hoping to extend to different regions and geophysical fields. She presented inter-comparisons of temperature fields in polar regions. She focused on a quantitative study of 6 data sets for cold Arctic winters in 1995-1996 and 1999-2000.

R. Swinbank gave an overview of the Stratospheric Data Assimilation at the UK Met Office. He described the Analysis Correction system, which produces a realistic quasi-biennial oscillation (QBO) in the analysed winds. He continued with a description of a newer 3D-Var system and a comparison of assimilated fields from the two systems. Differences of temperature sonde observations and model forecasts in the troposphere are smaller for the 3D-Var system. Planned development includes changes in the dynamical core, background error statistics, and a gravity wave drag scheme. He concluded that the stratospheric DA products are invaluable, and that stratospheric DA is becoming a part of the numerical weather prediction mainstream.

An overview of the meteorological analyses at the NASA/Goddard Data Assimilation Office (DAO) was given by **S. Pawson**. He showed how the scrutiny of the system products during mission support such as SAGE III Ozone Loss and Validation Experiment (SOLVE) leads to a better understanding of the system. A new DAO system GEOS-4 has reduced noise in meteorological fields that has a massive impact on trace gas transport, including an older age of air. The new system will be used for a reanalysis over the Upper Atmosphere Research Satellite (UARS) period for years 1991-1995. **Shuhua Li** showed that including travelling gravity waves has a large impact on DAO's GEOS-4 forecast and analysis fields, in the upper stratosphere.

S. Edouard presented the impact of the recent changes in the Global Environmental Multiscale (GEM) model: assimilation of radiances, a new quality control scheme, a new gravity wave drag scheme, and assimilation of cloud motion wind vectors. She presented the plans to change to a new hybrid vertical coordinate, assimilate new data types, and for development of a 4D-Var assimilation system.

S. Polavarapu described the development of a coupled meteorological and chemical assimilation system in collaboration of the Meteorological Service of Canada and Canadian Universities. They adapted the Canadian Meteorological Centre's operational 3D-Var scheme and coupled it to the Canadian Middle Atmosphere Model (CMAM). The system currently shows a reasonable comparison against UK Met Office analyses, and many improvements are planned.

A method for construction of proxy ozone fields based on the correlation of ozone measurements from occultation instruments and of smoothed potential vorticity (PV) fields on isentropic surfaces was presented by **C. Randall**. The proxy ozone based on Polar Ozone and Aerosol Measurement (POAM) data alone compares well with ozone sondes in mid to high latitudes. The addition of Stratospheric Aerosol and Gas Experiment (SAGE) and Halogen Occultation Experiment (HALOE) produces a better quality of the proxy ozone at low latitudes. This method can be used for construction of water vapour or aerosol surface area proxy fields. The method is limited by the noise in the PV field and during the period of the polar vortex break-up.

D. Allen presented a way of constructing another ozone proxy using a tracer equivalent latitude (TrEL). A synthetic tracer is advected with diffusion by non-divergent UKMO winds on isentropic surfaces. The tracer contours are used to define an equivalent latitude. Equivalent latitude/potential temperature bins are used to define an ozone proxy. The proxy is further constrained using Total Ozone Mapping Spectrometer (TOMS) level 2 data. This proxy was used to investigate an extreme ozone mini-hole event in November 1999.

S. Kondragunta gave an overview of the operational and reprocessed calibration of the Solar Backscatter

Ultra-Violet/2 (SBUV/2) instrument ozone data. She pointed out the changes in the operational calibration and the retrieval algorithm and their effects on the ozone product. She also presented a new method for producing global total column ozone maps by combining the SBUV/2 product in the middle and upper stratosphere with a TIROS Operational Vertical Sounder (TOVS) ozone product between 400 and 30 hPa.

J. Hornstein talked about using 3-D global ozone fields for testing of data assimilation and satellite retrieval algorithms. Global proxy ozone fields can be used to provide simulated data with a representative variability. They can also be used to construct a climatology and *a priori* error covariances matrices for satellite retrievals.

The ozone assimilation session started with the presentation given by **A. Dethof** about the ozone assimilation at the European Centre for Medium-Range Weather Forecasts (ECMWF). They have included TOMS and SBUV/2 ozone assimilation in the ERA 40 reanalysis and Global Ozone Monitoring Experiment (GOME) and SBUV/2 ozone assimilation in the operational system. They are planning to include a radiative feedback of ozone fields and a multivariate ozone-PV assimilation.

I. Stajner gave an overview of the ozone assimilation at the DAO. She demonstrated a positive impact of including SBUV/2 ozone data from the 63-126 hPa layer, and of modelling TOMS errors as spatially correlated on the quality of the lower stratospheric assimilated ozone. Both the inclusion of a parameterised chemistry model and the better quality of the GEOS-4 assimilated winds were shown to improve the assimilated ozone. She presented examples of successful monitoring of satellite instrument errors, and discussed plans for monitoring and assimilation of ozone data from new instruments.

D. Jackson described ozone data assimilation research at the UK Met Office. The goal is to include ozone as an analysis variable in the operational 3D-Var system by assimilating SBUV/2 ozone retrievals and TOVS channel-9 radiances. The ultimate goal is to show a positive impact on forecast scores of the operational system. Observing system simulation experiments for several future instruments (SWIFT, IASI, AMSU, GOME2) are planned.

H. Eskes showed results from GOME ozone data assimilation and ozone fore-

casting at the KNMI. In the system, that is driven by ECMWF winds, forecast error variances are evolved, and the correlations are fixed in time. Ozone forecasts are produced and have anomaly correlations above 60% for 6 days in the extratropics, and for 2 days in the tropics. Their plans include SCIAMACHY validation and assimilation, assimilation of nadir radiances, and estimation of tropospheric ozone from GOME or Ozone Monitoring Instrument (OMI) assimilation.

T. Sasaki presented the progress and plans for ozone assimilation within a coupled general circulation model (GCM) and chemistry and transport model (CTM) at the Meteorological Research Institute (MRI) and the Japan Meteorological Agency (JMA). This system uses TOMS total column ozone data through a nudging technique.

An approach to SBUV/2 radiance assimilation was presented by **P.-K. Bhartia**. He advocated the use of a linearised forward model around the retrieved ozone profile in the radiance assimilation. He also asked the ozone data assimilation community to help define the products needed for an effective assimilation of the new version 8 of SBUV/2 products.

The chemical data assimilation session opened with the talk by **W. Lahoz**. He presented a strategy for Envisat level 2 chemical data validation and assimilation at the Data Assimilation Research Centre (DARC). He showed results from GOME and/or UARS Microwave Limb Sounder (MLS) ozone assimilation. The assimilation results are better when data from both instruments are used than when either instrument is used alone.

H. Elbern presented observability tests with a variational data assimilation system. He showed that in an identical twin experiment evolution of most species in a box model can be recovered from the six species that will be provided operationally from MIPAS observations. This feasibility study indicates that a 4D-Var approach will provide estimates of unobserved species by assimilation of Envisat routine data.

D. Fonteyn showed the progress made towards operational chemical data assimilation BASCOE. It is based on a 4D-Var scheme for a 3-D Eulerian stratospheric CTM with heterogeneous chemistry and polar stratospheric cloud microphysics. Systematic differences were found in the assimilation of CRISTA chemical data.

Validated data from three Envisat instruments will be assimilated.

J.-F. Lamarque presented the recent work at NCAR on the tropospheric chemical data assimilation. He showed results on ozone and carbon monoxide assimilation in the MOZART-2 model with a tropospheric chemistry. Satellite data from TOMS, MLS and Measurements of Pollution in the Troposphere (MOPITT) instruments were used in a sub-optimal Kalman filter. The assimilated fields compare well with independent observations.

D. Lary presented his work on the chemical data assimilation in flow-tracking coordinates. The UARS chemical observations were assimilated using the Kalman filter into a box chemical model. Inconsistencies between measurements of different chemical species were found. They need to be addressed through a quality control of observations and by devising ways of conserving the budgets of chemical species in the assimilation.

The workshop concluded by a discussion of goals for an emerging SPARC DA working group. **I. Stajner** was appointed as convener. Yearly workshops and data assimilation sessions at scientific meetings are planned. Three near-term tasks were agreed on. **G. Manney** will coordinate collection of information about availability and quality of stratospheric meteorological and chemical data sets. After the data are available, process focused assessments of their quality will follow. For example, they can include a representation of polar processes, equatorial dynamics such as QBO, tape recorder in moisture, the subtropical barrier, or ozone mini-holes. **J.-F. Lamarque** will coordinate collection, validation and intercomparison of chemical assimilated data sets. The winter of 1999/2000 was suggested as one of the periods for an intercomparison and validation against independent measurements. **D. Fonteyn** will collect information on CTM and GCM assimilation systems that are available for intercomparisons and coupling.

More information and electronic presentations are available from: http://dao.gsfc.nasa.gov/sci_research/cooperative_ventures/sparc/report.php

Envisat Taking up Duty of Atmospheric Composition Sounding

The European Space Agency's GOMOS, MIPAS and SCIAMACHY Calibration and Verification Teams

Introduction

On the 1st of March 2002, the European Space Agency (ESA) launched Envisat, the largest Earth observing satellite ever built, with an Ariane 5 rocket into its 800 km, sun-synchronous, polar orbit. Three of the ten instruments onboard Envisat are dedicated to the observation of the atmospheric composition, namely, GOMOS, MIPAS and SCIAMACHY.

Since the launch, the instruments have undergone a variety of functional checks that aim at the verification of the overall health status of the instruments, their commandability and the data downlink. During the calibration and validation phase, which is being conducted in the period of one to nine months after launch, dedicated measurements are being acquired and analysed in order to verify or re-assess key instrument performance parameters, for example, re-characterisation of detector non-linearity, instrument line shape, line-of-sight mispointing. Once stable in-orbit measurement scenarios have been established, checks of critical on-ground algorithms will be performed, in order to identify necessary corrections to processor components and to compile error budgets. Non-Envisat measurements of geophysical parameters will be considered for first validations.

It is planned that around mid-July the first Level 1b and Level 2 data products will be released to the Atmospheric Chemistry Validation Team (ACVT) for intensive geophysical validation supported by dedicated campaigns, e.g., involving balloon and aircraft measurements. The Envisat data will be released to the user community once the Commissioning Phase and First Validation Phase have been completed.

In this article we present some first results of GOMOS, MIPAS and SCIAMACHY measurements. These results are, however, not yet conclusive and should be considered as preliminary. More details on the calibration and validation can be found in the "Envisat Calibration and Validation Plan" (<http://envisat.esa.int/support-docs/calval/CalVal.pdf>).

GOMOS

The primary objective of the Global Ozone Monitoring by Occultation of Stars (GOMOS) instrument is monitoring of the stratospheric and mesospheric ozone concentration with high accuracy via occultation of setting stars, providing comparable accuracy to solar occultation measurements, but with full global coverage. Ozone is measured in the Hartley, Huggins and Chappuis bands with a UV-VIS grating spectrometer (250-675 nm, 0.312 nm sampling, better than 1 nm resolution). The contiguous spectral coverage enables also observation of NO₂, aerosol extinction and possibly NO₃ and OClO. Atmospheric density can be derived from oxygen A-band measurements with a spectrometer covering 756-773 nm (0.2 nm resolution) and from Rayleigh scattering. Temperature can be derived with very high vertical resolution from the analysis of atmospheric scintillation signals recorded with two fast photometers (1 kHz sampling frequency) in the visible blue (470-520 nm) and red (650-700 nm) wavelength ranges. Furthermore, H₂O will be observed by a second near-IR spectrometer covering 926-952 nm. Level 1b data products are in particular atmospheric transmission spectra and associated variance. Level 2 data products are the retrieved geophysical data products, such as temperature and trace gas concentration and aerosol extinction profiles. The vertical resolution of the measured species profiles depends on the occultation obliqueness and is better than 1.7 km.

The instrument's line-of-sight can be pointed over a large contiguous range, reaching from the anti-flight direction (-10°) to 90° in azimuth and from 68° to 62° with respect to the nadir

direction. This enables GOMOS to acquire a star outside and follow it through the atmosphere. The instrument and mission objectives are described in [1].

GOMOS observations started on 20 March, 2002. Currently, the instrument performs already more than 500 occultations per day. The failure rate (due to loss of tracking) is currently below 2%. This happens with some faint (visual magnitude higher than 3) and hot (temperature above 15000 K) stars (low visual magnitude means bright, high visual magnitude means faint star). Stars up to a visual magnitude of 4.1 have been successfully tracked. Lowest tracking altitudes are below 10 km. The star detection threshold is currently under fine-tuning in order to increase the potentially observable star range.

The objective of the GOMOS calibration activities, which are on-going, is a complete instrument calibration, including a full in-flight calibration (e.g. band setting, wavelengths assignment) and re-characterisation of GOMOS (including non-linearity, pixel response non-uniformity, dark charge map), a complete verification and upgrade of the Level 1b data processor, definition of the routine calibration operations and observation plan. Four main tasks are being carried out in order to achieve this:

- 1 - Verification of instrument health,
- 2 - Derivation of instrument characteristics,
- 3 - Validation and tuning of the Level 1b algorithm chain,
- 4 - Level 1b data product verification.

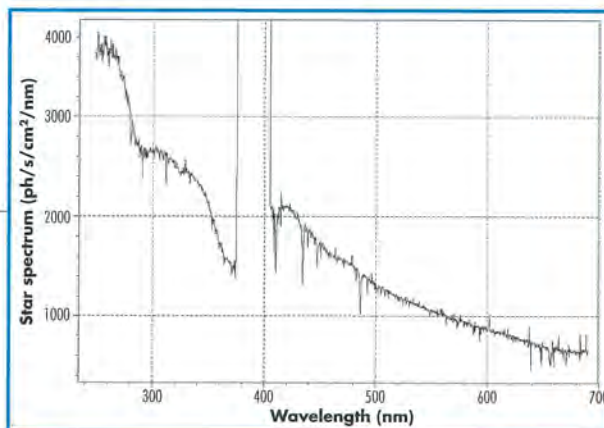


Figure 1. Calibrated stellar spectrum in the UV-visible spectrometer. The spectrometer is not specified in the region of 375-405 nm, therefore the spectrum is not calibrated in this region.

The data product quality varies with the visual magnitude and temperature of the occulted star. Scattered sunlight will furthermore degrade the measurements in the stratosphere and below on the orbit day side. An example of a stellar spectrum (of a weak and hot star of magnitude 2.4 and temperature 28000 K) in the UV-visible channel of GOMOS is shown in **Figure 1** (p. 5). From this occultation of 6 May 2002, the derived atmospheric transmission in the UV-visible is shown in **Figure 2** (p. I) for some tangent altitudes.

GOMOS uses a two-step Level 2 retrieval approach. In a first step, the trace gas densities integrated along the line-of-sight are being retrieved. In a second step, these "column densities" are converted into atmospheric profiles. The ozone absorption in the Hartley band allows good mesospheric ozone retrievals, but blacks out rapidly as the instrument scans downwards in the upper stratosphere. Absorption in the Huggins band is apparent, but most importantly, the strong Chappuis band signature enables ozone retrieval down to 20 km in this case. **Figure 3** shows the vertical profiles of ozone and NO₂ derived from the transmittances shown above. NO₃

Figure 3. Atmospheric ozone and NO₂ column density profiles along the line-of-sight (up) and local density vertical profiles (down) retrieved from the transmissions shown in **Figure 2**.

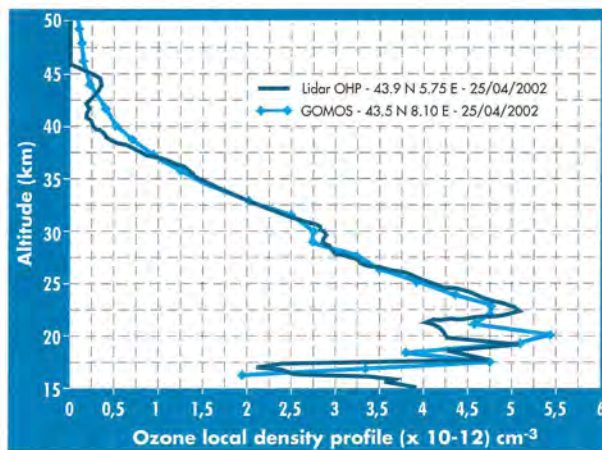
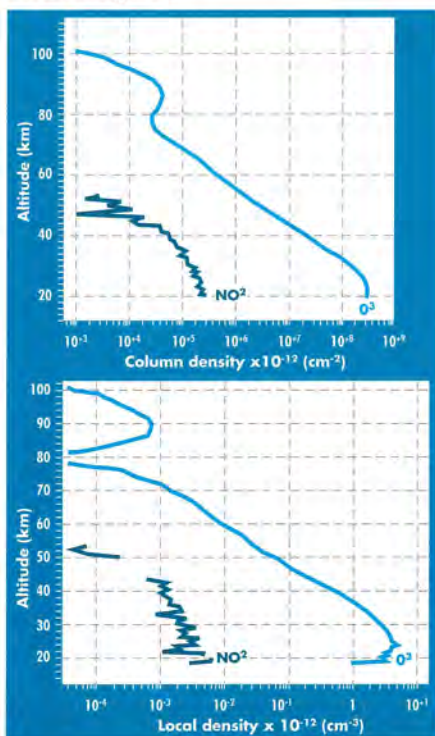


Figure 4. Comparison of GOMOS retrieved ozone profile measured on 25 April 2002 with collocated lidar measurement at Observatoire de Haute Provence.

will also be retrieved but has not yet been analysed in detail. First comparisons with climatology data are indicating very good agreement with GOMOS ozone, NO₂ and air density measurements. Also GOMOS-GOMOS inter-comparisons of measurements of the same air volume at subsequent orbits using different stars have shown very high consis-

istency in the retrieved geophysical data products. Furthermore, a first inter-comparison with a ground-based ozone lidar shows promising results (**Figure 4**).

Results of the retrieved atmospheric transmission with a bright and hot star (visual magnitude 0.61, temperature 28000 K) is shown in **Figure 5** (p. I). The Huggins ozone absorption structures are obvious as well as NO₂ absorption structures. Ozone and NO₂

retrievals are possible down to approximately 14 km. Good results can also be expected from the oxygen A band measurements, even though the calibration and Level 2 analysis of the two near infrared channels (oxygen and water vapour) have not yet been started.

Very promising are also first analysis results from the atmospheric scintillation measurements made with the two fast photometers. **Figure 6** shows the measured time delay in the two photometers and **Figure 7** shows the derived temperature profile with high resolution in comparison to the ECMWF analysis of the same time and location.

Figure 6. The measured time delay between the blue and the dark signal as measured by the GOMOS fast photometers (FP1 and FP2). This signal is being exploited for the retrieval of high-resolution temperature profiles.

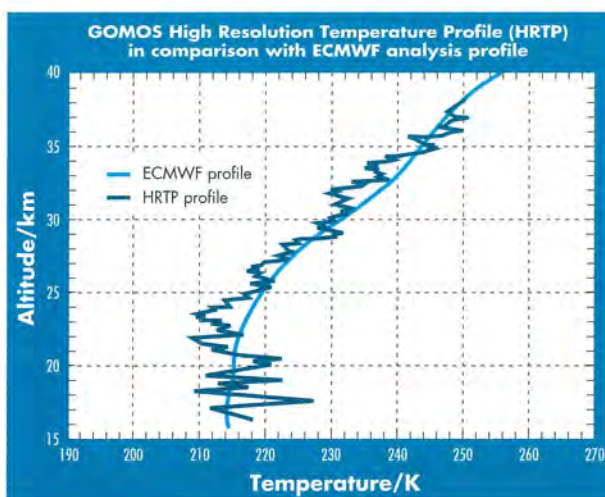
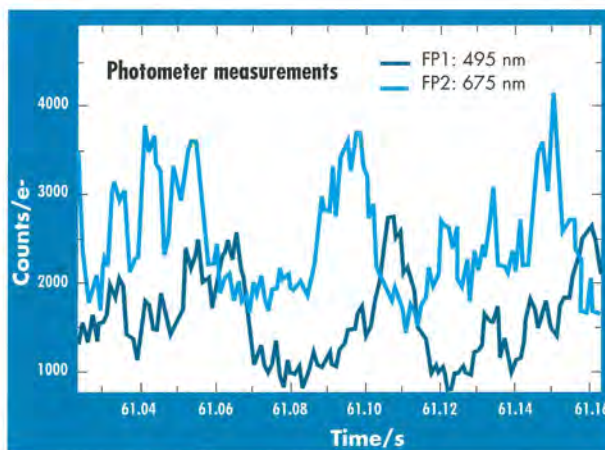


Figure 7. High-resolution temperature retrieval from GOMOS fast photometer measurements (dark curve, orbit 799, 25 April 2002) in comparison to collocated ECMWF analysis (blue curve).

MIPAS

The primary objective of the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is to advance the understanding of the chemistry and dynamics of the stratosphere and upper troposphere as well as the stratospheric-tropospheric exchange. It measures atmospheric limb emission spectra from which vertical profiles of atmospheric pressure, temperature and volume mixing ratios of a number of trace gases are derived with a vertical coverage of nominally 6 km to 68 km. The primary target species are O_3 , H_2O , CH_4 , N_2O , HNO_3 and NO_2 . The instrument covers a broad spectral range, from 685–2410 cm^{-1} (14.6 to 4.15 micron) at high spectral resolution (0.03 cm^{-1}). The field of view at limb tangent point is 3 km (vertical) by 30 km (horizontal). The line-of-sight viewing range is in the vertical 5 to 200 km (tangent height) and in the horizontal 35° about rearward (anti-flight) direction and 30° for sideways viewing geometries.

The instrument and mission objectives are described in [2]. The viewing geometry is depicted in Figure 8 (p. I).

The MIPAS activities during the Commissioning Phase are:

- 1 - Initial performance verification and update of instrument configuration and calibration,
- 2 - Level 1b and Level 2 algorithm characterisation and verification,
- 3 - Geophysical validation.

This paper focuses on first processing results of in-flight performance and Level 1b (collocated calibrated limb emission spectra) and Level 2 (geophysical data products) data. The implemented Level 2 retrieval algorithm is based on the global fit approach.

The initial switch-on of the instrument and first data transmission took place on 24 March (orbit number 334). MIPAS appears fully functional in flight. No serious hardware problems have been identified. Radiometric performance is excellent and very close to the performance model. An initial check of the line-of-sight direction using a planetary source shows little deviation from the commanded value. Spectral parameters such as resolution, linearity and stability have been verified to be within specifications.

Figure 9 shows calibrated stratospheric limb radiances in four spectro-meter bands. Other trace gas signatures

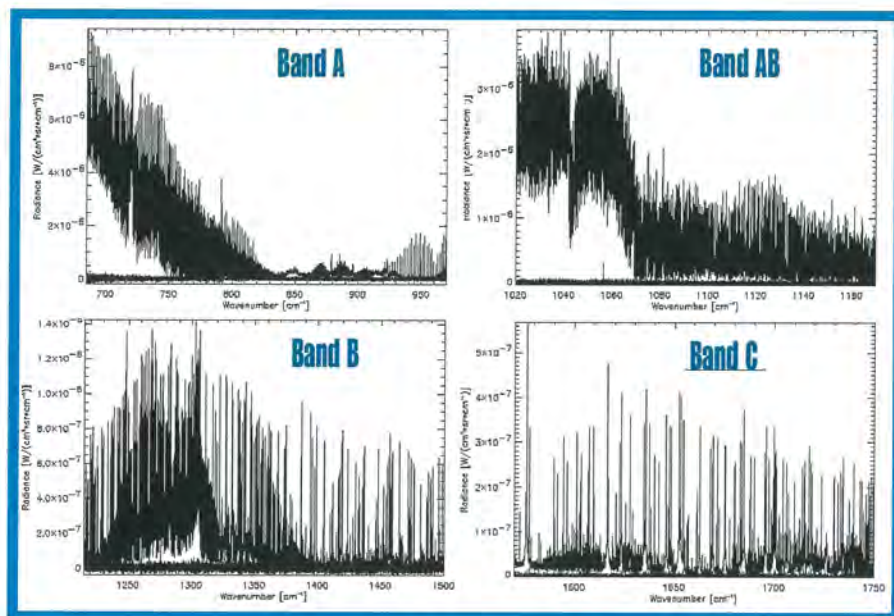


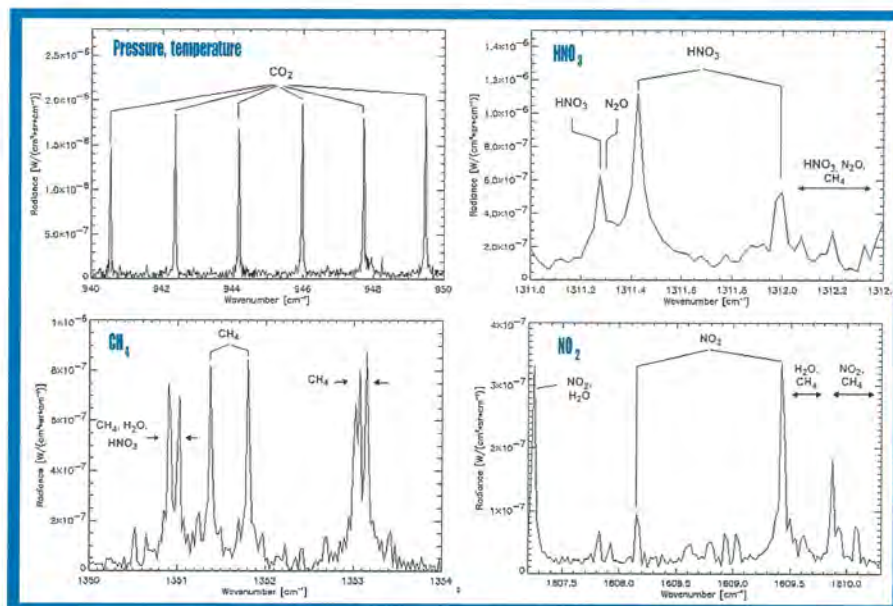
Figure 9. MIPAS calibrated stratospheric limb radiances in four spectral bands, measured on 24 March 2002, orbit number 334. The plots show both the real and the imaginary part of the spectrum. The latter shows only noise structures as expected. The expected strong signature of ozone emission can be seen in band AB around 1020 to 1070 cm^{-1} .

of various trace gases used for temperature, pressure and trace gas profiles retrievals can be identified when zooming in as shown in Figure 10. First temperature and ozone profile retrievals have been processed from orbit 504 (5 April 2002) as shown in Figures 11 and 12, plotted together with their standard deviations. Figure 13 shows the retrieved temperature profile over the full orbit 504. The vertical range of the retrievals is 12–68 km. The ozone retrievals from the same

data set are shown in Figure 14 (p. 9). NO_2 profiles are shown in Figure 15 (p. 9) and the HNO_3 profiles, which show a latitudinal concentration variation, are presented in Figure 16 (p. 9).

MIPAS data acquisition and analysis has started after the instrument switch-on 24 days after Envisat launch. Full functionality of the instrument and excellent radiometric performance have been achieved, so that calibration and validation mea-

Figure 10. Emission lines of minor species seen clearly when zooming in the spectrum. These spectra have been recorded by MIPAS on 24 March 2002, orbit 334.



measurements were started as planned on the 5th of April. A dedicated characterisation measurement period is currently ongoing with very encouraging results of up to the Level 1b and Level 2 processing. So far, only minor routine modifications of the algorithms and auxiliary data were necessary. Cloud detection turns out to be an essential part of the processing scheme. From July 2002 onwards, a stable Level 1b processing is expected coinciding with the start of the first intensive balloon and aircraft geophysical validation campaign.

SCIAMACHY

The Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) is a cross-track scanning double spectrometer, which can look at the atmosphere in either nadir or limb geometry, as well as via solar and lunar occultation. The spectrometer covers eight channels:

- 1 - 240-314 nm (0.24 nm resolution),
- 2 - 309-405 nm (0.26 nm),
- 3 - 394-620 nm (0.44 nm),
- 4 - 604-805 nm (0.48 nm),
- 5 - 785-1050 nm (0.54 nm),
- 6 - 1000-1750 nm (1.48 nm),
- 7 - 1950-2040 nm (0.22 nm),
- 8 - 2265-2380 nm (0.26 nm).

The polarisation measurement devices have 7 channels:

- 1 - 310-377 nm,
- 2 - 450-525 nm,
- 3 - 617-705 nm,
- 4 - 805-900 nm,
- 5 - 1508-1645 nm,
- 6 - 2265-2380 nm,
- 7 - 802-905 nm

The objective of SCIAMACHY is to measure a wide range of tropospheric and stratospheric constituents (O_3 , H_2O , CH_4 , N_2O , NO_2 will be systematically processed and distributed) as well as temperature and aerosol.

SCIAMACHY data are processed, similar to GOMOS and MIPAS, into Level 1b (radiances) and Level 2 (geophysical products). Level 1b differs from the GOMOS and MIPAS products insofar as the user has to apply the corrections and calibrations himself in order to obtain geo-located calibrated radiance. This specific interpretation of Level 1b is based on the GOME (ERS-2) heritage, in order to have as much as possible raw data information in the data product. Calibration software is delivered together with the Level 0 data. More information on SCIAMACHY mission

objectives and measurement modes can be found in [3].

The first steps in the calibration process are to verify the in-flight behaviour of the instrument. This will be achieved by analysing measurements made with various on-board calibration sources as well as with sun, moon and atmosphere as calibration targets. Calibration activities focus on the characterisation of:

- Dark current,
- Dead and bad pixels,
- Etalon and pixel-to-pixel gain,
- Spectral calibration,
- Straylight,
- Polarisation sensitivity,
- Throughput.

This will lead to an update of the calibration auxiliary data before starting the Level 2 data geophysical validation.

During launch, the instrument is protected by three mechanical covers for the two mirrors and the radiant cooler. First instrument functional tests after switch-on in mid-March made use of the on-board calibration

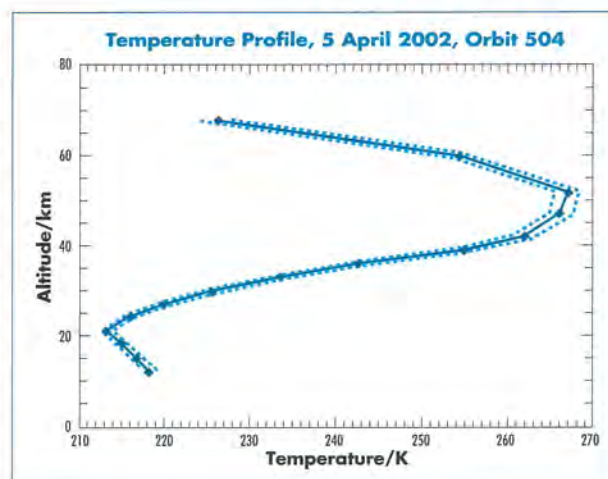


Figure 11. First temperature retrieval with statistical error from measurements in orbit number 504, 5 April 2002.

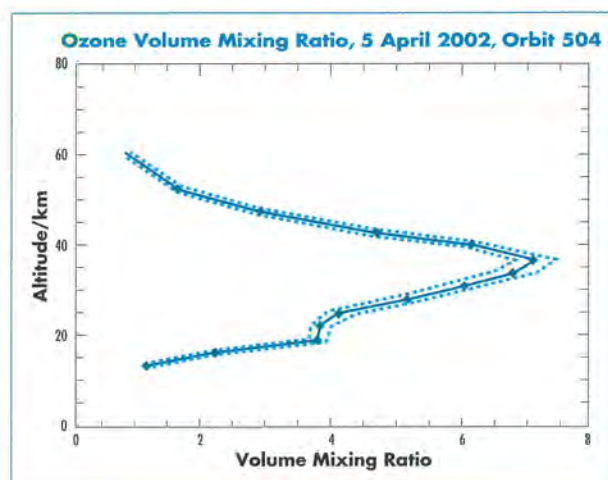
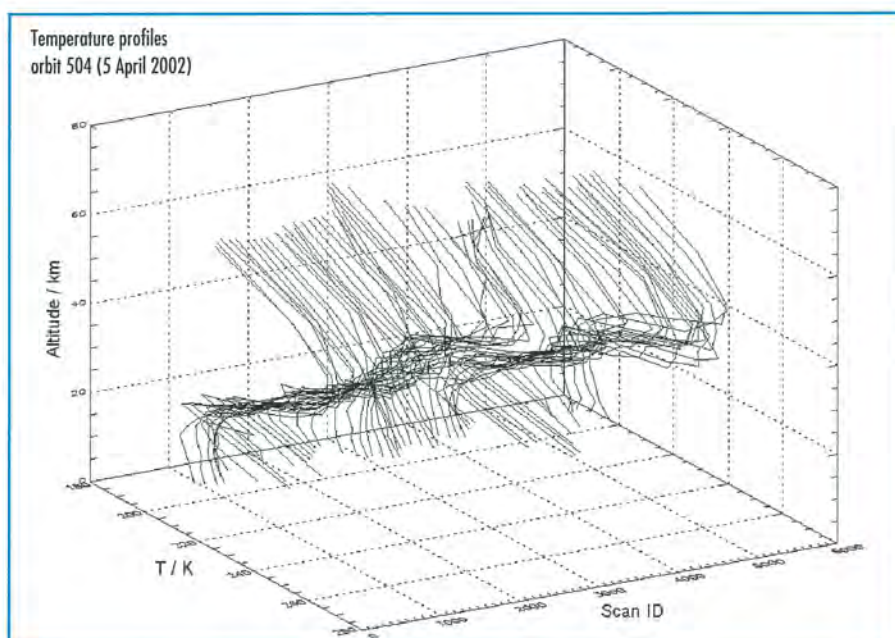
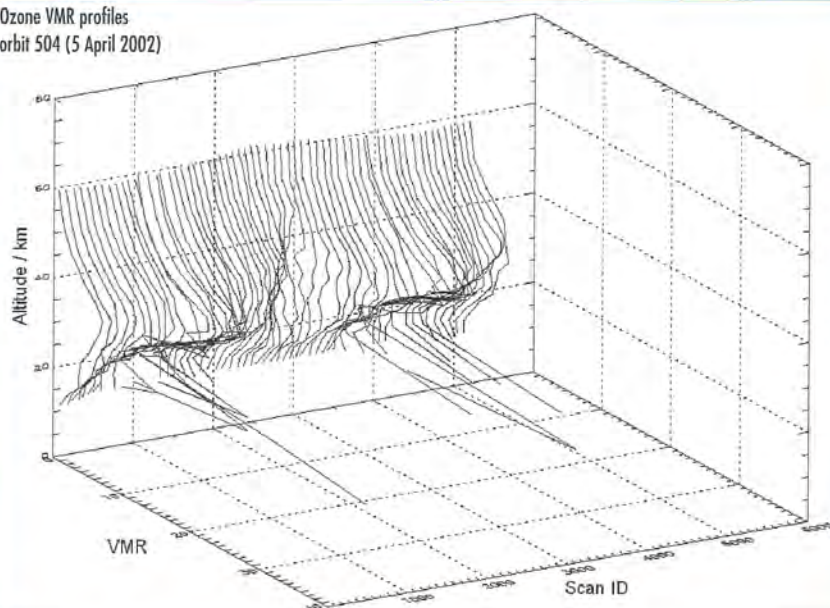


Figure 12. First ozone volume mixing ratio retrieval with statistical error from measurements in orbit number 504, 5 April 2002.

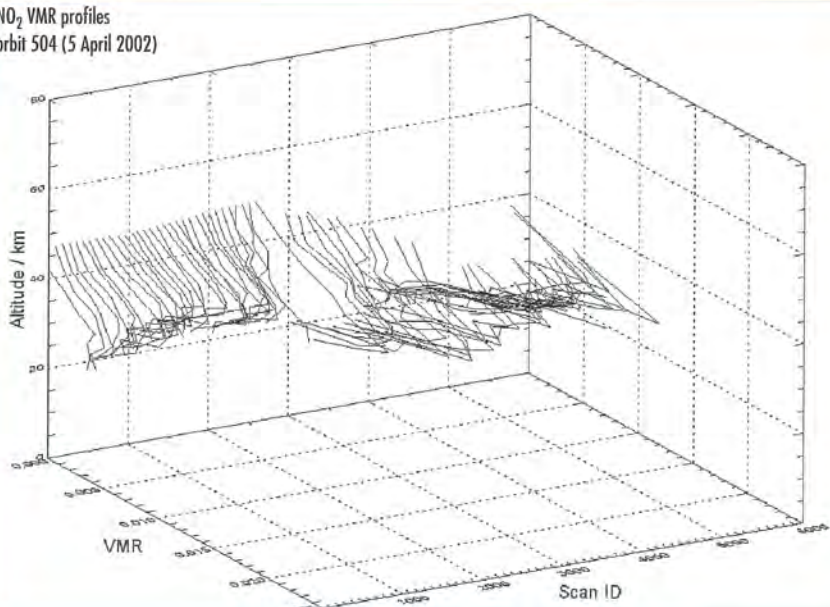
Figure 13. MIPAS retrieved temperature profiles, orbit number 504.



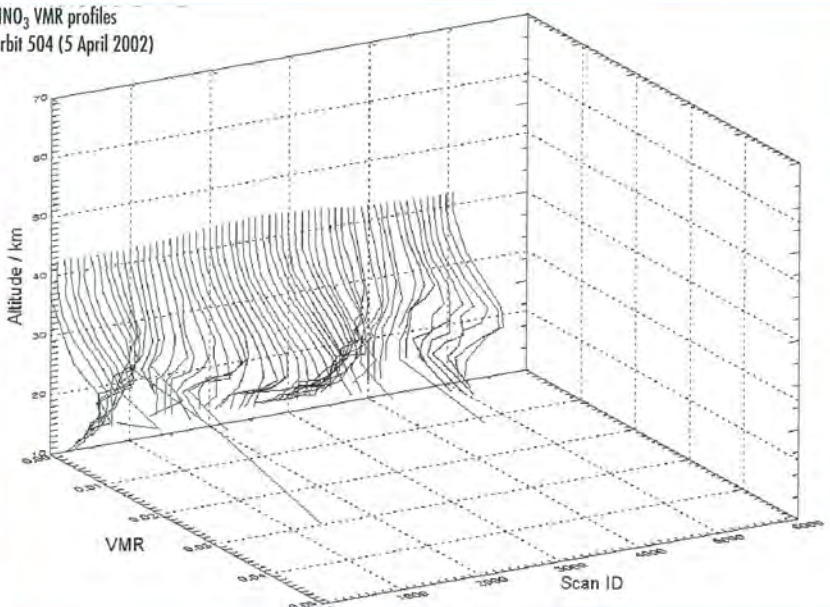
Ozone VMR profiles
orbit 504 (5 April 2002)



NO₂ VMR profiles
orbit 504 (5 April 2002)



HNO₃ VMR profiles
orbit 504 (5 April 2002)



◀ Figure 14. MIPAS retrieved ozone VMR profiles, orbit 504.

▼ Figure 15. MIPAS NO₂ VMR profile retrievals showing diurnal cycle, orbit 504.

▼ Figure 16. MIPAS HNO₃ VMR profile retrieval showing latitudinal variation in HNO₃ concentration. Orbit 504.

lamps. After a first decontamination of the optics, for which the instrument optical bench is heated up in order to release water vapour and other contaminants, this phase ended with opening the azimuth mirror cover mechanism. Functional tests have continued and first atmospheric and solar measurements have been taken in limb and occultation mode, respectively. At that stage the infrared channels could not be interpreted as they were not yet cooled to operating temperature. After the radiant cooler has been activated, the instrument was cooled down to achieve its nominal operation temperature, followed by characterisation measurements. In parallel with the first in-flight test, calibration data (dark current, spectral calibration and etalon correction) have been analysed and their systematic and operational derivation has been started. This phase has been completed on 20 June 2002 with the opening of the last cover protecting the nadir port.

The status as of end of June is that all covers are released and the instrument is fully functional. The instrument temperature (optical bench) and detector temperatures are nominal. All mechanisms are working. The wavelength calibration has been executed with expected results (shift smaller than 1 pixel). Radiance response and leakage current are as expected.

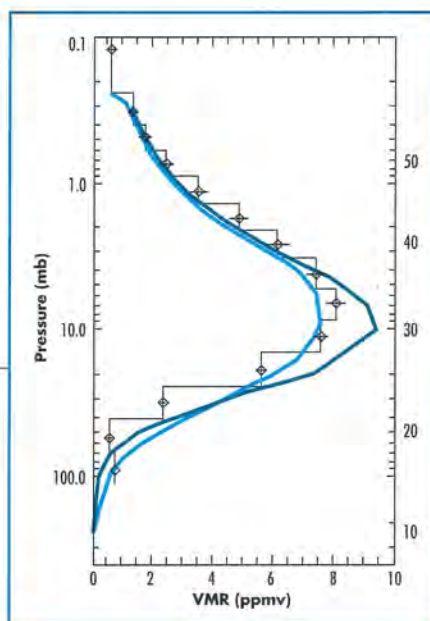
Due to the much longer and more complicated commissioning procedure of SCIAMACHY compared to MIPAS and GOMOS, geophysical data and spectra are more sparsely available.

Figure 17 (p. II) shows the preliminarily calibrated solar reference spectrum acquired during orbit number 814. A first comparison of ozone profile retrieval with GOME measurements is shown in Figure 18.

Outlook

The first results of GOMOS, MIPAS and SCIAMACHY are very encouraging. The Commissioning Phase is currently going on and will be concluded in

Figure 18. A retrieved ozone profile (black line) from SCIAMACHY limb scan measurements processed with the DLR limb prototype processor. The dark blue line shows the initial guess used for the retrieval. The blue line shows an ozone profile retrieval from a collocated GOME (ERS-2) measurement (processed with the NGONG algorithm). The observations have been taken over the Sahara desert (Envisat orbit number 913, 3 May 2002) with preliminary SCIAMACHY calibration and 30 minutes time difference to the GOME observation.



September 2002. The initial Envisat validation will be completed by December.

Further information can be found at <http://www.esa.int/> and <http://envisat.esa.int/>

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- Information on the internet: <http://www.esa.int/> and <http://envisat.esa.int/>

The Odin Aeronomy Mission - an Update

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Introduction

The Odin satellite was launched on 20 Feb 2001 into a sun-synchronous 18:00 hour ascending node near polar orbit. Odin is a Swedish-led mission in co-operation with Canada, Finland and France using sub-mm spectroscopy for astronomical and atmospheric studies [Murtagh *et al.*, 2002]. This is the first time sub-mm frequencies have been used from space for such studies. Earlier instruments such as the MLS instrument on the Upper Atmosphere Research Satellite [Waters *et al.*, 1996] and the MAS instrument on the Space Shuttle operated at mm-wave frequencies which limits their sensitivity and height resolution for a

given antenna size. In addition to the Sub-mm Radiometer (SMR), an Optical Spectrometer and Infrared Imaging System (OSIRIS) is included in the payload to complement and enhance the atmospheric studies. OSIRIS is one of the first limb viewing spectrometers operating in scattered light. Earlier instruments were carried on Solar Mesosphere Explorer [Mount *et al.*, 1986] and the space shuttle [Flitner *et al.*, 2000].

The satellite

Odin has been designed and built by the Swedish Space Corporation (SSC) as the main contractor to the Swedish National Space Board (SNSB).

Platform components have been provided by several of the nations involved. At 240 kg Odin is a small satellite and demonstrates a number of new technological applications including an advanced antenna design based on carbon composites, low power digital auto-correlator spectrometers, an advance 3-axis attitude control system that can point the entire satellite with an accuracy of <10 seconds of arc. The attitude control system is used both for pointing at specific objects in astronomy mode but also to scan the fields of view of the instruments through the earth's limb. The satellite has no consumables and has full redundancy for all spacecraft systems.

Short description of the instruments

SMR

The sub-mm radiometer consists of 4 tunable sub-mm receivers and 1 mm-wave receiver fixed at 118.7 GHz, three spectrometers and a calibration subsystem. The Schottky mixers are operated at 100 K to reduce noise. A Sterling cycle mechanical cooler provides the cooling. Each sub-mm channel is tunable over 17 GHz but the instantaneous bandwidth is only 1.2 GHz due to the low intermediate frequency of 3.9 GHz. One of the spectrometers is based on acousto-optical techniques with a frequency coverage of 1 GHz and about 1 MHz resolution, the other two spectrometers are hybrid autocorrelators specially designed for Odin and consisting of eight correlator chips configurable to provide a number of frequency coverage and resolution combinations. For atmospheric measurements they are normally operated in the 800 MHz mode with 1 MHz resolution. One major advantage of the autocorrelator spectrometers is the possibility to configure each block anywhere within the 1.2 GHz instantaneous band pass of the receivers allowing us to target lines that are near the two extremes of the band pass. Telemetry and power considerations only allow us to operate two spectrometers at any given time so several different operating configurations of the receivers have been designed to address the scientific goals.

OSIRIS

The OSIRIS instrument consists of 2 parts: The spectrometer covering 280–800 nm with 1 nm resolution using an aspherical grating, a path bending prism and order sorting filter to create an image of the earth's limb on a 1353 × 286 element CCD. The field of view of the spectrograph subtends a region 30 km along the limb by 1 km in altitude. Since the OSIRIS instrument requires sunlight, measurements are made only over half of the orbit. Because of the local time of the orbit, OSIRIS makes measurements predominantly in the Southern Hemisphere during the period late September to late February and in the Northern Hemisphere for the remaining part of the year. The infrared imager part of OSIRIS is actually three separate co-aligned single lens imagers operating at 1263 nm, 1273 nm and 1530 nm. The spectral regions are selected using interference filters and the imaging is achieved with 1-dimensional InGaAs (128 pixel) linear arrays that are thermoelectrically cooled. Various adapta-

tions of the limb DOAS technique are used to derive species profiles from the optical spectrograph while tomographic methods are used to provide the volume emission profiles of the 1.27 μm emission that may then be related to the distribution of ozone in the sunlit mesosphere following the techniques developed for rocket flights (Evans and Llewellyn, 1972) and the SME spectrometers.

Measurement strategy

As Odin has a joint astronomy and atmospheric mission, the observation time has been equally divided between the disciplines. To ensure both continuous coverage and provide for campaign-oriented observational periods, the atmosphere is observed every third day with an additional day in each third cycle. Further periods of 1–2 weeks of uninterrupted atmospheric operations can be scheduled in accordance with geophysical conditions. Such periods are available during the boreal and austral springs and in the northern hemispheric summer period. One day of observations (15 orbits) provides global coverage in the sense that all longitudinal ranges have been sampled. Measurements are normally made in the plane of the orbit covering the latitude range 82°S to 82°N.

As mentioned above, the SMR is highly flexible, however a limited number of modes are used in normal operations. On the regular observation days it is operated in the so-called basic stratospheric mode with target gases ozone, chlorine monoxide, nitric acid and nitrous oxide, while the OSIRIS spectrometer measures ozone, nitrogen dioxide, bromine oxide. On the additional days or in campaign mode, the SMR is retuned to make various measurements of water and its isotopomers, odd nitrogen and odd hydrogen species and carbon monoxide.

Data retrieval

Retrieval algorithms have been developed for both instruments and in most cases employ an optimal estimation approach. For the SMR, the algorithms have been jointly developed by the groups at Chalmers, the Dept of Meteorology, Stockholm University and the Observatoire de Bordeaux [Eriksson *et al.*, 2002; Baron *et al.*, 2002; Merino *et al.*, 2002]. At least two independent models have been used allowing quality assurance of the algorithm implementations. For the OSIRIS spectrometer mea-

surements the relative novelty of the measurements has inspired a range of modelling and data analysis techniques [McDade *et al.*, 2002; Strong *et al.*, 2002; McLinden *et al.*, 2002; Haley and McDade, 2002; Griffioen and Okarienen, 2002]. Von Savigny *et al.* [2002] at York University in Toronto have employed a modified version of the algorithm used by Flittner *et al.* [2000] to retrieve ozone profiles. DOAS techniques have also been used to retrieve ozone and NO₂ both in Canada (Sioris *et al.*, 2002) and in Sweden. At the Finish Meteorological Institute a modified onion peel global fit approach is being developed.

History and early results

After launch the early operations phase proceeded well and instrument turn on was nominal. Initial problems were encountered with the mechanical cooler but have been solved by running it at a higher power than originally intended and careful management of its thermal environment. In addition, the harmonic oscillator in one of the sub-mm channels failed soon after turn on, which initially seemed to be going to prohibit any measurements in the 575 GHz band, which includes the CO line, but experience has shown that the receiver is sufficiently stable to allow measurements if account is taken of the slow frequency drifts around the orbit. The first atmospheric limb scans were made in May 2001 and the first validation balloons were flown by CNES in June from the Gap launch site (France). Following a period of astronomy commissioning in July, problems were encountered in returning to limb scanning mode in August. While limb scanning was re-established the spacecraft would lose pointing quite often and the problem grew gradually worse until it was impossible to maintain limb scanning mode for a complete orbit during late September and October 2001. The problem was finally traced to a software error and corrected at the end of October with a great improvement in the pointing precision that now more than fulfilled the design requirements.

All of these early problems have complicated and delayed the processing of the data but this is now coming under control. To illustrate the type of data that Odin has been gathering, some examples are given here both of single orbits of data and complete days.

Figure 1 (p. II) shows the retrieved ClO for a single orbit in Jan 2002. The spacecraft moves northward from the equator to the maximum latitude of 82°N and then back southward to 82°S and back to

the equator. The variation of the solar zenith angle at the observation point is also shown. The main ClO peak at around 45 km is clearly seen, as is the expected dependence on local solar illumination conditions. Figure 2 (p. II) shows the zonal mean N₂O distribution, combining 15 orbits of data, on 6 Nov 2001. The descent into the remaining Antarctic polar vortex is clear, as are the equatorial bulge and the edges of the tropical pipe.

The OSIRIS instrument provides high quality ozone retrievals using both the modified Flittner method and DOAS. Figure 3 (p. III) shows the first observations of the ozone hole by OSIRIS derived using the Flittner method on 10 October 2001 despite major problems with the satellite pointing system. Figure 4 (p. III) shows another example on 11 Nov 2001, this time using a DOAS retrieval and after the satellite pointing problem had been corrected. In both cases the typical lowering of the altitude of the ozone peak with latitude is seen together with the accumulation of ozone outside the vortex edge. The strong depletion of the layer within the vortex is also clear.

Work is ongoing to validate the products both internally as shown in Figure 5 for ozone and externally using the data from the validation balloon, ozone sondes and the POAM instrument. Comparisons with models are also under way as illustrated in Figure 6 (p. IV), which shows a ClO data from Odin and output from the REPROBUS model sampled at the same local time and locations as the measurements.

Conclusions

After some initial problem the Odin satellite and its two instruments are working well and providing data of the excellent quality that we expected. Data processing is now underway and the products are being subject to validation both internally between the both instrument where possible and against external measurements. We are aiming to have a public product available in time for the coming winters' VINTERSOL programme organised under the auspices of the EC.

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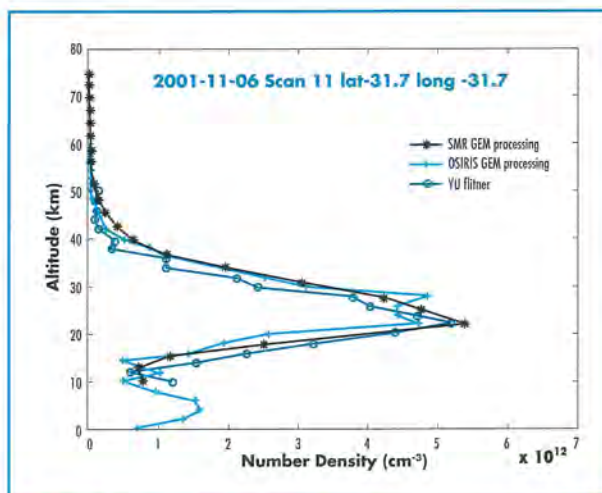


Figure 5. Comparison of Ozone profiles measured by SMR and the OSIRIS instrument. The SMR result is from the ozone line near 501 GHz and the two OSIRIS curves have been derived using two different algorithms: line with circles uses the modified Flittner method (York Univ) and the line with crosses uses the DOAS method and a single scattering forward model (Chalmers). Error analysis is not yet complete so no error bars are shown.

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Arctic Polar Stratospheric Clouds Observed with the ILAS Sensor: Inference of their Composition and Possible Relation to Denitrification

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Polar stratospheric clouds (PSCs) are recognised as a key factor in ozone destruction over the polar regions as a result of heterogeneous reactions occurring on their surface, which convert inactive reservoir chlorine into active chlorine. Recent stratospheric data show a trend in decreasing temperature [WMO, 1998] and it is of current scientific interest to detect any trend in the frequency of PSCs. PSCs are also closely related to denitrification (irreversible removal of nitric compounds that inactivate chlorine radicals). Waibel *et al.* [1999] showed that conditions in the Arctic are at the threshold for denitrification. A temperature decrease of one-degree would enhance PSC formation, which might cause significant denitrification and therefore prolonged ozone loss over the Arctic.

Our research group in the Nara Women's University has been analysing various kinds of satellite data focusing on chemical mechanisms related to aerosols/PSCs in the stratosphere. Most of our recent work is concerned with the Improved Limb Atmospheric Spectrometer (ILAS) onboard the Advanced Earth Observing Satellite (ADEOS). ILAS was designed to observe the profiles of minor stratospheric species, such as ozone, nitric acid, and water vapour, and that of the stratospheric aerosol extinction coefficient (780 nm) at 1-km height intervals [e.g., Sasano *et al.*, 1999; Yokota *et al.*, 2002]. ILAS observed 14 circumpolar points in each hemisphere every day at high latitudes (57.1–72.7N and 64.3–88.2S) from November 1996 until the end of June 1997.

Arctic PSCs observed with ILAS in winter/early spring of 1997

ILAS captured more than 60 PSC profiles in the Northern Hemisphere during the winter and early spring of 1997. Hayashida *et al.*, [2000a] showed the highest probability of

sighting PSCs in mid-January at an altitude of approximately 23 km, with subsequent occurrences of PSCs observed intermittently at lower altitudes until mid-March. The 1997 Arctic winter was characterised by the prolonged appearance of PSCs until mid-March, associated with a long-lasting polar vortex. As the ILAS PSC measurements were the only spaceborne measurements made on a regular basis (about 14 times daily) during that period, our study provided an additional data set for the long-term PSC data archive to examine the long-term trend in PSC frequency. Besides, simultaneous measurements of nitric acid and PSCs by ILAS made it possible to infer the composition of PSCs and their effects on denitrification.

PSC composition inferred from satellite data

The ILAS extinction and nitric acid data were compared with theoretically predicted values assuming the existence of Supercooled Ternary Solution (STS) and nitric-acid-containing solid particles (NAD or NAT) [Saitoh *et al.*, 2002]. As the amounts of nitric acid and water vapour in the atmosphere are closely concerned with PSC composition, it is important to estimate those amounts properly in inferring PSC composition. The details of our scheme to determine the values of ambient nitric acid and water vapour that should be in thermodynamic equilibrium with a specific type of PSCs such as STS, NAT, and NAD, are described in Hayashida *et al.* [2000b] and in Saitoh *et al.* [2002].

Our analysis indicated that both the extinction coefficient and nitric acid level for some of the PSC events observed in mid- and late-January 1997 over the Arctic agreed with the theoretical values for STS better than with those of NAT or NAD. **Figure 1** shows scatter-plots of UKMO temperature vs. the ILAS extinction coefficient (a1, a2), and UKMO temperature vs.

the ILAS nitric acid value (b1,b2), at 20 km (a1, b1) and 21 km (a2, b2) in mid-January. Solid circles represent the data identified as PSCs. The theoretical curves for STS (blue lines), NAD (black line), and NAT (dark blue line) are shown in the figure. In **Figure 1**, STS formation curves are indicated with the thick solid blue lines with the proper conversion factors (mass-to-extinction ratio) depending on temperatures: STS droplets are expected to form at cold temperatures, while the background conversion factor should be used at warm temperatures. In the figure, the blue circles indicate events whose extinction and nitric acid values are closest to theoretical STS values among the three types. It is found that the enhancement of the volume corresponds to the decrease in the ambient nitric acid, suggesting the uptake of nitric acid into particles as STS forms.

Figure 2 (p. 15) shows the vertical profiles of the extinction coefficient (solid line with a notation 'E'), nitric acid (solid line with a notation 'N'), and the collocated UKMO temperature (upper scale: 'T') on these two days. The 10-day averaged background profile of nitric acid for mid-January is also shown in the figure (dashed line). The black circles indicate the data that correspond to the STS formation curve. Comparison of the ILAS nitric acid profile with the background profile illustrates that nitric acid decreased significantly in the region where STS-PSCs were observed.

However, some gaseous nitric acid data corresponding to PSC events indicated less decrease in gaseous nitric acid than predicted for STS, which leaves an uncertainty in identifying PSC type. On the other hand, Pan *et al.* [2001] reported a corresponding decrease in water vapour up to ~2.5 ppmv in late-January and discussed the possibility of ice cloud formation. They argued that freezing of water would be a much faster process than forming nitric acid containing

particles, which could lead to dehydration before denitrification, or in some cases, without substantial denitrification. It would be possible that the STS particle growth was limited in dehydrated air to explain the synchronous decrease in nitric acid and water vapour with less amount of nitric acid decrease than predicted in STS formation. Although the mixture of STS and ice in a large sampling volume of ILAS would be another possible interpretation, those studies brought up a question in PSC formation process at any rate.

According to our analysis for the late PSC season in the same year, many of the characteristic PSC events were categorised as the nitric-acid-containing solid PSC events [Saitoh *et al.*, 2002]. Those PSC events experienced temperatures below NAT saturation temperature for more than several days. They had not passed over typical mountainous area before their measurements, so the formation mechanisms of these solid particles should be explained from their

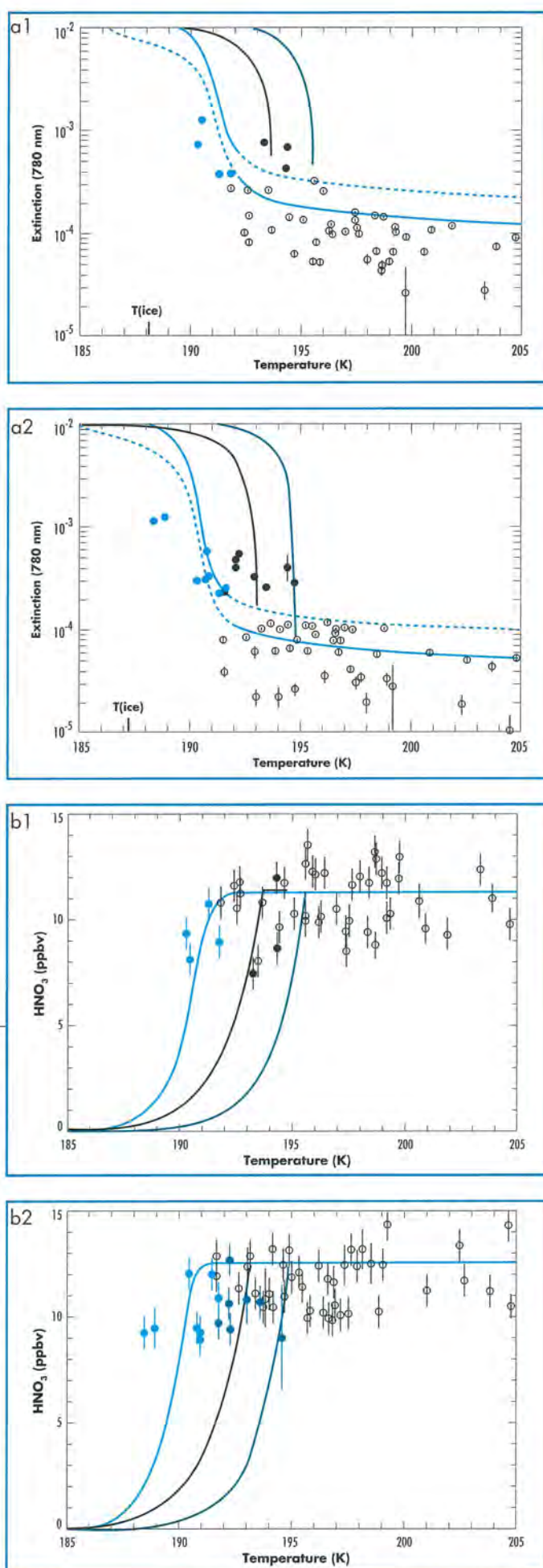


Figure 1. Scatter-plots of UKMO temperature vs. the ILAS extinction coefficient (a1, a2) and UKMO temperature vs. the ILAS nitric acid (b1, b2) at 20-km (a1, b1) and 21-km (a2, b2) in mid-January. Solid circles represent the data identified as PSCs, blue ones are more likely to be STS considering the extinction coefficient and nitric acid concentration. The theoretical curves for STS (blue lines), NAT (black line), and NAT (dark blue line) are shown in the figure. Error bars on ILAS data are from data set of version 5.20. Details on the errors are described in Yokota *et al.*, [2002].

synoptic scale temperature histories, without considering lee waves. They maintained relatively high nitric acid hydrate saturation ratios along their trajectory, which suggests their homogeneous freezing [Tabazadeh *et al.*, 2001]. In our analysis, some of the PSC events indicated low concentration of nitric acid and less volume than predicted from temperature. Kondo *et al.* [2000] and Irie *et al.* [2001] derived clear denitrification in February 1997 from ILAS nitric acid data. It seems that the shortage of nitric acid limited particle growth, even if the temperature did fall low enough to generate PSCs in February.

Recently, S. Oshchepkov (NIES) examined IR channel aerosol extinction data of ILAS in aerosol type analyses using a spectral fitting approach [Oshchepkov *et al.*, 2002]. We are now continuing collaboration on this issue with Oshchepkov and the NIES group. Combined use of our approach with infrared spectral analysis will shed light on unknown microphysical processes of PSCs.

Effects of denitrification on ozone destruction - a new approach with assimilated chemical model

Finally, the effect of PSCs and denitrification on ozone loss was examined by means of our newly developed scheme named Chemical Species Mapping on Trajectories (CSMT) [Kagawa and Hayashida, 2002]. The CSMT is a method to construct synoptic maps of chemical species by combining "trajectory mapping" [Morris *et al.*, 1995, 2000] with a photochemical box model. Minor constituents are time-integrated in a photochemical box model along trajectories that start from satellite measurement points until a target time. In this study, we calcu-

lated a 7-day forward trajectory for each observed data. The initial values of ozone, HNO_3 , and N_2O at the initial trajectory points were taken from ILAS version 5.20 data. All other initial data were taken from the climatological data derived in a similar way to Becker *et al.*, [2000]. Many long and short-lived species in the stratosphere were successfully mapped by the CSMT. Figure 3(a) (p. IV) and 3(b) (p. V) are the examples among those maps for ozone and nitric acid on February 20, 1997 on 475-K isentropic surface. Though ILAS measurements are geographically limited, the CSMT scheme can be used to expand the area of data coverage, which furthers the potential of data usage.

The ozone loss rate was determined by the CSMT scheme. Figure 4 (p. V) shows the time evolution of ozone loss rate on 475-K isentropic surface with the level of gaseous nitric acid (the latter is shown as color codes). Although sedimentation process was not involved in this calculation, denitrification was implicitly included as initial values of gaseous nitric acid that were observed with ILAS. As reported by Kondo *et al.*, [2000] and Irie *et al.*, [2001], significant denitrification was observed after late-February. As shown in Figure 4, the values of ozone loss rates in late-February are distributed in two clusters, with high and low ozone loss rates. The high ozone loss rate was due to low deactivation of chlorine and the low ozone loss was due to less PSC formation. Although the analysis is still preliminary, it suggests that denitrification has a significant impact on ozone loss and recovery as expected. Our analysis shown here is based on the observed nitric acid data that are almost equivalent to NO_y , and therefore the partitioning of NO_x/NO_y would be more realistic than the result from a mechanistic chemical-transport-model.

Acknowledgements

I wish to thank all of my graduate students, especially Dr. A. Kagawa and Ms. N. Saitoh. I also thank the members of the ILAS science team and their associates.

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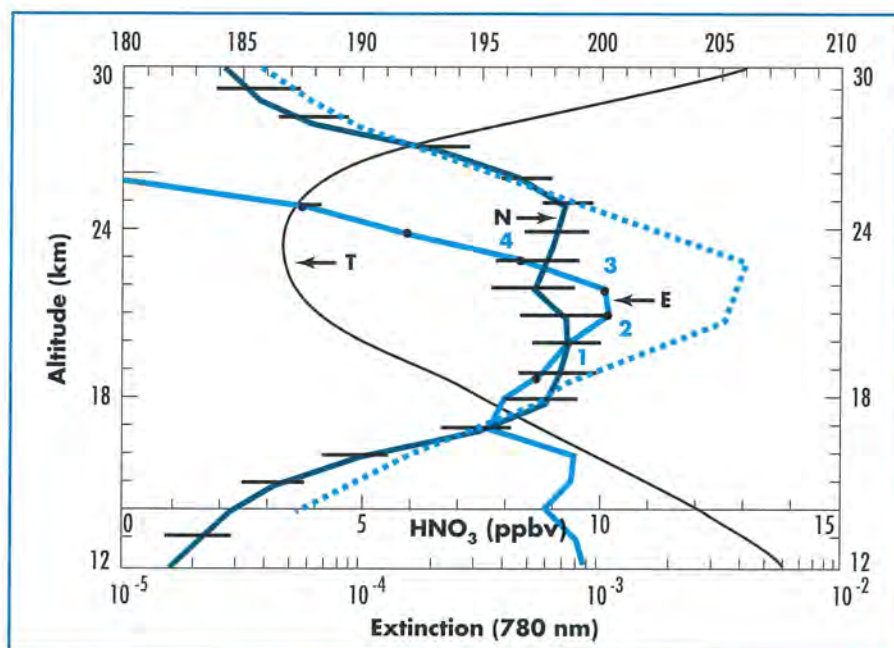


Figure 2. The vertical profiles of the extinction coefficient (E), nitric acid (N), and collocated UKMO temperature (T) observed on January 19 (65.8 N, 21.6 E). The 10-day averaged background profile of nitric acid for mid-January is also shown in the figure (dashed line). The black circles indicate the data that categorised as STS.

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Workshop on Laboratory Studies of Upper Troposphere/Lower Stratosphere Processes

Breckenridge, Colorado, USA, 22-27 July 2001

A.R. Ravishankara, NOAA, Boulder, USA (ravi@al.noaa.gov)

Organizing Committee:

R. A. Cox, Cambridge, UK, IGAC representative

M. J. Kurylo, NASA/NIST, Washington, DC, USA, NASA and SPARC representative

A. R. Ravishankara, NOAA, Boulder, CO, USA, SPARC representative

K. A. Wolfe, CSC, Boulder, CO, USA

The upper troposphere/lower stratosphere (UT/LS) region of the Earth's atmosphere is unique in many ways and has been the focus of a large number of research activities in recent years. This interest stems from a desire to understand the observed trends in ozone column abundances (as well as the vertical distributions of these trends), polar stratospheric ozone depletion, the oxidation mechanisms that impact the delivery of short-lived tropospheric compounds to the stratosphere, the oxidative capacity of the troposphere, and the possible impacts of aviation on UT and LS.

There have been a large number of field measurements that have unearthed interesting compositional information that suggests the need for additional data on gas-phase reactions, photochemical processes, and heterogeneous/multiphase reactions that occur within the UT/LS. From a chemist's point of view, this region (Figure 1 p. VI) is a challenge because of the low temperatures accompanied by significant pressures, the presence of condensed matter, and highly variable levels of ozone and water vapour. The laboratory research community in kinetics and photochemistry met in October 1996 in Strasbourg (France) to take stock of current progress in our understanding of heterogeneous and multiphase reactions (see SPARC Newsletter N°9, 1997, pp. 6-15). However, the state of gas-phase kinetics and photochemistry had not been assessed for a long time. Therefore, a workshop was held during 22-27 July 2001 in Breckenridge (Colorado) to assess the state of gas-phase and photolytic parameters relevant to the above issues.

SPARC, IGAC, NASA, NOAA, EC, NERC UT/LS, and EC-IPO sponsored this workshop, which brought together a few key atmospheric modellers and field measurement scientists with researchers from the laboratory com-

munity. The specific areas that were covered were:

- Photolytic processes,
- Pressure-dependent reactions and equilibrium processes,
- Low-temperature oxidation of volatile organic compounds,
- Halogen chemistry in the UT/LS,
- Short-lived trace gases and their impact on the UT/LS,
- Nitrogen oxides in the UT/LS region,
- Experimental methods in laboratory studies.

The topic of short-lived compounds and their impact on UT/LS was included because it is a major topic of the 2002 WMO/UNEP Scientific Assessment of Ozone Depletion and it was thought important to air out the chemistry issues involved in this topic as input for the assessment activities.

The workshop programme consisted of scene-setting talks, followed by extensive discussions. There were two opportunities to present posters, which were displayed throughout the workshop period. All attendees were encouraged to bring a few view graphs of their results to aid a comprehensive discussion, and most attendees took advantage of this opportunity.

The following summaries highlight the discussions and findings of this workshop in the seven areas listed above and are based on the rapporteurs' reports. These reports were done in collaboration with the speakers and the session chairs.

Photolytic processes in the UT/LS

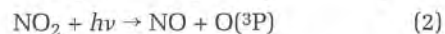
The scene setting talks in this session were given by R. Salawitch (NASA/JPL) and P. Wine (Georgia Institute of Technology). The session chair was P. Wennberg (California Institute of Technology) and the rapporteur was P. Monks (University of Leicester).

Photodissociation of atmospheric molecules by solar radiation plays a fundamental role in atmospheric chemistry. The photodissociation of trace species such as ozone and formaldehyde contributes to their removal from the atmosphere, but probably the most important role played by these photolytic processes is the generation of highly reactive atoms and radicals from stable molecules. Photodissociation of trace species and the subsequent reaction of the photoproducts with other molecules are the prime initiator and driver for the bulk of tropospheric chemistry.

The first order rate coefficient for the photolytic destruction of a molecule is given by the expression,

$$j = \int_{\lambda_{\min}}^{\lambda_{\max}} \sigma(\lambda, T) \phi(\lambda, T) F_{\lambda}(\lambda) d\lambda \quad (1)$$

where σ is the absorption cross-section (cm^2), ϕ is the quantum yield for the destruction of the molecule, F is the wavelength dependent solar flux density ($\text{photons cm}^{-2} \text{s}^{-1}$), and T is the temperature. If we are interested in a specific process, the quantum yield will be for that specific outcome following the absorption of light by the molecule under consideration. For example, in the photolysis of NO_2



the rate of removal of NO_2 is given by

$$\frac{d[\text{NO}_2]}{dt} = j_2[\text{NO}_2] \quad (3)$$

where the photolysis frequency, j_2 , is the first order rate coefficient for the removal of NO_2 and ϕ is the quantum yield for the dissociation of NO_2 .

The solution of equation (1) under both the physical and chemical conditions encountered throughout the UT/LS lies at the heart of understanding photolytic processes and their role in the chemistry of these regions. The photolysis rate or j value can be either

measured in the atmosphere or computed using parameters measurable in the laboratory (σ , ϕ) and the actinic flux, which is computed from either extraterrestrial flux or observations. In either case, high quality laboratory measurements are required to evaluate the factors in equation (1) to design and validate measurements of j values.

The current state of our information on the actinic flux was discussed and some recommendation for future work was made. They included the following research activities:

- a - The evaluation of the O_3 cross section as a function of T ,
- b - The resolution of the differences in the absolute values of $\sigma(O_2)$ in the Herzberg continuum,
- c - Recommendation of a top-of-the-atmosphere flux, which takes into account both seasonal and solar cycle effects for use in modelling studies,
- d - Atmospheric transmission measurements in the O_2 Schumann-Runge absorption region to test model parameterisations of this spectral region,
- e - Atmospheric measurements of $O(^3P)$ as a critical check on ozone photolysis rates.

Following the discussions on the actinic flux, the available laboratory data were reviewed and the following issues of high priority for UT/LS were noted:

- a - Extension of the absorption cross section measurements to longer wavelengths,
- b - Extension of the absorption cross section measurements to typical UT/LS temperatures,
- c - Extension of quantum yields to wavelength regimes (and temperature/pressure as appropriate) where atmospheric photodissociation actually occurs in the UT/LS,
- d - Assessment of the low energy (electronic) transitions,
- e - Assessment of the missing transitions,
- f - Assessment of the metastable states,
- g - Assessment of the weak absorbers,
- h - Assessment of the overtone transitions,
- i - Assessment of the H_2O complexes.

These suggestions were followed by discussions of the experimental factors involved in such research as well as issues such as parameterisation of the cross sections, extrapolation and interpolation of laboratory data, and the limitations and needs of such undertakings. It was further noted that a number of criteria must be considered when evaluating the atmospheric

importance of a given photolysis frequency. These include composition with respect to lifetime (production vs. loss routes), the role of the photoproducts, the influence of clouds and aerosols, the sensitivity of the action spectrum to changing values of σ and ϕ , and the variation of the action spectrum and atmospheric sensitivity with respect to changing solar zenith angle.

Pressure-Dependent Reactions

The scene setting talks in this session were given by J. Troe (University of Gottingen), D.M. Golden (SRI International and Stanford University), and H. Hippler (University of Karlsruhe). The session chair was J. Troe (University of Gottingen) and the rapporteur was J. Barker (University of Michigan).

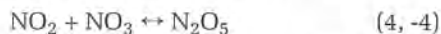
This was a very lively session with a great deal of debate. The discussions clearly showed the emerging approaches to addressing this important, but complex, area of kinetics.

Chemical species from the planetary boundary layer, the middle troposphere, and the middle stratosphere are found near the tropopause and thereby influence the composition of the UT/LS. Conditions there are such that a wide variety of pressure-dependent reactions may be important. This is both because of the large number of organic species important in the troposphere and because of the low pressures and temperatures that occur near the tropopause. In this session, pressure-dependent reactions were categorised into several classes. Some experimental and theoretical tools used for determining the rate constants needed for accurate atmospheric models were subsequently described. The protocols currently in use for analysing and tabulating conventional fall-off data for recombination and decomposition reactions were discussed. Finally, a summary of future needs for determining, evaluating, and tabulating pressure-dependent reactions important in the UT/LS were listed.

Reactions are pressure-dependent when the rate of collisional energy transfer is competitive with the rate of a chemical process that depends on internal energy. Even "inert" gases like argon (Ar) and nitrogen (N_2) participate in energy transfer. Since the rate of energy transfer depends on the total pressure (including "inert" gases), the over-all reaction is pressure-dependent. The following classes of reactions were noted and discussed:

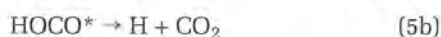
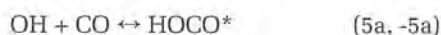
a - Recombination/Decomposition Reactions:

These reactions are important in all regions of the atmosphere. In recombination reactions, chemical energy is released and a highly vibrationally excited product is produced. If energy transfer is too slow, the excited product re-dissociates and there is no net reaction. If energy transfer is very fast, then the excited product is efficiently stabilised. The fall-off curve is a quantitative representation of the efficiency of stabilisation as a function of the total pressure. Decomposition reactions are the reverse of recombination reactions: a stable molecule is activated by collisions and the highly vibrationally excited molecule decomposes. The efficiency of the collisional activation is described by the fall-off curve. Fall-off curves for recombination and decomposition reactions for the same chemical system are connected by microscopic reversibility and thus are described by the same physics and can be represented using the same functional forms. Reactions of this type are currently included in the NASA/JPL and IUPAC data evaluations. An example of such a reaction is the recombination/decomposition reaction:



b - Chemical Activation Reactions: In this general class, a bimolecular reaction leads to a single, highly vibrationally excited intermediate that is capable of further decomposition, isomerisation, or collisional stabilisation (**Figure 2**). The product branching ratio depends on pressure because collisional stabilisation of the excited intermediate results in an increased yield of the stabilized intermediate at the expense of decomposition or isomerisation products. Reactions of this type are *not* currently included in the data evaluations in a systematic way.

An example of such a reaction, which is included empirically in data evaluations, is the extremely important reaction of OH with CO.



c - Chemical Excitation Reactions: This is a reaction sequence that has found renewed importance under atmospheric conditions. An example of such a sequence is the reaction between the RO_2 radical and NO, where a product (alkoxy radical) is left with a large amount of internal energy so that it can undergo other reactions (for example, decomposition).

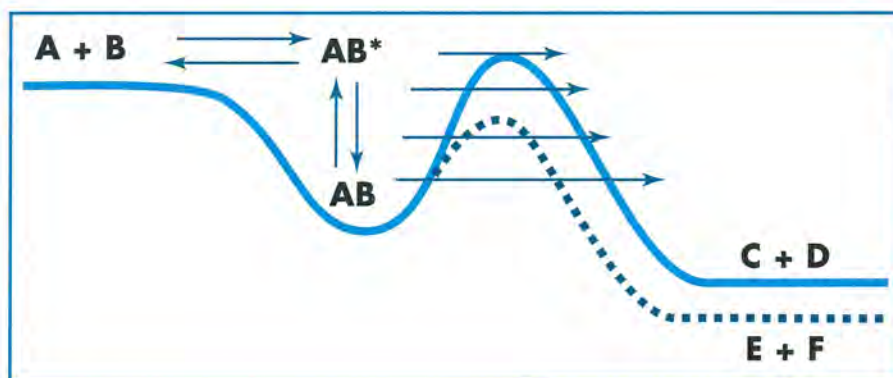
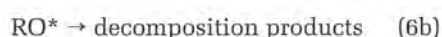
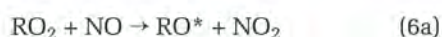
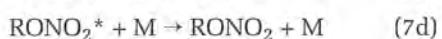
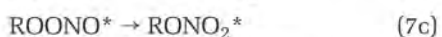
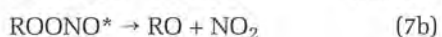


Figure 2. A reaction proceeding through the formation of an adduct. [Courtesy of A. R. Ravishankara].



d - Multi-Well, Multi-Channel Reactions: This class includes reactions in which vibrationally excited species are produced by chemical activation, thermal activation, photoactivation, or some other process, and then undergo competitive reactions via several pathways with rates that depend on the amount of excitation. Collisional deactivation slows the energy-dependent reaction rates and hence causes changes in branching ratios, etc. Reactions of this type are *not* currently included in the data evaluations. Free radical isomerisation/decomposition reactions fall into this category. In the atmosphere, alkoxy radicals can undergo decomposition and isomerisation reactions, which depend on vibrational energy, as well as bimolecular reaction with O_2 (it is not known whether this bimolecular reaction depends on vibrational energy). Another example involves nitrate formation in the reaction of alkyl peroxy radicals with NO.



Theory has played, and will continue to play, a major role in describing, deriving, and extrapolating association/dissociation reaction rate coefficients. In this endeavour, electronic structure calculations continue to be very useful for elucidating reaction mechanisms and identifying transition state structures. As computational capabilities have improved, the accuracy of calculated thermochemical quantities has approached that needed for chemical kinetics calculations for high temperature combustion systems. In contrast, the low temperatures

found in the UT/LS require thermochemical accuracy that can only be achieved for a few small molecular systems (and then, only with great difficulty). To make useful chemical kinetics predictions for the UT/LS, considerable progress will be necessary in developing computing resources and computational tools. Recent calculations on the reactions $\text{OH} + \text{HONO}_2$, $\text{ClO} + \text{OH}$, and $\text{RO}_2 + \text{NO}$ illustrate the usefulness of such electronic structure calculations. Several possible transition state structures for the reaction of $\text{OH} + \text{NO}_2$ have been identified by *ab initio* calculations, but some can be eliminated because their predicted isotope effects contradict experiments. Branching ratios for the $\text{ClO} + \text{OH}$ reaction have been calculated based on calculated transition state properties.

In addition to the *ab initio* calculations, theoretical treatment of reaction kinetics and dynamics is an important venue for better atmospheric data. The study of the dynamics of elementary reactions leads to improved theoretical rate constants. Variational Transition State Theory and the Statistical Adiabatic Channel Model were developed as a result of fundamental investigations on theoretical reaction dynamics. These theories provide an essential connection between macroscopic elementary rate constants and the fundamental dynamics on *ab initio* potential energy surfaces. The theories give good insight into the expected behaviour of observed elementary rate constants and hence they are valuable as background for evaluating experimental data.

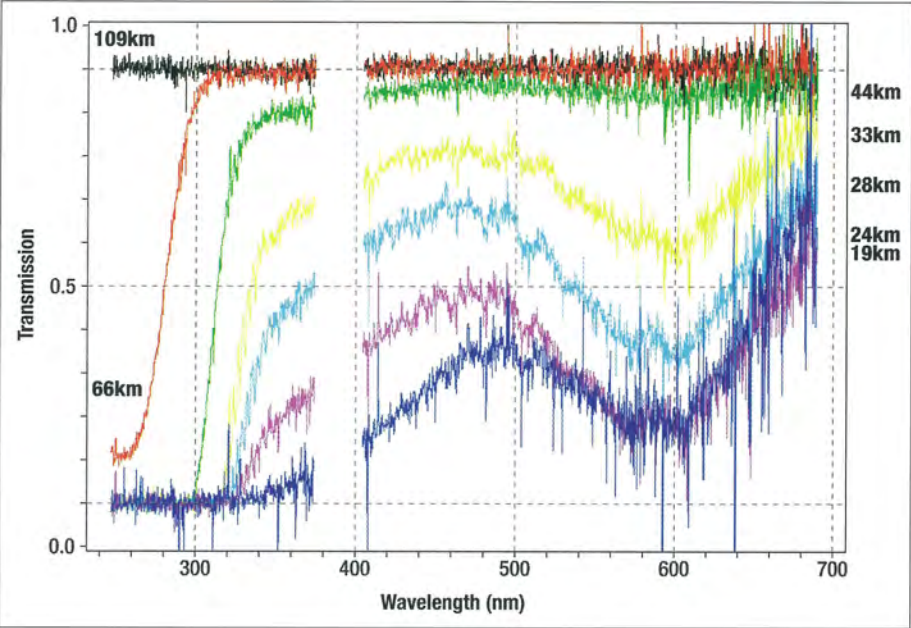
Master equations that describe the simultaneous interplay of energy-dependent collisional energy transfer and energy-dependent chemical reactions are necessary for the most accurate descriptions of pressure-dependent reactions. Master equations of varying complexity are needed for the various classes of energy-dependent reactions

listed above. The most complex pressure-dependent systems involve multiple potential energy wells and multiple reaction pathways. Although several methods have been developed for solving the resulting master equations, each method has strengths and weaknesses. Considerable work is needed to increase the speed and accuracy of the existing methods and to identify which methods are most suitable for certain classes of problems.

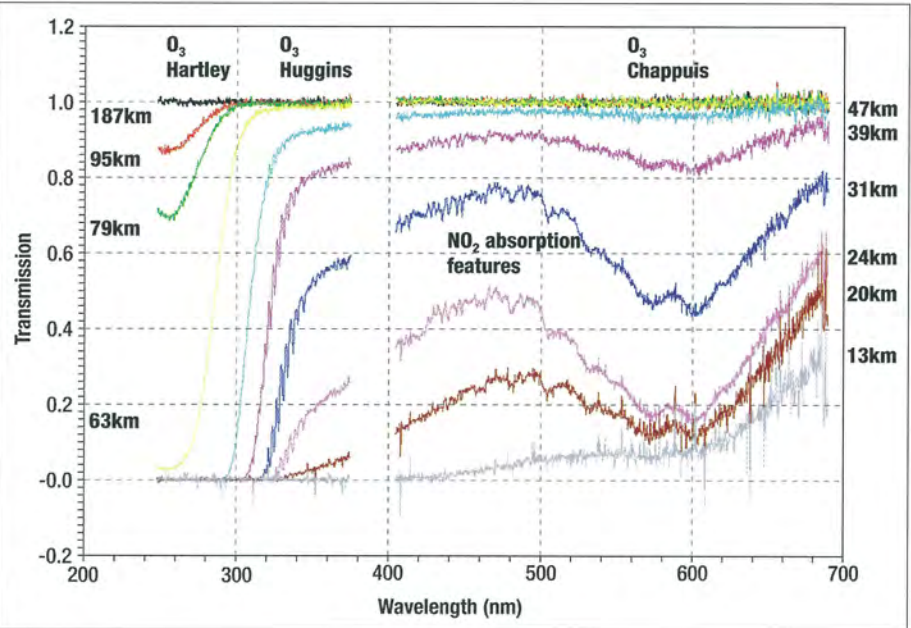
Semi-empirical formulations (for example of Troe, Oref, Frenklach, and others) exist for the purpose of analysing, evaluating, and summarising experimental fall-off data for single-channel, single-well unimolecular/recombination reactions. The formulation published by Troe is the most popular of these, although further evaluation is needed to determine whether it is the most accurate (Figure 3 p. VI). These formulations are far more practical for data analysis than master equation calculations, and they are of good general accuracy. The use of semi-empirical formulae by the NASA/JPL and IUPAC evaluation panels is discussed below.

Data evaluation is an essential component in atmospheric chemistry research. Multiple investigations of the same reaction are needed to establish reproducibility and to cover the wide ranges of temperature and pressure important in the atmosphere. Inevitably, the various data sets are of uneven quality and the experimental results must be spliced together in order to obtain complete understanding of a reactive system. Data evaluation panels' function by compiling data from different sources, analysing the similarities and differences, and making informed judgments of relative quality. The end result is a set of recommendations that must be communicated to all interested parties. In the atmospheric science community, the recommended rate constants are adopted by modellers for baseline comparisons, as well as by experimentalists. In this way, the atmospheric science community attacks problems more efficiently, using the best available current data. Data evaluation is the final essential step necessary for efficient utilisation of the resources spent on laboratory measurements. Currently, the evaluation panels summarise bimolecular reactions, recombination (and

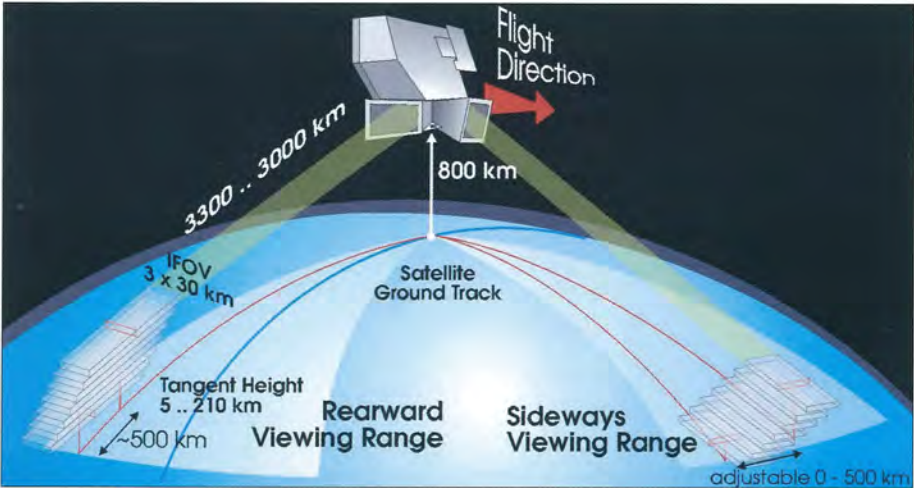
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◀ **Figure 2**
Atmospheric transmission spectra measured on 6 May 2002 by occultation of a weak and hot star (visual magnitude 2.41, temperature 28000 K). For clarity, only a subset of the measurements of this scan is shown with the tangent altitudes indicated.



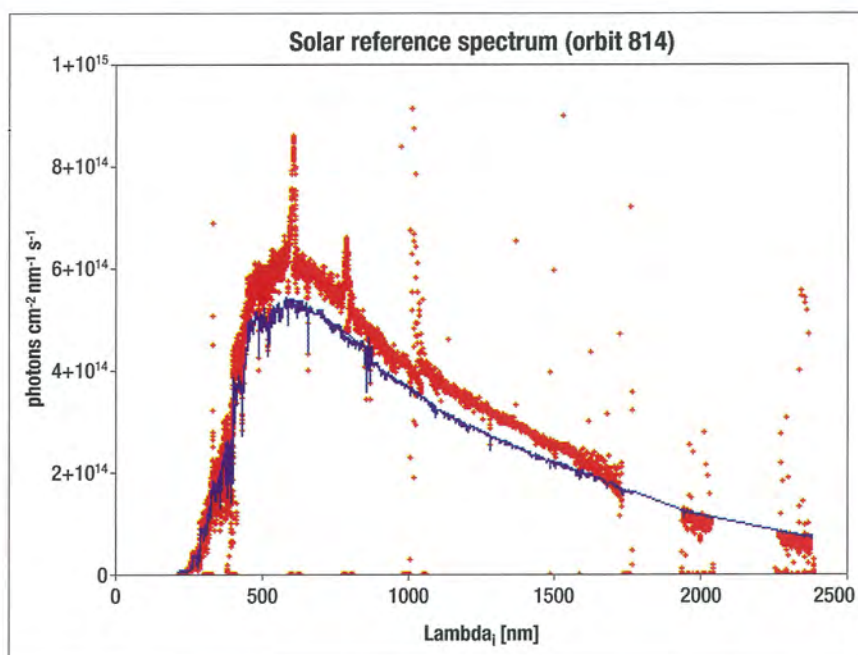
◀ **Figure 5**
Atmospheric transmittances in the UV and visible measured by GOMOS on 6 May 2002 with a bright (visual magnitude 0.61) and hot (28000 K) star. NO_2 absorption structures are clearly visible in this measurement. The measurement tangent altitudes are indicated.



◀ **Figure 8**
MIPAS viewing geometry.

► **Figure 17**

A preliminarily calibrated solar reference spectrum measured by SCIAMACHY (red curve) during orbit number 814. The outliers and sharp spectral features are expected to disappear as soon as masking of bad pixels and spectral calibration has been completed. The blue curve shows for comparison a solar spectrum from MODTRAN.

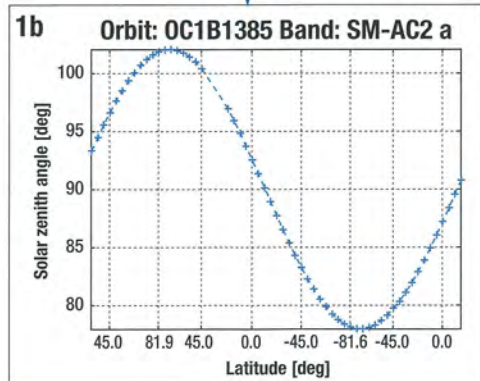
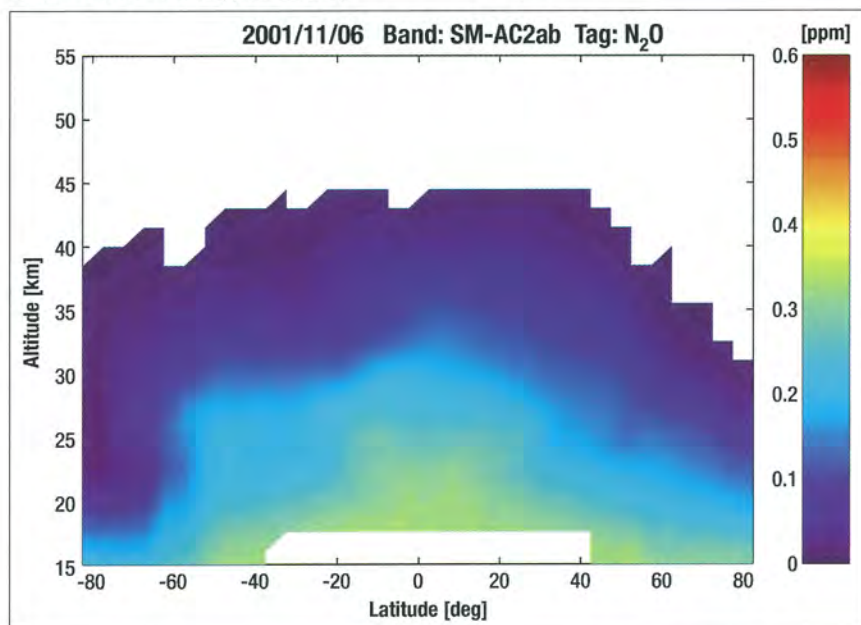
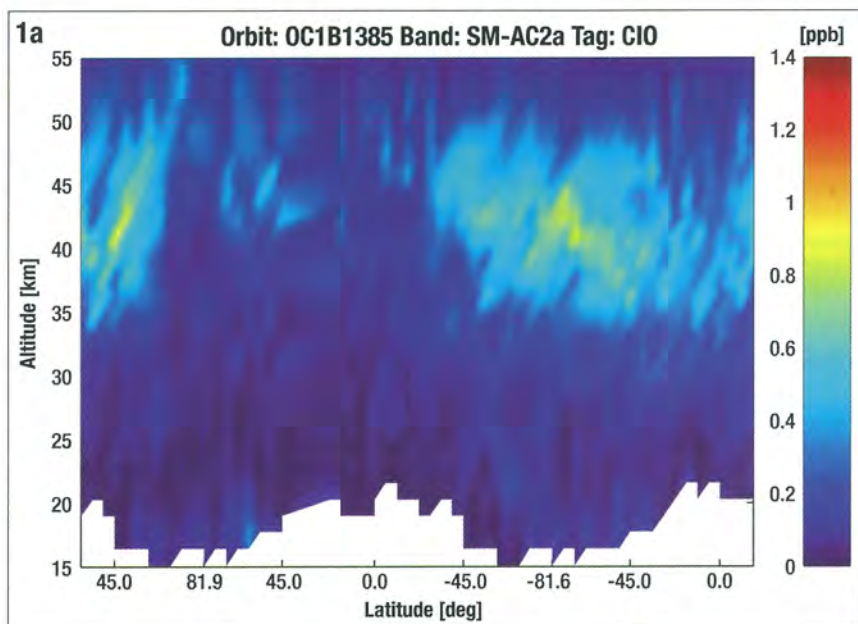


The Odin Aeronomy Mission - an Update

► **Figure 1**

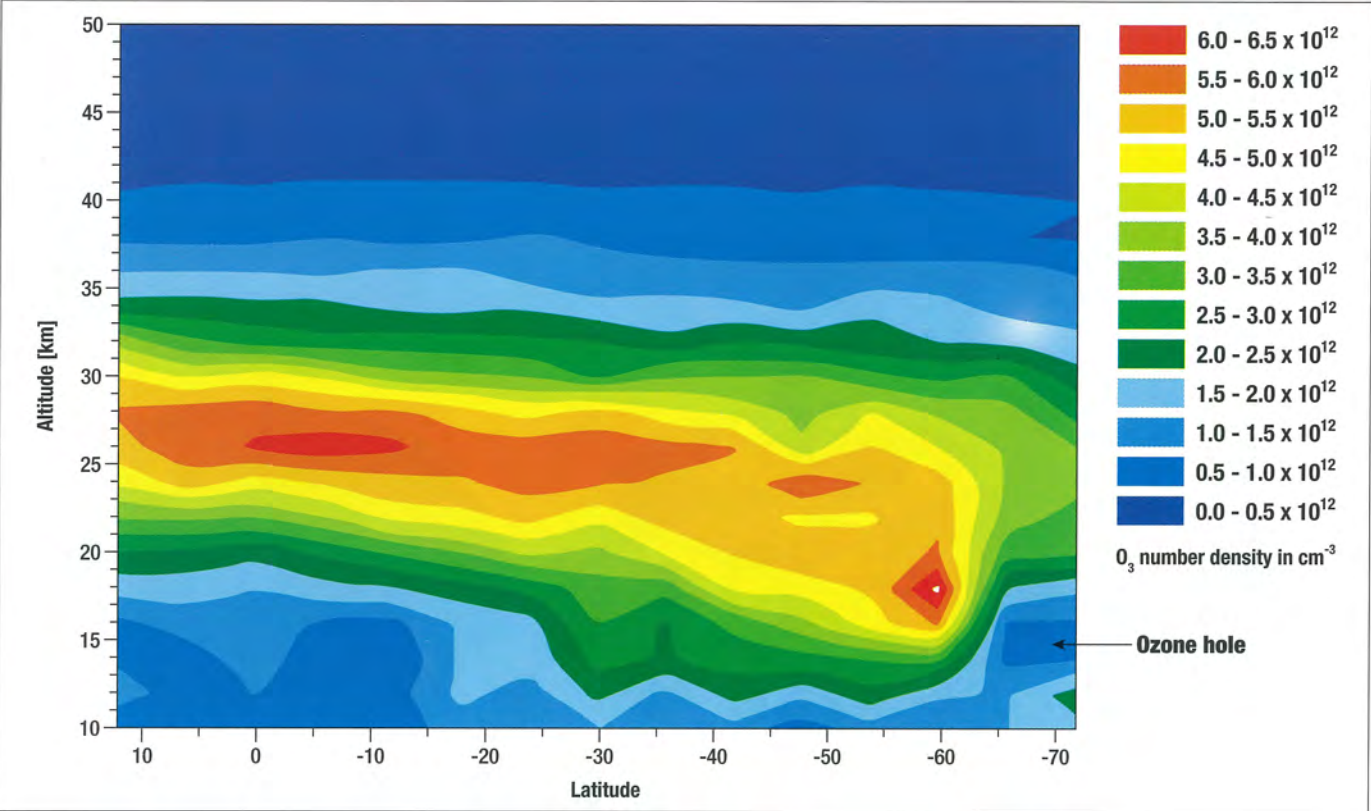
a - Chlorine monoxide measured by Odin-SMR along a single orbit in January 2002.

b - The solar zenith angle at the measurement position. Throughout the figures negative and positive latitudes correspond respectively to southern and northern hemisphere. [Courtesy C. Jiménez, Chalmers University, Sweden].

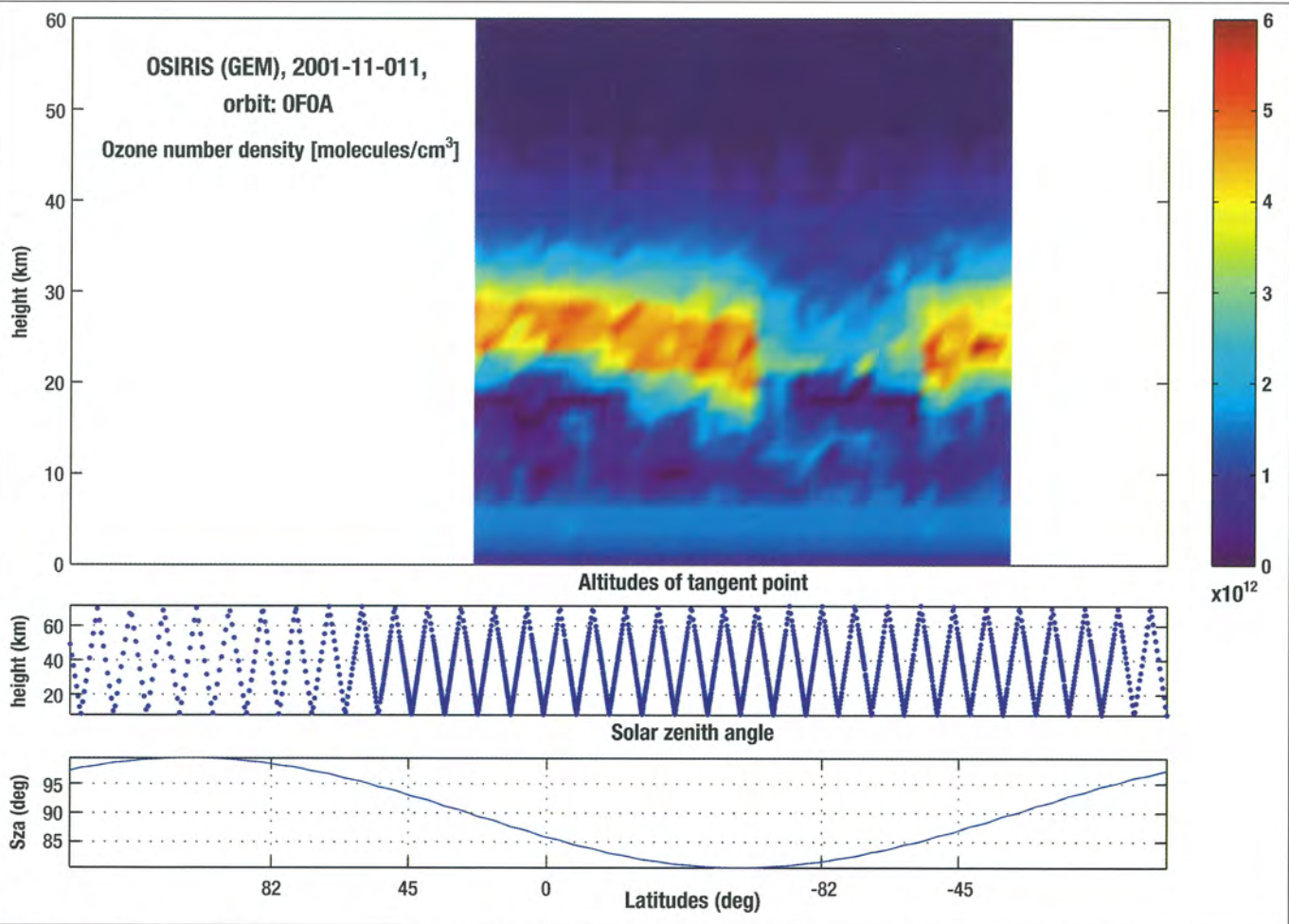


► **Figure 2**

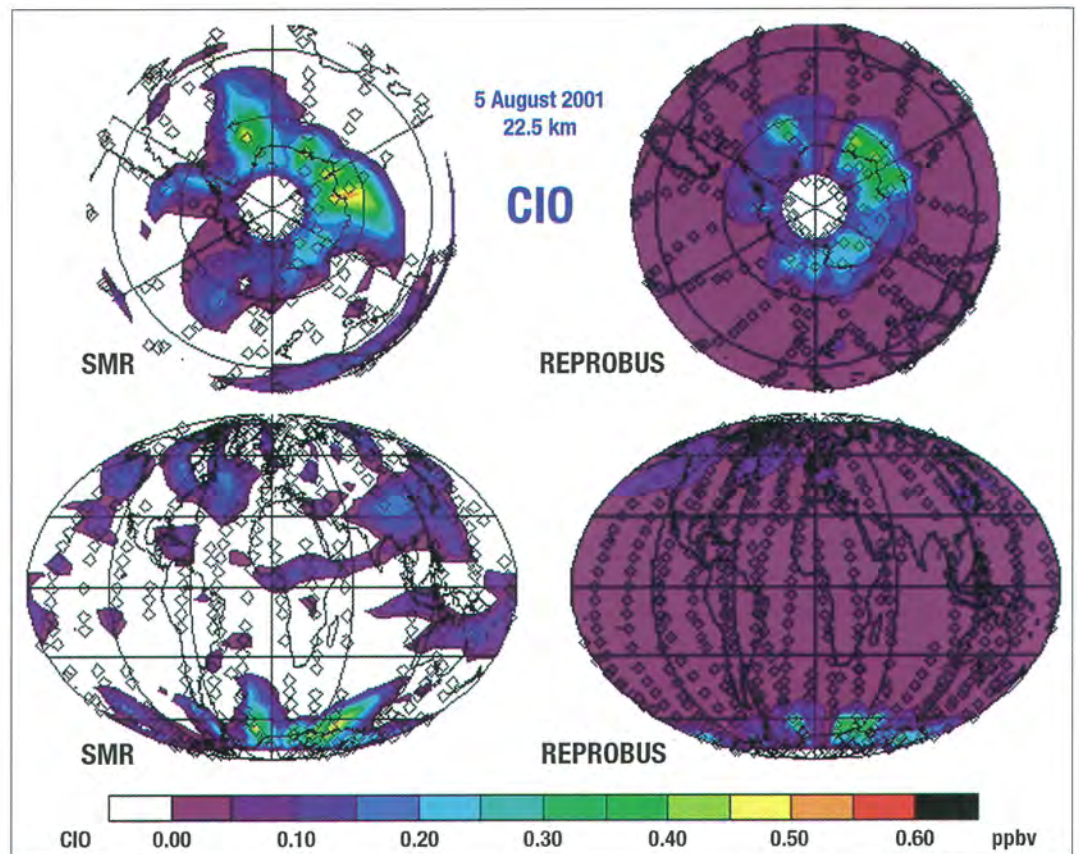
Zonal mean N_2O distribution on 6 Nov 2001 from 15 orbits of SMR measurements. [Courtesy C. Jiménez, Chalmers, Sweden].



▲ **Figure 3** - The first observation of the ozone hole by the OSIRIS instrument on Odin. Ozone profiles derived using a modified Flittner method. [Courtesy Ch. Von Savigny and C. Haley, York university, Canada].

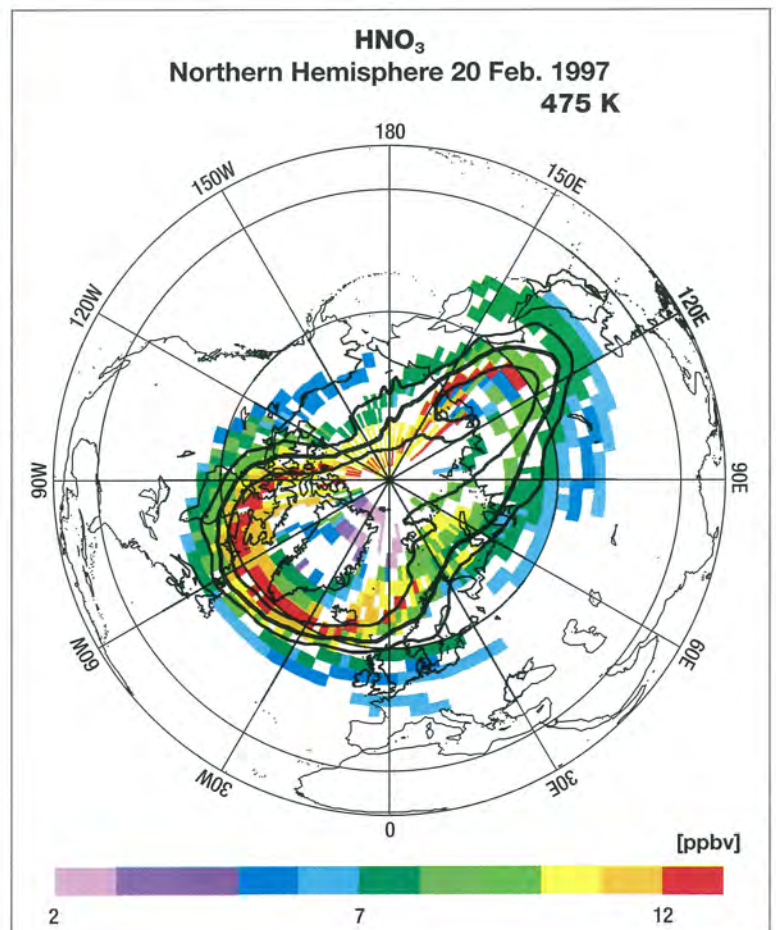


▲ **Figure 4** - Ozone hole seen in November 2001 by the OSIRIS instrument. Retrieval using the DOAS method combined with optimal estimation and a single scattering forward model.



▲ **Figure 6** - Comparison between the CIO measured by Odin and the Reprobus model sampled at the same local time and positions as the Odin measurements. Note that the measurements were made with a solar zenith angle > 90°. [Courtesy Ph. Ricaud, Obs. de Bordeaux and F. Lefèvre, CNRS, Paris].

Arctic Polar Stratospheric Clouds Observed with the ILAS Sensor: Inference of their Composition and Possible Relation to Denitrification



► **Figure 3a**
A CSMT-derived ozone map on the 475-K isentropic surface on February 20, 1997. Colors indicate ozone-mixing ratios.

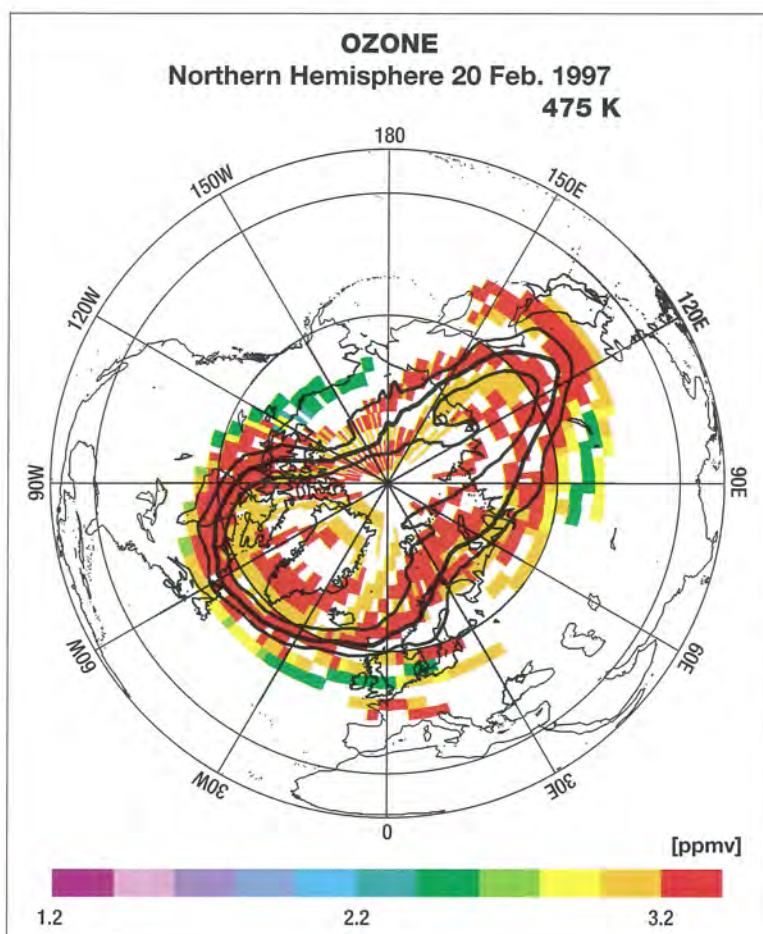
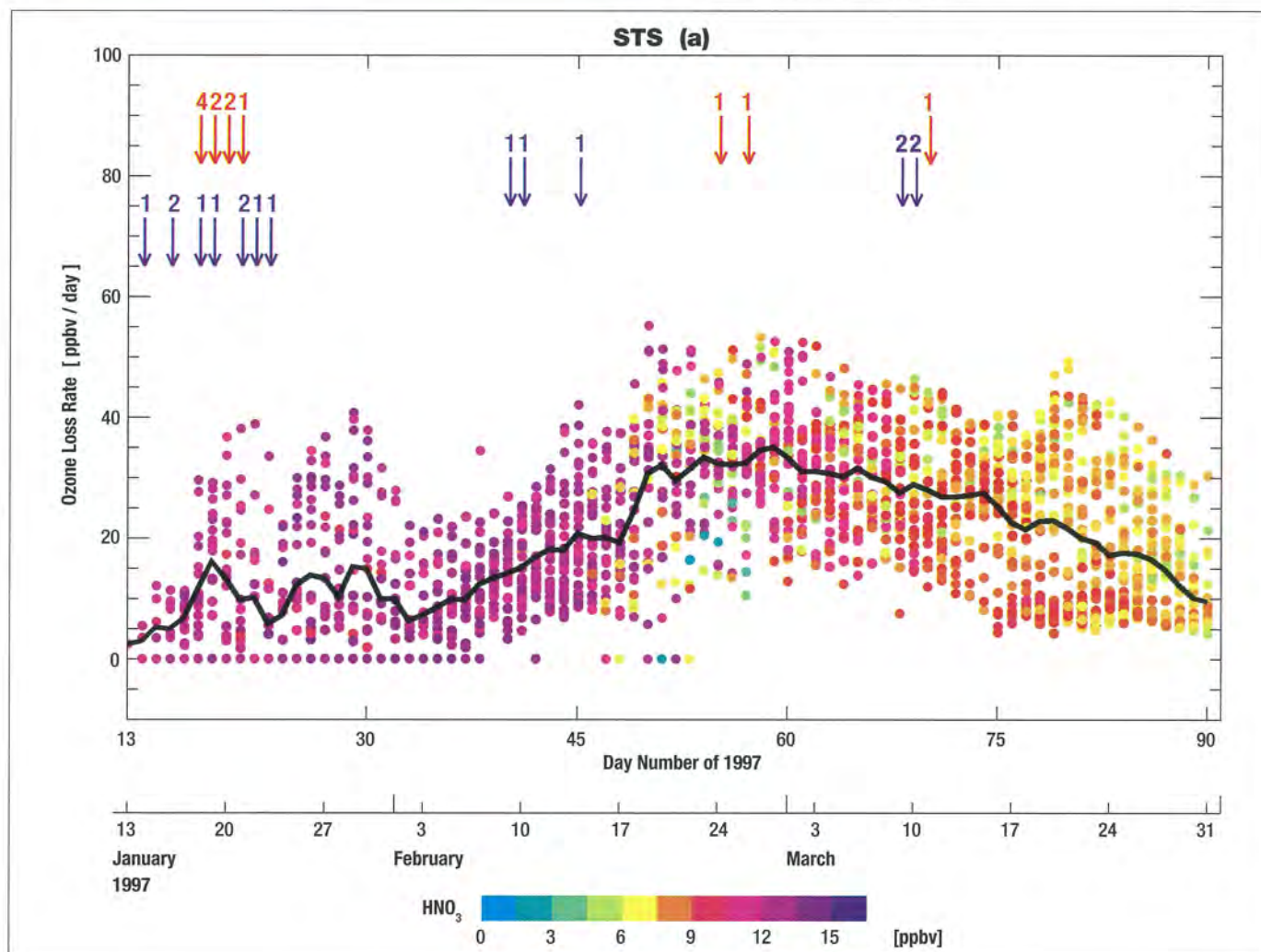


Figure 3b

Same as Figure 3(a) but for nitric acid.

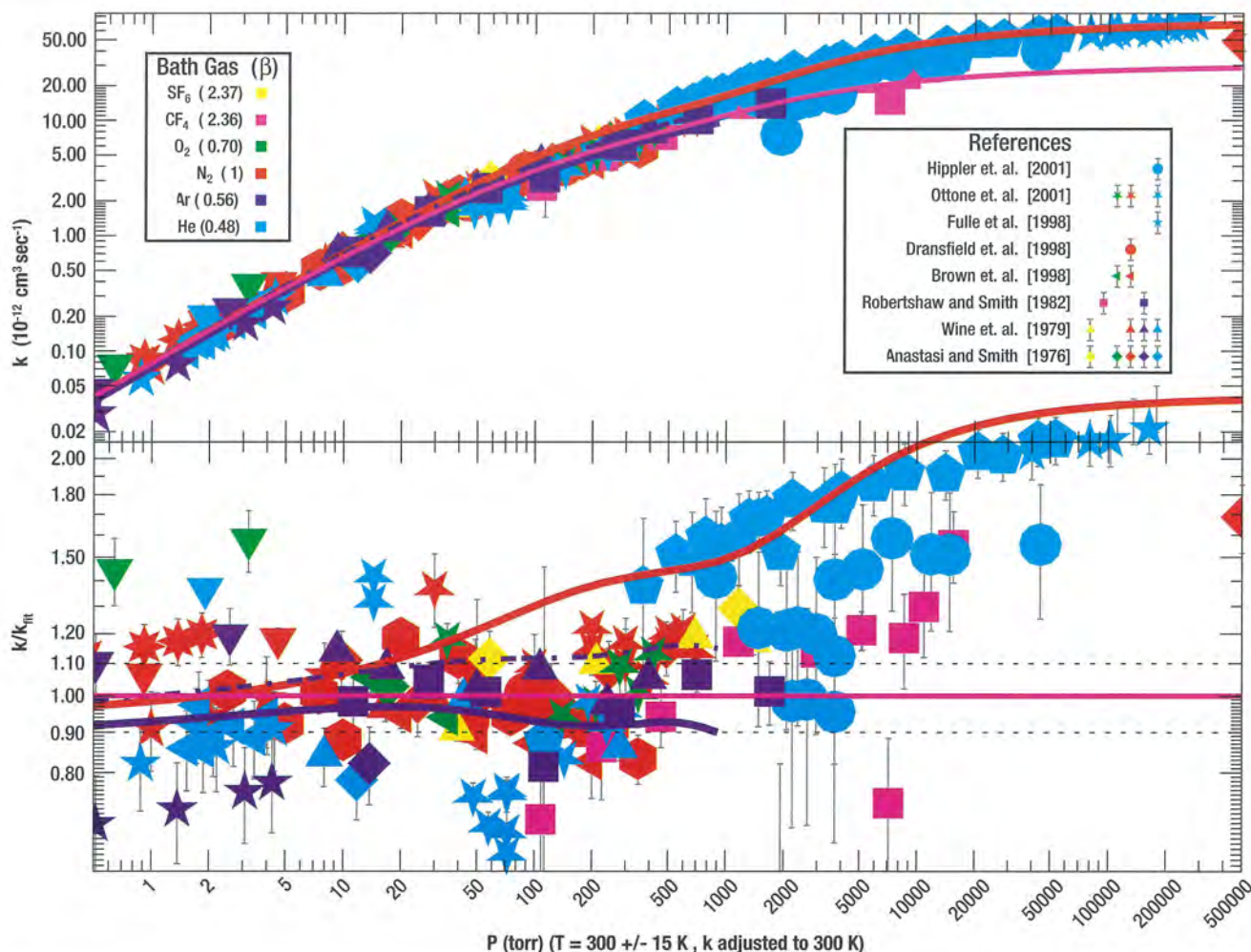
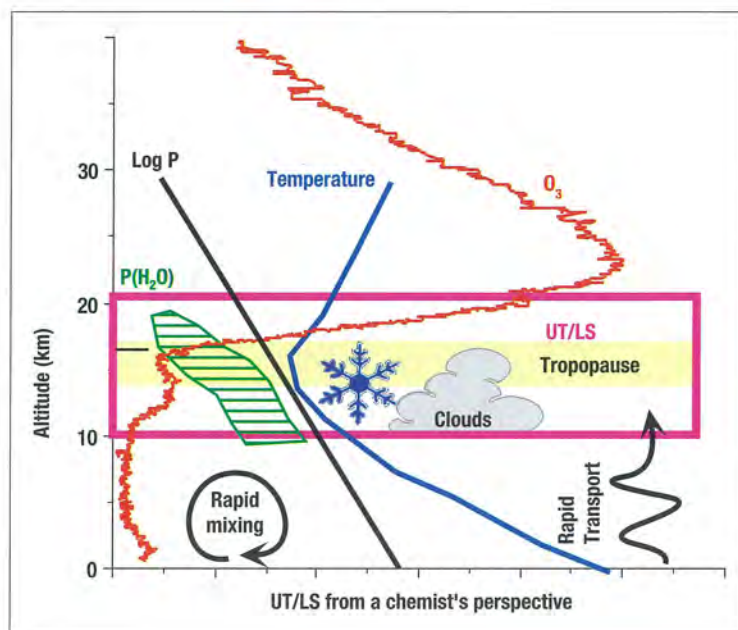
Figure 4

Calculated ozone loss rate in ppbv/day. Ozone decrease is taken to be positive. Each dot indicates the ozone loss rate calculated for the target day along different trajectories. Ozone loss was estimated from the difference between the first calculated output of the target day and the value 24 hours later. The color indicates the corresponding nitric acid level. The arrows shown in the figure are the PSC events categorised with Saitoh *et al.*, [2002]: red and blue arrows indicate STS and NAT with numbers of the events.



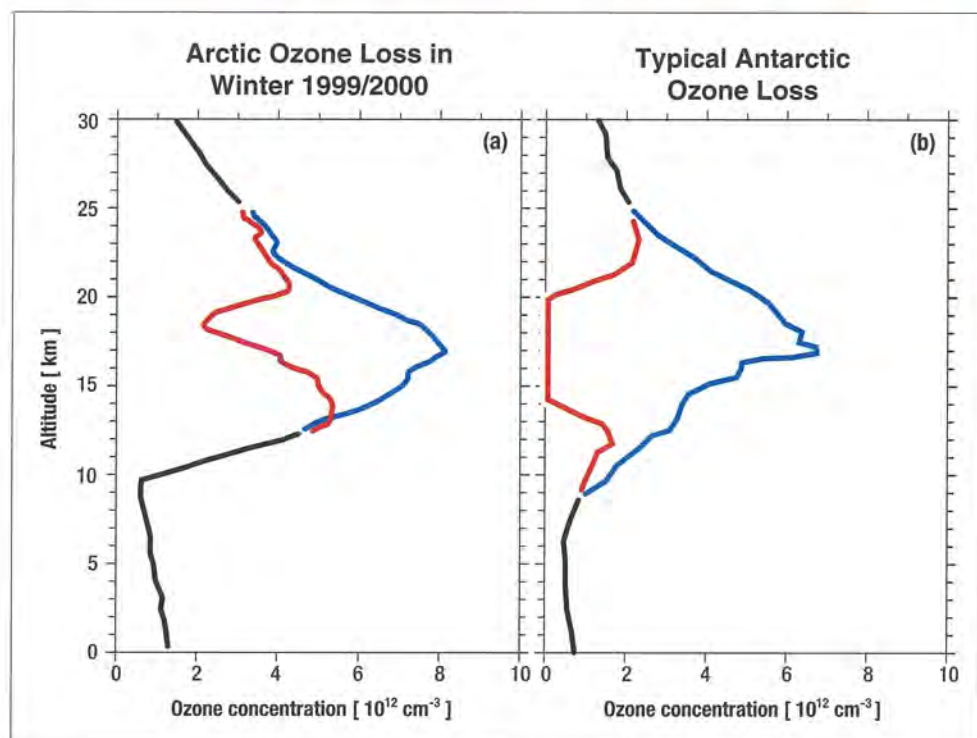
Workshop on Laboratory Studies of Upper Troposphere/Lower Stratosphere Processes Breckenridge, Colorado, USA, 22-27 July 2001

► **Figure 1**
Chemist's view of UT/LS. [Courtesy
A.R. Ravishankara].



▲ **Figure 3**
Fall-off curve for the reaction of OH with NO_2 . [Courtesy N. Donahue].

Report on the Arctic Ozone Loss Workshop Postdam, Germany, 4–6 March 2002



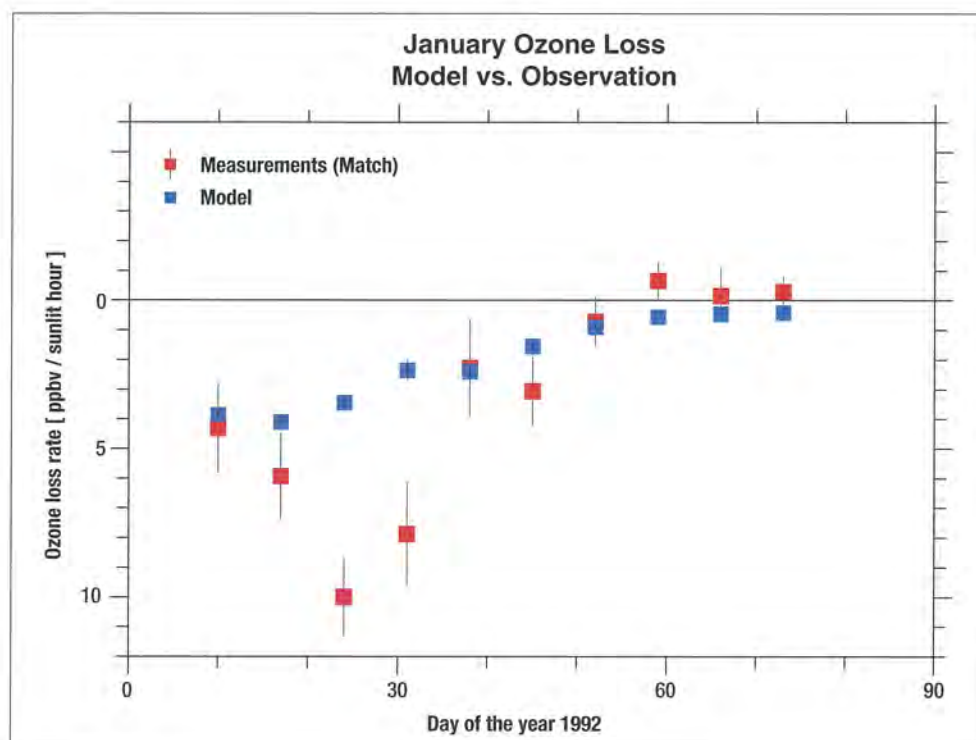
◀ **Figure 2**

Illustration of the degree of ozone loss in the Arctic winter 1999/2000, the coldest Arctic winter on record, compared with the typical ozone loss over Antarctica.

a - Concentration profile of O_3 during late winter from ozone-sonde observations between 20 and 30 March 2000 (red). The profile of O_3^* (blue), i. e. the abundance of O_3 expected in the absence of any chemical loss, is estimated by allowing the early winter vortex average O_3 mixing ratio profile from ozonesondes

to descend by amounts based on cooling rates from the SLIMCAT CTM. The difference between the profile of O_3^* and O_3 (hashed) is an estimate for the accumulated chemical loss of ozone during the winter, based on the vortex average approach. The black lines represent a typical late March ozone profile above and below the vertical region where significant ozone loss occurred. Adapted from Rex *et al.*, Chemical depletion of Arctic ozone in winter 1999/2000, *J. Geophys. Res.*, in press.

b - Illustration of the typical degree of ozone loss in the Antarctic. Typical mid-winter (15 July 1997, blue) and late winter (13 October 1997, red) ozone profiles measured inside the Antarctic polar vortex at the Neumayer station at 71°S . This panel is for illustration only and no attempt has been made to correct for transport effects, which are weaker in the Antarctic compared to the Arctic.



◀ **Figure 3**

Ozone loss rates from Match (red) compared with model calculations (blue) along the air mass trajectories used in the Match study [Becker *et al.*, Ozone loss rates in the Arctic stratosphere in the winter 1991/92: Model calculations compared with Match results, *J. Geophys. Res.*, 1998]. The plot shows an underestimation of the observed ozone loss by up to date chemical models during January. Since Becker *et al.*, 1998, this underestimation has been confirmed by independent studies that were reported at the Workshop and for all cold Arctic Januaries that have been studied so far (i.e. 1992, 1995, 1996, and 2000).

The First Network for the Detection of Stratospheric Change (NDSC) International Symposium

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decomposition) reactions, and a few complex bimolecular reactions, as well as photochemistry and heterogeneous reactions. The pressure dependence of the complex bimolecular reactions is currently approximated as a linear function, while the fall-off of the recombination reactions is treated in more detail. Troe's semi-empirical formulation is the basis for both the NASA/JPL and IUPAC evaluations of experimental fall-off data, although the details differ in the ways the two evaluation panels have chosen to apply the formulations.

At the workshop, several key questions were articulated and discussed. It was concluded that further experimental and computational work could help answer the questions:

- What is needed for improved data on recombination reactions?
- Is the high pressure limiting rate coefficient, k_{∞} , independent of T?
- Is the rate constant for vibrational relaxation a useful surrogate for k_{∞} ?
- How important is the radical-complex (chaperone) mechanism for energy transfer and radical-radical recombination? Can it be predicted? How can it be incorporated into master equation calculations?
- Should the NASA/JPL data evaluation protocol for representing pressure fall-off be changed?
- Should the NASA/JPL data evaluation panel develop protocols for other classes of pressure-dependent reactions?

Low Temperature VOC Oxidation

The scene setting talks in this session were given by **R. Atkinson** (University of California, Riverside) and **L. Jaegle** (University of Washington, Seattle). The session chair was **C. Zetzsch** (Fraunhofer Institute, Hannover) and the rapporteur was **G. Tyndall** (National Center for Atmospheric Research).

The presence of VOCs (Volatile Organic Compounds) in the lower troposphere has long been recognised as necessary for the production of ozone. However, their role in the overall chemistry of the UT/LS is less certain. VOCs in the UT/LS could impact the formation of odd-hydrogen radicals, the production and/or enhancement of aerosols, and *in situ* ozone formation. The study of VOC oxidation at low temperature is not as complete as might be desired, partly due to experimental difficulties encountered when handling low-volatility compounds at reduced temperature.

A thorough discussion of the current state of rate coefficients and product data was carried out. The database for the reactions of OH, Cl, NO₃, and O₃ with alkanes, alkenes and oxygenated hydrocarbons were reviewed. The case of OH reaction with acetone was highlighted and it was revealed at this meeting by Orlando *et al.* that the reaction of OH with acetone was unlikely to produce acetic acid.

A discussion of peroxy radical reactions followed. It was noted that the recent SPARC-IGAC evaluation of peroxy radical reactions (see <http://www.sparc.sunysb.edu/html/tyndall/index.html>) discussed most of the issues involved in these processes. In addition to HO₂ and CH₃O₂, other peroxy radical reactions may play a role in the UT/LS, such as the reactions of acyl peroxy radicals with other peroxy radicals. Consensus has only recently been reached on the values of the rate coefficients for some of these reactions, while the products have been the subjects of only limited study at temperatures other than 298 K. The reactions of HO₂ and CH₃O₂ with acetyl peroxy, CH₃C(O)O₂, are both thought to have minor channels to form acetic acid at room temperature. The occurrence of these channels in increasing amount at low temperature could be very important with regard to aerosol composition in the UT/LS.

It was concluded that better and more widely applicable detection methods need to be developed for both peroxy and alkoxy radicals. Most rate coefficients for peroxy radicals have been measured by UV absorption spectrometry, which is not very sensitive or specific for a given radical. Alkoxy radicals have the advantage that they can be detected by laser-induced fluorescence; however, this technique becomes increasingly less sensitive as the pressure and temperature increase, and also as the size of the molecule increases. A number of laser techniques appear promising, and mass spectrometric techniques should also be investigated. In addition, methods for the detection of stable reaction products should be investigated. In this respect, interactions with the field measurement community may be invaluable. Continued collaboration between experimentalists and theoreticians should further improve our understanding of reaction mechanisms at the molecular level, which will assist in the prediction of reaction rates in regimes that are difficult to access in the laboratory.

Based on modelling efforts and field measurements, it was shown that short-

lived species could be transported vertically in the atmosphere via rapid convection and play a major role in remote areas such as the upper troposphere. A related issue is the range of lifetimes of species transported to the UT/LS by convection. Some of the products of isoprene oxidation have lifetimes of several hours, and it is possible that such compounds, as well as brominated and iodinated hydrocarbons, can be transported locally to the UT by convective activity. This requires a much more detailed speciation in models than is usually included.

The roles of organic aerosol were also discussed. It was noted that to predict the composition and growth rates of aerosols at low temperatures, a suite of parameters for relevant organics are necessary. These include vapour pressures, solubilities in sulfate solution of the appropriate strength, and uptake coefficients (all at temperatures encountered in the UT/LS).

Halogen Chemistry in the Lower Stratosphere and Upper Troposphere

The scene setting talks in this session were given by **J. Rodriguez** (University of Miami) and **S. Sander** (NASA/JPL). The session chair was **R. Friedl** (NASA/JPL) and the rapporteur was **D. Rowley** (University College, London).

Halogens play a key role in the UT/LS region of the atmosphere due to their participation in catalytic cycles that destroy ozone. Since halogenated source gases in the atmosphere include both natural and anthropogenic compounds, understanding the photolytic release of halogen atoms from these compounds, and the subsequent gas phase chemistry is central to elucidating the role of halogen chemistry in the ozone budget. The halogen families of particular interest in the UT/LS are chlorine, bromine and iodine. Fluorine is not considered to play a significant role in the atmosphere due to its inefficient release from the source gases and the rapid formation and high stability of the inactive reservoir species HF. The bonding strengths of the halogen atom and the reactivity of halogenated free radicals dictate, along with the magnitude of the atmospheric source, the role of other halogens in the atmosphere.

A detailed discussion of the current state of halogen reactions was conducted. It was noted that recent measurement campaigns have greatly

improved the ability to test gas phase and heterogeneous chemistry schemes against atmospheric composition. For chlorine in particular, simultaneous measurements of HCl, ClONO₂, ClO and Cl₂O₂ from aircraft and balloon observations have been reported from recent campaigns such as POLARIS, SOLVE and THESEO-2000. While POLARIS data showed that total Cl_y correlated well with N₂O abundances, as would be expected for long-lived chlorine source gases, data from the SOLVE campaign indicated that the sum of individual inorganic chlorine species abundances was lower than the expected total inorganic chlorine content based upon decomposition of source gases. For bromine, far fewer data have been obtained on the abundances of the key species. BrO measurements indicate concentrations between 10 and 20 pptv in the LS, and thereby confirm the involvement of Br in ozone loss. HBr measurements of ca. 1.5 pptv however, are systematically not reproduced in models. This has led to speculation that the BrO + HO₂ reaction and/or the OH + BrO reaction produce HBr via minor reaction channels. The presence of iodine in the UT/LS region is as yet unconfirmed by measurements. While the first attempts to measure iodine abundances (as IO) in this region essentially reported zero abundance, more recent work has indicated IO abundances between 0.65 and 0.80 pptv in the LS.

Laboratory studies of many of the key kinetic and photochemical parameters for halogens have been reported. However, a number of these studies exhibit serious disagreements, and further work is required with improved techniques and methodologies. Individual rate-limiting reactions for important atmospheric ozone loss cycles, and reactions controlling halogen partitioning were discussed individually, along with recommendations for further study.

It was noted that many "new" techniques have been adopted from other fields of research. In addition, data from chemical dynamics studies, such as state-resolved measurements of differential cross-sections, can be used to calculate thermal rate constants and to provide mechanistic insight into reactions and their temperature and pressure dependencies. Theoretical studies are also

contributing increasingly to the database on gas phase halogen chemistry. *Ab initio* studies allow calculation of energies of reaction intermediates and transition states. RRKM-type calculations using these energetics can then be used to calculate rate constants.

Short-Lived Compounds

The scene setting talks in this session were given by **M. Ko** (AER) and **P. Seakins** (University of Leeds). The session chair was **R.A. Cox** (University of Cambridge) and the rapporteur was **J. Burkholder** (NOAA, Aeronomy Laboratory).

A comparison of atmospheric transport times versus chemical lifetimes suggests that any compound with a globally averaged lifetime of less than 30 days would be called a short-lived compound. Examples of short-lived compounds are alkenes, some alkanes, oxygenates, some haloalkanes, and certain sulfur (SO₂, CS₂) and nitrogen (RO_xNO_x) species. The session was limited to haloalkanes and sulfur species, which are a focus of the 2002 WMO/UNEP Ozone Assessment.

Atmospheric model studies (2D and 3D) have demonstrated the importance of including short-lived compounds and their atmospheric degradation products in the calculation of ozone depletion potentials (ODP). The scope of short-lived compounds is however not limited to the evaluation of ODPs but may impact the stratospheric sulfate layer as well as the HO_x and NO_x budgets.

There are three major issues associated with short-lived compounds.

- Short-lived source gases are not well mixed in the troposphere and therefore cannot be treated in model calculations in the same way as long-lived compounds such as CFC-11 and CFC-12.
- Model results are dependent on location and time of emission (variation of OH field and actinic flux with season) of the short-lived compound making it difficult to define a single-valued ODP.
- Stratospheric residence times and tropospheric washout lifetimes are an important parameter in model calculations but are currently poorly defined.

The implications of the short lifetimes are that the degradation pathways and the formation of intermediate products need to be evaluated for each source gas on an individual basis. A guide to the degradation pathways is obtained by comparison with the more comprehensively studied analogous alkanes. Laboratory measurements of OH rate coefficients, photochemical processes, and heterogeneous processes for source gases and degradation products under UT conditions are needed for this evaluation. The emphasis in this session was placed on the evaluation of haloalkanes that have been observed in the atmosphere (CH₃I, CH₂ClI, C₂H₅I, CH₂I₂, CH₃CHICH₃, and CH₃CH₂CH₂I) along with 1-bromopropane, a proposed future emission. All the processes that need to be evaluated to estimate the effect of short-lived compounds on stratospheric ozone are shown in **Figure 4**.

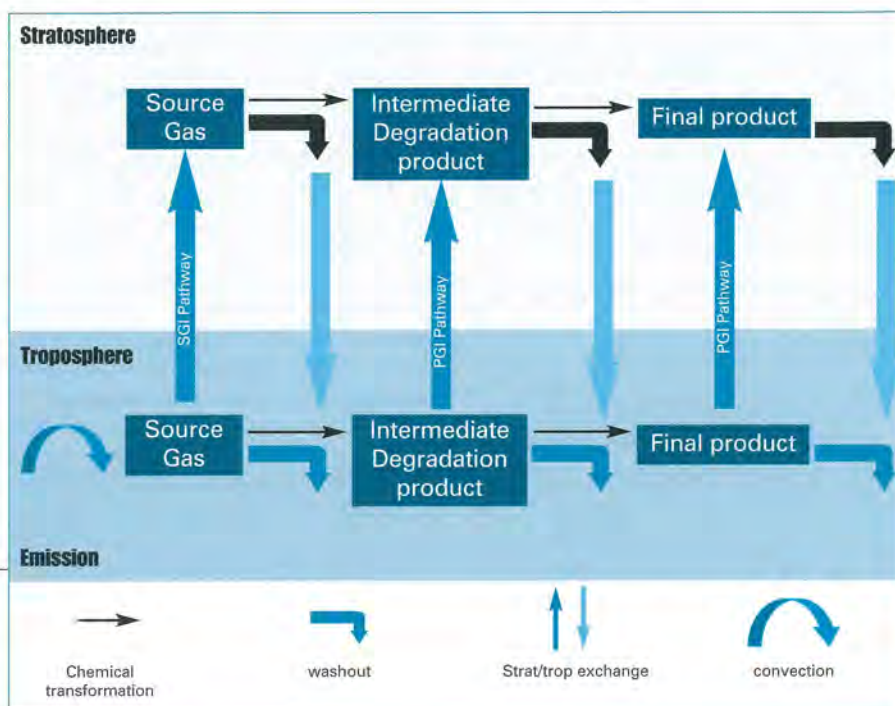


Figure 4. The pathways by which halogens in a short-lived molecule can reach the stratosphere and be re-transported into the troposphere for their eventual removal. [Courtesy of M. Ko].

In addition to the haloalkanes, sulfur species are also important short-lived compounds. The formation of aerosol particles in the UT and subsequent transport to the LS can change the sulfate surface area without changing mass burden. Convection may change how particles are formed in the UT. Laboratory studies of the degradation pathways and formation of aerosol particles under UT conditions are required. These studies include, but are not limited to, the evaluation of the degradation pathways for dimethyl sulfide (DMS) and the formation of sulfuric acid aerosol under UT conditions.

Nitrogen Oxides in the UT/LS Region

The scene setting talks in this session were given by D. Fahey (NOAA, Aeronomy Laboratory) and N. Donahue (Carnegie-Mellon University, Pittsburgh). The session chair was M. Kurylo (NASA and NIST) and the rapporteur was A. Wahner (KFA-Juelich).

Nitrogen oxides play important roles in ozone production and destruction in the UT/LS regions and influence the chemical composition and reactivity of UT/LS aerosols. Kinetic data needed to improve our understanding in these roles were identified at the workshop. In the reaction of OH with HNO_3 , which is one key reaction that controls NO_2 and HNO_3 abundances and provides a sink for lower stratospheric HO_x , more studies at UT/LS temperatures ($< 230 \text{ K}$) are needed. A better theoretical understanding of the origin of temperature and pressure dependence would also be useful. In the reaction of OH with NO_2 (Figure 3), which is another key reaction for NO_2 and HNO_3 abundances, the possible production of HOONO at low temperatures and the value of the rate coefficient for the channel that produces HNO_3 are uncertain; they need to be investigated further. Also of interest is the production of peroxy nitrates, ROONO , in the reaction of RO_2 with NO and the pressure and temperature dependence of this production.

Heterogeneous chemistry of the UT/LS has many unexplored reactions because the area is relatively new compared to gas-phase studies and because of the chemical complexity in the UT/LS. The studies of the N_2O_5 heterogeneous loss reactions provide an interesting example of the inherent complexity of the heterogeneous process. The reactive uptake is lower

on crystallised aerosols than on liquid aerosols and much lower on nitrate-containing aerosols (up to a factor of 50) or on aerosols with an organic coating (5 to 10 times). Especially for the UT, this detail for the N_2O_5 heterogeneous reaction is important because of the role of N_2O_5 as a reservoir of NO_x .

Observational studies in the UT/LS have provided substantial detail and coverage for the speciation and sources of the reactive nitrogen reservoir, NO_y . In the LS, most of the NO_y reservoir is comprised of only a few species and variability is low. In the UT, the complexity is increased by the presence of organic source gases. Budget studies in both regions have been successful in accounting for the principal NO_y component species. Global coverage in NO_y measurements is very sparse overall. Most measurements have been made of NO and NO_2 . Satellite observing systems are not available yet for UT/LS measurements of NO_y . The first commercial aircraft data for NO has proven to be of value.

Accurate rate constant for the reactions involving NO_y species are essential for maintaining progress in key UT/LS issues. Leading issues include calculations of the ozone tendency, the production and loss balance of NO_x in the UT, and the partitioning of HO_x and NO_y reservoirs. The study of the NO_x/NO_y ratio in the summer lower stratosphere stands as an important example of how improved accuracy in fundamental rate constants improves our confidence in LS photochemistry.

The Heidelberg NO_x/NO_y workshop in March 2000 discussed in detail many modelling, laboratory, and observational issues related to nitrogen oxides in the UT/LS. The value of possible future reaction rate studies was prioritised. The workshop report is available on the web at: http://www.aero.jussieu.fr/~sparc/News18/18_Fahey.html

Experimental Methods in Laboratory Studies

The scene setting talk in this session were given by M. Pilling (Leeds University). The session chair was C. Kolb (Aerodyne Research) and the rapporteur was V. Orkin (NIST).

It is clear that laboratory measurements of kinetic and photolytic processes remain key area of research in atmospheric chemistry. The future needs for atmospheric modelling pur-

poses demand increasing accuracy and precision in photochemical data. Data evaluation, an important element of the kinetic support for atmospheric studies, places additional demands on laboratory data of good quality. Therefore, a discussion of the role of laboratory studies used to obtain such parameters was carried out during this workshop.

It was concluded that the reliability of evaluations would be improved if experimental data were always made available in the original scientific publications together with a clearly described uncertainty analysis. Furthermore, every attempt should be made to conduct laboratory measurements over pressure and temperature ranges representative of the real atmosphere. This is particularly important for termolecular reactions as well as for bimolecular reactions that exhibit non-Arrhenius behaviour at low temperatures. Also, in some cases, measurements over the relevant range of water vapour pressures are critical.

The measurements of branching ratios and reaction products are very important for correct/complete modelling and should be conducted in concert with absolute rate constant measurements. Similarly, measurements of the rate constants for the reactions of isotopically labelled compounds can help in the determination of the reaction channels and, thus, can be of atmospheric importance.

The collaboration and inter-comparison of the results obtained via laboratory studies, theoretical calculations, atmospheric modelling, and field measurements are essential for further progress in understanding the chemistry of the atmosphere. Such collaboration can also provide information on the accuracy of laboratory measurements of certain rate constants. Sensitivity analyses of modelling studies can also help prioritise reactions for further laboratory study as well as define required improvements in the accuracy of reaction rates and photolysis parameters. Finally, various experimental methods used to obtain kinetics and photolytic data were described and discussed, and future measurement methods that are coming on line were described.

Report on the Workshop on Molecular Spectroscopy for Atmospheric Sensing

San Diego, USA, 23-26 October, 2001

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Introduction

Remote sensing and *in situ* measurements play critical roles in developing an understanding of the chemistry and physics of the Earth's atmosphere and of its susceptibility to change as a result of natural and anthropogenic forcings. Improvements in laboratory spectroscopic measurements are required to meet the needs of these endeavours, particularly in light of the increasing demands of current sensing technology and of the increased accuracy and precision required to address current atmospheric science issues. Nevertheless, the laboratory spectroscopy needs for atmospheric sensing have not been assessed since the early preparations for the UARS (Upper Atmosphere Research Satellite) observatory [1]. Accordingly a workshop on Molecular Spectroscopy for Atmospheric Sensing was organised in San Diego, CA during October 23-26, 2001 (<http://atmoschem.jpl.nasa.gov/>). The workshop brought together laboratory molecular spectroscopists and investigators who use spectroscopic techniques to probe atmospheric processes to stimulate discussion, to define the needs of the atmospheric sensing community, and coordinate these needs with the current capabilities of laboratory spectroscopy. The programme was balanced between invited oral presentations, posters, and discussions of the issues raised.

Even though there are many spectroscopic issues related to atmospheric sensing that are common to all wavelengths, the workshop was divided into sessions devoted essentially to specific wavelength regions with a separate session concentrating on aerosol spectroscopy. This was done primarily because most atmospheric sensing instruments individually cover one wavelength region due to instrumentation limitations. Each wavelength region had two sessions, one oral session with two or more invited overview presentations with concentrations on the current atmospheric sensing instruments and

state of the art laboratory spectroscopy and a poster session with presentations of specific laboratory and atmospheric sensing projects.

The overview talks for each of the sessions were given by **J. Sloan** and **R. Niedziela** (aerosol session); **J. Waters** and **F. Delucia** (microwave session); **D. Johnson** and **M. Birk** (far infrared session); **P. Bernath**, **Ch. Webster**, **J.-M. Flaud**, and **Ch. Benner** (mid and near infrared session); and **E. Hilsenrath** and **J. Orphal** (visible and ultraviolet session). Overview presentations can be viewed at <http://atmoschem.jpl.nasa.gov/>

The workshop was attended by 70 researchers and was split evenly among the atmospheric sensing community and laboratory spectroscopists. The institutions represented included the Jet Propulsion Laboratory (JPL), NASA Headquarters, NASA Langley, NASA Goddard, NASA Ames, National Institute of Standards and Technology, University of Denver, UCLA, Harvard-Smithsonian Center for Astrophysics, Depaul University, William & Mary College, University of Massachusetts Lowell, Massachusetts Institute of Technology, State University of New York, Ohio State University, Computer Sciences Corporation, University of Waterloo, University of Paris, DLR (Germany), Université Libre de Bruxelles, Japanese Meteorological Research Institute, Communications Research Laboratory (Tokyo), Institut für Meteorologie und Klimaforschung (Karlsruhe, Germany), and National Institute of Environmental Studies (Japan).

Aims

The main aims of the workshop were to:

- identify current and future spectroscopic needs for existing and planned atmospheric remote sensing technologies,
- review the status of current spectroscopic parameters for important atmospheric species,

- prioritise the needs stemming from the above considerations.

Discussions and findings

A number of topics were common to the sessions of all the wavelength domains and are presented first to emphasize their importance. The topics include:

- the need for a recommendation panel for molecular spectroscopic parameters,
- the need for more thorough investigation of temperature dependent pressure broadening line shapes and intensities,
- the imminent need for improvements to the spectroscopy of water vapour over the entire spectrum.

There was extensive discussion on the need for the formation of a recommendation panel for data that is included in molecular spectroscopy databases (e.g., HITRAN). An advisory group will comprehensively review and provide detailed specific recommendations for generating complete sets of parameters (e.g., line intensities, air-broadening coefficients, absorption cross sections as a function of temperature, sulphate aerosol optical constants as a function of temperature, etc.) for all atmospheric species with sufficient absorption to effect atmospheric absorption and emission observations and atmospheric radiation calculations. This panel will assign sub-panels assigned to specific molecules and/or wavelength region. The panel also will set guidelines for data submission, level of scientific review, validation procedures, quantification of uncertainties, and format of data. This has been performed in the past in an informal fashion for databases like HITRAN and the JPL sub-millimetre wave database. While the exact structure and procedures of this panel has yet to be determined, it was envisioned to operate in a fashion similar to that used previously for recommendations of spectroscopy in the

visible and UV for the current ESA satellite instruments [2], the NASA Chemical Kinetics and Photochemistry panels (<http://jpldataeval.jpl.nasa.gov/>) and the IUPAC Gas Kinetics data evaluation panel (<http://iupac.gas-kinetic.ch.cam.ac.uk/>). NASA will sponsor this structure in the form of travel support for the panels to meet on a regular basis.

Uncertainties in pressure broadening coefficients can have a significant impact on the retrievals of molecules for instruments with high spectral resolution and for transitions that saturate over observational path lengths. Pressure broadening uncertainties also affect the use of line shape for the inference of altitude in nadir and zenith observations. Many of the laboratory observations of pressure broadening are taken at room temperature and not typical atmospheric temperatures. There is an obvious need for future pressure broadening line shape information, especially for water vapour, at all wavelengths.

Water vapour absorbs strongly from the microwave through the visible and is a significant contributor to the radiative budget of the atmosphere, convective transport, and atmospheric photochemistry. As a result, accurate spectroscopic parameters for water are especially important. However, many complications have prevented the spectroscopy of water vapour to be represented with sufficient accuracy to address the scientific questions being asked about it. These problems include the difficulty in determining the quantity of the water in the gas cell, the low vapour pressures at the lower atmospheric temperatures, the high centrifugal distortion values which confuse the calculations for line strengths, and the non-Lorentz line shapes that give a continuum opacity over a broad spectrum.

Potential solutions for solving these problems include improved rotational/vibrational coupled non-rigid-rotor models, performing the laboratory spectroscopy with multiple wavelength regions, and using atmospheric spectra directly in order to obtain longer pathlengths and colder temperatures.

Aerosol Spectroscopy

J. Sloan (University of Waterloo) and **R. Niedziela** (DePaul University) addressed the instrument characteristics and aerosol indices needed for remote measurement of Earth's atmo-

sphere and the identification of atmospheric aerosols and the many aspects of laboratory studies of aerosol particles, respectively.

Although the UV/Visible region has good signal-to-noise characteristics for sizing aerosols, there is little spectral information about particle composition in this wavelength regime. The infrared region contains information about the chemical composition of observed particles, but sizing is more difficult. An instrument that can measure continuously over both wavelength regimes (e.g., ACE) offers distinct advantages over past mid-infrared measurements (e.g., ATMOS, ILAS). Retrievals of polar stratospheric clouds (NAT and $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$) over Antarctica using low-resolution ILAS spectra were shown. The largest uncertainty in the retrieval was the incomplete fitting of gas absorptions in a low-resolution spectra. High-resolution and high signal-to-noise ratio spectral measurements would alleviate many existing problems in aerosol retrieval. The presentation and discussion on laboratory measurements of the refractive indices of materials known or presumed to exist in particles of the upper troposphere and lower stratosphere focused on sulphates, organics, and biomaterials. An algorithm was presented for determining refractive indices from laboratory aerosol extinction measurements combined with series of spectra with no scattering components and with Mie scattering only.

From the discussions following the oral and poster presentations and a Thursday afternoon break-out session the spectroscopic requirements that are deemed important for atmospheric sensing are: (1) self-consistent sets of refractive indices across the UV to infrared spectral regions, (2) ternary solution refractive indices at polar stratospheric temperatures, (3) far-infrared refractive indices of sulphate, ice, and water at stratospheric temperatures, and (4) refractive indices of organics, mixtures, dusts, and urban pollution materials to characterise future satellite instruments that will probe into the troposphere.

Microwave Spectroscopy

J. Waters (Jet Propulsion Laboratory) and **F. DeLucia** (Ohio State University) addressed the spectral database and laboratory measurements necessary for remote sensing in the microwave, respectively. Currently ground-based,

air-, balloon-, and space-borne sub-millimetre radiometers (e.g., MLS, ASUR, SLS, ODIN, SMILES) measure a long list of tropospheric and stratospheric molecules (H_2O , O_3 , HCl, CO, N_2O , HNO_3 , HCN, H_2CO , CH_3CN , H_2O_2 , HNO_4 , ClO, OH, etc.). The principal spectroscopic deficiencies in microwave spectral parameters are linewidths and non-resonant absorption continuum (i.e., H_2O). For both, the laboratory data are sparse and theoretical models imprecise. Although number of institutions (JPL, OSU, Ibaraki University, DLR) are performing highly precise rotational linewidth measurements, statistically relevant discrepancies persist. Inter-comparison of microwave and infrared spectral lineshape measurements could be made to resolve this issue. Similarly, combination of microwave and far- and mid-infrared measurements could assist in understanding air and H_2O continua as no physical models exist to explain the phenomena.

From the discussions following the oral and poster presentations and a Thursday afternoon break-out session the spectroscopic requirements deemed important for atmospheric sensing are: (1) estimate uncertainties in linewidths, lineshifts, and continuum parameters, (2) a combined microwave and infrared investigation of spectral parameters for important but "challenging" gases (e.g., H_2O , O_3 , HNO_3) to ascertain the ability of current data set to reproduce spectrally resolved atmospheric measurements, (3) precise dipole moment measurements for important isotopomers (^{18}O , HDO, BrO, acetone), and (4) frequency predictions for tropospheric and stratospheric species beyond 1 THz.

Far-, Mid-, and Near-Infrared Spectroscopy

D. Johnson (NASA, Langley Research Center), **C. Webster** (Jet Propulsion Laboratory) and **P. Bernath** (University of Waterloo) addressed the far-, mid-, and near-infrared spectroscopic parameters needed for *in situ* and remote measurement of Earth's atmosphere. In the context of the meeting the region covers 20–10,000 cm^{-1} (or 1–500 μm). **C. Webster** noted that *in situ* measurements using narrow-band (0.005 cm^{-1}) tunable diode and quantum cascade lasers operating in the 1–3 μm region achieve sensitivity currently not obtainable by remote sensing instruments. Measurements of linewidths and their temperature

dependence were identified as a critical need for the *in situ* community. Spectral line parameters for H_2O and CO_2 isotopomers with 0.1 % accuracy are needed to understand transport of water vapour across the tropical tropopause and the sources and sinks of atmospheric carbon, respectively. The remaining presentations and discussions in infrared sessions focused on the immediate need for consistent and precise O_2 and CO_2 spectroscopy (needed by remote sensing instruments for pressure and temperature retrievals), O_3 line strengths and widths, H_2O continuum, and HNO_3 band strengths (hot bands in particular).

M. Birk (DLR), **J.-M. Flaud** (University of Paris), and **C. Benner** (William and Mary College) addressed the many aspects of current laboratory studies and future needs for infrared remote sensing. These presentations were less of a review and more in form of requirements on the quantifiable quality of laboratory measurements. The metrology required for highly accurate spectroscopic measurements was thoroughly discussed including need for precise characterisation of instrument line shape, detector performance (i.e., non-linearity, baseline, and channelling), calibrations (i.e., wavenumber, pressure, and temperature), gas cell geometry, and isotopomer mixing ratio of measured gas. There was general agreement that high correlation between the measured spectral parameters (strengths, widths, and their temperature dependence) often results in unrecognised systematic errors. However, simultaneously analysis of spectra recorded over a wide range of conditions (i.e., pressure, temperature, resolution) could reduce systematic uncertainties. An important discussion focused on the SNR characteristics of atmospheric measurements necessary to discern errors in spectroscopic parameters. It was illustrated that while a SNR of 1000:1 was sufficient to measure a 1 % error in halfwidths, a SNR of 50000:1 was needed to detect a 1 % error in zero level.

From the discussions following the oral and poster presentations and a Thursday afternoon break-out session the spectroscopic requirements deemed important for atmospheric sensing again are: (1) high precision near-IR measurements of H_2O and CO_2 (and their isotopomers) line intensities, widths, and their temperature dependence to support *in situ* tunable diode laser measurement programs

aiming for sub-parts per billion accuracy, (2) accurate and consistent sets of O_2 and CO_2 spectroscopy (position and intensity measurements) in the mid- and far-IR, (3) O_3 intensities and air-broadening coefficients in the 10- μm region since current measurements differ by about 4%, and (4) absolute band intensities of HNO_3 between 390–3600 cm^{-1} for precise retrieval of nitric acid abundance.

Ultraviolet and Visible Spectroscopy

J. Orphal and **E. Hilsenrath** gave the visible and ultraviolet overviews of the current states and needs for laboratory and atmospheric spectroscopy, respectively. A number of general outlines for laboratory data were given to ensure consistency and usefulness of the data. These include:

- instrumental lineshape to be reported for all spectra,
- simultaneous measurements in other spectral regions where possible,
- wavelength standards should be reported where possible (e.g. I_2 , hollow cathode lamps),
- validation of laboratory spectra from atmospheric observations useful in many cases.

The topic of a well calibrated (both in frequency and intensity) high resolution solar spectrum was given considerable discussion. Such a spectrum would be invaluable for atmospheric observations from the near-infrared through the UV. To be most useful, the spectra should cover the range from 115 nm to 2.5 μm with a spectral resolution of 0.05 cm^{-1} . The spatial resolution on the disk should be 1/10 and include a full disk average and be taken over a full solar cycle. Such a project might require collaboration with solar physics projects.

For specific molecules, the main focus were on O_2 , O_3 , NO_2 , and H_2O , with some discussion on molecules like BrO , ClO , and organic compounds. For some, the current laboratory is sufficient or nearly sufficient for the current and upcoming atmospheric observations. This includes O_2 , which needs some minor improvements in the Wulf bands, the Herzberg continuum, and the B-band, ClO , and OClO .

O_3 requires more observations of the temperature dependence of the cross sections throughout the visible and UV down to 180 K, preferably with high resolution FTS observations. H_2O has

significant problems. Most of the transitions cannot currently be assigned. As a result, the temperature dependence of the strengths cannot be characterised. Temperature dependence of the pressure broadening coefficients and shifts are also needed. Other molecules that require some work are O_2 complexes, NO_2 , NO_3 , IO , BrO , and many organic compounds.

Acknowledgements

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Report on the 2nd National German SPARC Workshop: Status and Perspectives of Atmospheric Research in Germany in the Context of International Strategies

Frankfurt, Germany, April 08-09, 2002

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Several international research programmes have started discussions to re-define their scientific structure and main objectives. For example, a closer co-operation between WCRP/SPARC and IGBP/IGAC is planned in the future, in particular due to common interests of both programmes in studying the chemistry and dynamics of the UTLS region. New foci such as chemistry/climate coupling are also being discussed in order to jointly develop and link important areas of atmospheric research activities. On the other hand, the European Commission has implemented a substantially modified strategy for funding research during the 6th Framework programme. Atmospheric research as well as all other R&D activities will primarily be supported in the frame of Integrated Projects (IP) and Networks of Excellence (NoE). Last not least, the national funding of atmospheric research in Germany is also likely to be reorganised during the coming years. The national scientific community will have to respond to these changes in the programmatic definition as well as in the structure of funding in order to maintain its role in the international scientific efforts.

In this context, a two-day national workshop was convened and hosted by our research group at the Johann Wolfgang Goethe Universität, Frankfurt am Main, Germany, on 8 – 9 April 2002. About 60 scientists from almost all German atmospheric research groups in particular SPARC-related research groups attended the meeting, which to a large part was sponsored by BMBF.

The scientific programme of the first day was dedicated (1) to review the results of the German activities related to SPARC that have been obtained during the last five years and (2) to document their actual status. The following list of the presentations illustrates the broad range of national scientific activities in the field of the different SPARC foci.

Chemistry and dynamics of the UTLS region

Reviews were given by **H. Fischer** (Mainz) on experimental studies of transport and mixing processes at mid-latitudes, by **V. Wirth** (Mainz) on numerical modelling, by **M. Volk** (Frankfurt) on the structure and composition of the UTLS in the tropical region, by **J. Crowley** (Mainz) on photo-oxidation processes, by **B. Kärcher** and **U. Schumann** (Oberpfaffenhofen) on atmospheric effects of aircraft emissions, and by **M. Rex** and **P. V. D. Gathen** (Potsdam) on Arctic ozone depletion.

Long-term-changes in the stratosphere

Several German scientists were involved in the preparation of the recent SPARC assessments. **B. Naujokat** (Berlin) presented a summary of the climatology of the NH stratosphere based on the FU-Berlin data. Short reports were given by **K. Labitzke** (Berlin) on stratospheric temperature trends, by **C. Schiller** (Jülich) on stratospheric and upper tropospheric water vapour, and by **H. Smit** (Jülich) on ozone trends. **A. Engel** (Frankfurt) reviewed the recent observations of GHGs (others than H₂O) and **F.-J. Lübken** (Kühlungsborn) talked about trends in the mesosphere. The issue of a potential change in the stratospheric circulation was addressed by **W. Steinbrecht** (Hohenpeißenberg).

Global processes

Overview talks of recent research results on halogen chemistry and on NO_y-chemistry were given by **F. Strohm** (Jülich) and by **H. Oelhaf** (Karlsruhe). **G. Schmitz** (Kühlungsborn) talked about the results of recent work on the role of gravity waves and **M. Riese**

(Jülich) discussed the global observations of dynamical processes performed by the shuttle experiment CRISTA. **G. Seckmeyer** (Hannover) reviewed the national contributions to the investigation of global UV-B trends.

Modelling stratospheric effects on climate

Numerical simulations of the effects of natural processes (AO, NAO etc.) were discussed by **H. Graf** (Hamburg), while **U. Langematz** (Berlin) reviewed the results of model experiments to investigate the impact of anthropogenic changes in global distributions of ozone and GHGs.

The programme of the second day focussed on presentations of national activities in other programmes that are of interest to SPARC. The talks included reports on EUROTRAC (by **A. Volz-Thomas**, Jülich), on the NDSC (by **K. Kunzi**, Bremen), and on the observational programme for GAW (by **P. Winkler**, Hohenpeißenberg). **S. Bühler** (Bremen) presented the actual status of the implementation of the new European COST Action 723 on UTLS research.

The successful launch of Envisat on the 1st March 2002 was a new exciting challenge, in particular for the national scientific community, to make use of the new global data sets that will be provided by the three chemistry instruments on board the Envisat. Overview presentations on SCIAMACHY and MIPAS were given by **J. Burrows** (Bremen) and **H. Fischer** (Karlsruhe), respectively.

Discussion of future structures

The open discussion of the structure of future national contributions to international atmospheric research

programmes started after a talk by **M. Dameris** (Oberpfaffenhofen) who presented an overview of the present status of the German national "Atmospheric Research Programme (AFO 2000)". **H. Bauer** (Munich) summarised the available information about the future funding policy of the European Commission.

The plenum presented and discussed further the available information about

future directions and planned activities in some international programmes such as SOLAS/IGBP (Surface Ocean Lower Atmosphere Study) and IGACO, the atmospheric chemistry component of the IGOS project. The European Commission recently published a call to submit 'Expressions of interest (EoI)' for "Integrated Projects (IP)" and "Networks of Excellence (NoE)". Plans and existing initiatives for this action were discussed as well as some

large joint projects in the field of atmospheric research to be proposed to the major funding agencies BMBF and DFG in the frame of a possible future national research programme.



Report on the Arctic Ozone Loss Workshop

Potsdam, Germany, 4-6 March 2002

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With contributions from the rapporteurs: **A. Dörnbrack**, **S. Godin**, **G. Millard**, **M.L. Santee**, **H. Schlager**, **A. Schulz**, **B.-M. Sinnhuber**, **R. Stimpfle**, **R. Ruhnke**, and **Y. Terao**

Introduction

Over the past decade tremendous progress has been made toward quantifying and understanding ozone loss in the Arctic stratosphere. Today a variety of approaches exist to quantify the degree of chemical loss over the course of an Arctic winter. Some have been used in a consistent way for many years and have produced a record of the inter-annual variability. On the other hand, a wide range of chemical models have been used to understand the processes in the wintertime Arctic stratosphere and to calculate the degree of ozone loss.

An active scientific discussion has started about the level of maturity of up to date chemical models of the polar stratospheric chemistry. How well are observations of the ozone loss rate reproduced? How complete is our current quantitative understanding of the involved chemical and microphysical processes? Are discrepancies between model results and observations larger than the combined known uncertainties?

In the published literature the answers to these questions are controversial. Over the next few years one of the major challenges for the stratospheric research community will be to predict the future of the Arctic ozone layer in a scenario of decreasing stratospheric halogen loading and possible changes

in climate. A solid assessment of our ability to reproduce currently observed ozone losses with model calculations is indispensable to determine the requirements for future research and to correctly interpret the reliability of model based predictions.

To address these issues, the Arctic Ozone Loss Workshop was held on 4-6 March in Potsdam, Germany, hosted by the Alfred-Wegener-Institute for Polar and Marine Research. The conveners (the authors of this summary) were joined in a programme committee by **G. Amanatidis**, **M. Kurylo**, **P. Newman**, and **J. Pyle**. About 70 scientists from Europe, the US, Japan, Russia and New Zealand have participated. The workshop was mainly based on poster presentations and discussion sessions. It was part of DYCHO, a research project within the German AFO-2000 program and of QUOBI, an EC funded research project, which are both part of the EU research cluster SOLO. The workshop was supported by SPARC.

In his opening remarks **M. Kurylo** highlighted the role of the workshop as an arena for focused discussions where the current status and the requirements for future research should be identified. The workshop covered five sessions that are summarised in the following.

Ozone Loss: Observations

The opening session was on the empirical determination of ozone loss. A variety of techniques have been developed in recent years:

- those which use explicit transport calculations based on meteorological data,
- those which use long-lived tracers.

There are now estimates of ozone loss based on measurements for nearly every winter since 1988/89. Scientists involved with almost all these analyses were present at the workshop. **F. Goutail** presented multi-annual results from comparing a passive ozone tracer in the chemical transport model (CTM) REPROBUS with ozone observations from the SAOZ ground-based network and from the Polar Ozone and Aerosol Measurement (POAM) satellite instrument. The same technique was used by **G. Hansen** with the SLIMCAT CTM and ozone lidar measurements. **G. Manney** showed ozone loss estimates for various years based on measurements from the Microwave Limb Sounder (MLS) and ozone advection by trajectory calculations. **M. Rex** reported one decade of results from Match campaigns, a lagrangian approach to observe chemical ozone loss. In presentations based on POAM data [**K. Hoppel**], ozonsonde profiles [**G. Braathen** and **M. Rex**] and airborne lidar measurements [**W. Grant**] chemical ozone losses were derived

using the vortex average technique. **V. Dorokhov** used ozone soundings from Siberia to estimate ozone loss. **S. Hayashida** presented results from a trajectory mapping approach based on measurements from the Improved Limb Atmospheric Spectrometer (ILAS). **A. Schulz** derived the temperature dependency of ozone loss rates from Match data. **Y. Terao** applied the Match approach to ILAS data, and **S. Tilmes** presented a homogenised multi-annual re-evaluation of ozone/tracer correlation studies based on data from the HALogen Occultation Experiment (HALOE).

The discussion centred on the level of agreement between these techniques. The general result is illustrated by the four coloured boxes in **Figure 1**, which indicate different degrees of reliability of current observationally based techniques.

In region (i) many techniques have been used with consistent results. All agree that in cold Arctic winters the main ozone loss occurs in this region. Recent work comparing results for well-defined time periods and geographical locations indicate quantitative agreement between the various independent approaches better than 20% (95% confidence). The largest local ozone loss that was observed in the Arctic so far occurred in winter 1999/2000. In **Figure 2** (p. VII) this loss is compared with typical Antarctic conditions.

In region (ii), fewer studies have been carried out, with some disagreement as to whether significant ozone loss is occurring. However, the majority of analyses showed clear evidence that it does indeed occur, predominantly at the higher levels of region (ii), i.e. above the flight levels of the ER-2. Losses up to 500 ppbv (at around $\theta = 500$ K) were observed in cold winters with daily loss rates of up to 40 ppbv/day.

There are considerably fewer studies for the regions marked (iii) and (iv). Uncertainties associated with heating rates are greater in these regions and rigorous horizontal mixing particularly in region (iv) is an insuperable challenge for all currently known approaches.

Dynamics

Ozone changes in the Arctic winter and spring are the result of both chemistry and transport. Presentations in this session focused on the relative contributions of both to the variability

and long-term changes of the total ozone column in the Arctic [**S. Anderson**, **R. Kivi**, **M. Proffitt**, **M. Rex**, **M. Weber**], long-term changes and the accuracy of meteorological parameters [**G. Braathen**, **B. Knudsen**, respectively], the influence of mixing and net transport on ozone abundances [**A. Dörnbrack**, **R.-S. Gao**, **G. Manney**, **Y. Orsolini**], the processes that govern the initial ozone distribution in the early polar vortex [**R. Kawa**], and on the processes that determine the temperature in the Arctic stratosphere [**P. Newman**].

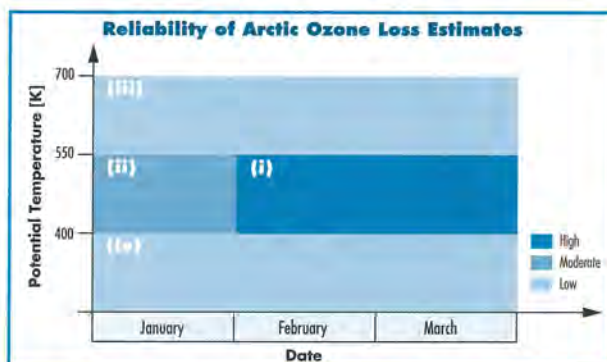


Figure 1. Schematic illustrating the level of reliability of current approaches to estimate chemical ozone losses from ozone observations.

In her overview, **G. Manney** stressed the importance of interannual variability of stratospheric dynamics on the abundance of ozone in the Arctic polar vortex. She discussed the effects of wave activity, diabatic descent and tropopause heights on Arctic ozone fields based on meteorological data and MLS observations.

P. Newman showed that March temperatures in the polar vortex are correlated with wave fluxes into the stratosphere during winter. Models show this qualitatively, but not quantitatively, raising concerns about the ability to accurately simulate polar temperatures and, hence, chemical ozone losses in a changing climate.

B. Knudsen showed that the variability in Arctic total column ozone is correlated with the chemical ozone loss within the vortex. **M. Rex** quantified the dynamical supply of ozone to the Arctic and the wintertime chemical loss for the past decade. Both concluded that dynamics and transport contribute about equally to the observed interannual variability of the Arctic ozone columns. **B. Knudsen** also reported that about 75% of the Arctic ozone decline during the nineties was due to chemistry and discussed the accuracies of temperature fields from various assimilation models.

The discussion for this session focused on the uncertainties in descent, their impact on ozone loss studies, and what steps can be taken to improve model simulations of polar dynamics.

The general view of the participants was that it could be shown that chemistry accounts for approximately half of the interannual variability of column ozone and that the largest fraction of the decrease of ozone since the eighties was due to chemical depletion. It was noted that large discrepancies remain in temperature analyses,

and it will be difficult to achieve the accuracy desired for simulating highly non-linear chemical processes.

Halogen Observations

Abundances of ClO and BrO and their temporal variability are critical in order to calculate chemical ozone destruction. This session featured presentations that addressed issues related to the accuracies of halogen measurements [**L. Avallone**, **M. Santee**, and **R. Stimpfle**], the

partitioning of inorganic chlorine [**K. Kreher**, **J.-P. Pommereau**, **H. Oelhaf**, **M. Santee**, **I. Wohltmann**], ozone loss rates based on measured ClO and BrO [**K. Pfeilsticker**, and **F. Stroh**] and long-term trends in BrO [**D. Toohey**].

During SOLVE/THESEO-2000 there were a number of opportunities when *in situ* and remote measurements of ClO overlapped. **L. Avallone** showed that reported abundances of ClO typically agreed within the combined uncertainties when the measurements were nearly co-located and differences in solar zenith angles are taken into account. But in individual cases differences of ~30% were found, which would imply a difference in chemical ozone loss of over 50%.

Abundances of ClO measured from the NASA ER-2 during SOLVE/THESEO-2000 based on preliminary data were smaller than those measured by other techniques. **R. Stimpfle** reported that, based on post-mission laboratory calibrations, the final ClO data will increase by 10-25% (depending on temperature). He also showed that this change reduces the apparent inorganic chlorine budget discrepancy that had been discerned from the preliminary data. **M. Santee** showed that the better vertical resolution in version 5 of MLS algorithms results in a significant reduction in the abundances retrieved at 20 km altitude.

The agreement between measurements of BrO by different techniques was addressed during the discussion session. Remote techniques report abundances of BrO in the polar vortex that are ~10-20% larger than *in situ* measurements. **K. Pfeilsticker** showed that remote observations of BrO in 2000 are consistent with a total bromine budget of 23 ± 2.5 ppt, whereas previous *in situ* observations have supported a budget between 15 and 18 ppt. **D. Toohey** showed that BrO abundances have increased in the Arctic vortex at a rate of ~3% per year since 1989, thus explaining a significant fraction of the discrepancies between the remote and *in situ* observations (the latter having been carried out between 1992 and 1995). Because abundances of chlorine source gases are expected to decrease faster than those of the bromine source gases, the relative role of bromine in polar ozone destruction will further grow in importance.

K. Kreher showed that column abundances of ClO, HCl, and ClNO₂ over Scott Base, Antarctica, are reproduced well by the SLIMCAT CTM during the period of major ozone destruction. This indicates that the budget and partitioning of inorganic chlorine are reasonably well understood during the period of maximum activation, but the model does underestimate ozone loss both in the Antarctic [**K. Kreher**] and in cold Arctic years [**I. Wohltmann**]. Using MLS data for 7 years, **M. Santee** showed that ClO abundances are more variable in the Arctic than in the Antarctic, but that during the cold mid-1990s years in the Arctic, chlorine activation was nearly as extensive as over Antarctica. **F. Strohm** presented results from the TRIPLE balloon flights in 2000 that can be used to infer photochemical rate parameters. The results were broadly consistent with model results based on the current recommendations of the JPL panel.

K. Pfeilsticker reported that some simultaneous observations of OClO and NO₂ suggest high abundances of active chlorine could coexist with non-negligible abundances of NO_x, in contrast to expectations based on photochemical models. Such an observation could imply activation of chlorine in darkness, and the possibility for unrecognised reactions that destroy ozone.

W. Bloss presented results from a recent laboratory study indicating that the rate constant for the reaction ClO+ClO is ~15-30% larger than cur-

rently recommended by the JPL panel at low temperatures (< 200 K) that prevail during the period of chlorine activation and ozone loss.

The general conclusion from the halogen session was that the various techniques used to detect ClO and BrO provide comparable results, but that specific intercomparisons would be very useful for reducing uncertainties that limit the ability to bring more consistency to the observations of ozone loss and calculations of chemical ozone destruction. The possible co-existence of NO_x and active chlorine and the implications for ozone destruction need further investigation, especially in the context of unexplained ozone losses that have been observed at high solar zenith angles in mid-winter.

Polar Stratospheric Clouds and Denitrification

The primary factor that determines the rate of chlorine deactivation in springtime and, hence, the cessation of ozone loss is the abundance of reservoirs of reactive nitrogen (NO_y) that can be depleted by sedimenting PSC particles – a process termed denitrification. Presentations in this session covered topics ranging from observations of denitrification [**R. Bevilacqua**, **A. Kleinböhl**, **M. Santee**], observations of particles [**D. Fahey**, **M. Müller**], particle microphysics [**K. Drdla**, **B. Luo**], and the relationship between denitrification and ozone loss [**K. Drdla**, **R.-S. Gao**, **R. Ruhnke**].

Measurements obtained during SOLVE/THESEO-2000, summarised by **D. Fahey**, demonstrated that denitrification can occur by formation of a small number of very large (> 10 mm diameter) NAT particles. However, the mechanism by which these particles form is unclear. **B. Luo** showed that initial particle growth and sedimentation in the supersaturated lower edge region of NAT 'mother clouds' downstream of ice clouds could be the source of such particles, but argued that the accuracies in temperature fields necessary for accurate model descriptions of this process may be difficult to achieve.

R. Bevilacqua presented a multi-year climatology of polar stratospheric clouds based on POAM data. By analysing the threshold temperature for PSC formation some information about the degree of denitrification can be inferred, indicating that denitrification may be more common in the Arctic than previously thought.

K. Drdla argued that 50% of the ozone loss observed in the Arctic in 2000 resulted from heterogeneous reactions that occurred after March 1, but that chlorine reactivation is very effective on liquid aerosols, not on NAT particles.

In the break-out discussion the importance of future studies of the PSC formation process, the evolution of the particle composition and phase during their life cycle, and the extent of denitrification they are causing were stressed. These studies will benefit from a much higher level of coordination between different observational efforts than in the past.

Ozone Loss (2): Models

The reliability of predictions of the future evolution of the ozone layer over the Arctic depends on the degree of maturity of current chemical models of the polar ozone loss processes. Presentations during the session focused on comparisons of model calculations with empirically determined ozone losses.

R. Salawitch focused on model runs constrained by measurements of ClO and Cl₂O₂ by the ER-2 during the SOLVE/THESEO 2000 campaign. The model results were compared with ozone losses determined from the ER-2 ozone measurements. Using the current (preliminary) version of the ClO data, the model underestimates the observed ozone loss considerably for all ER-2 flights. However, taking into account expected revisions of the ClO data (as was discussed in halogen session) reduces the discrepancy and results in reasonable agreement between the model and the observations for most of the flights, perhaps with the exception of the missions early during the year.

J.-U. Gross reported box model calculations along trajectories used in Match ozone loss studies for the years 1992 and 1995. During January of both years the observed ozone losses along the trajectories were significantly larger than the model could reproduce. The discrepancy for 1992 is shown in **Figure 3** (p. VII). Using the CLAMS CTM, he analysed whether the Match results inside the polar vortex may have been impacted by dynamical supply of ozone poor air from outside. He found that in January 1992 some mixing occurred, but that the estimated impact was by far too small to explain the discrepancy.

T. Hanisco focused on the balance between active chlorine species and

their passive reservoirs during the recovery period. Based on ER-2 observations and model studies he reported that the relevant processes are extremely sensitive to surface reactivity, calling into question how accurately they can be represented in models of the Arctic stratosphere.

Results from a multiannual integration of the SLIMCAT CTM were presented by **M. Chipperfield**. Using a microphysical scheme that requires the formation of ice particles before substantial denitrification can occur, SLIMCAT has not produced significant denitrification in any winter before 1999/2000 and has generally underestimated ozone loss during cold Arctic winters, with the exception of 1999/2000 [**B.-M. Sinnhuber**]. In 1999/2000 a cold bias in the UKMO temperature fields led to unrealistically intensive formation of ice particles in the model, resulting in widespread denitrification and more realistic ozone loss. Using the same model **G. Millard** addressed the interannual variability of ozone loss and argued that in the Arctic the ClO-BrO cycle is the predominant loss cycle.

M. Rex showed that unrealistically high levels of active chlorine would be required to explain Match observations of ozone loss rates in cold Arctic Januaries with the known photochemistry. Based on a statistical analysis of Match data, he showed that the January ozone loss occurs most likely during short sunlit periods at high solar zenith angles. For March 1996, he found good agreement between the Match ozone loss rates and model calculations constrained by MLS ClO measurement, using version 5 data.

An overview over results from coupled chemistry-climate models were given in a contribution by **J. Austin**, presented by **V. Eyring**. The range of predictions from different models is broad. The initial concern raised by the GISS model that very low Arctic ozone levels can occur around the year 2020 due to increasing greenhouse gas concentrations was not confirmed by the majority of subsequent studies with other models. Some are showing a rapid recovery within the next two decades and even a positive impact of greenhouse gas emissions on Arctic ozone recovery.

The discussion in this session focused on the discrepancies between ozone loss observations and models. Two points were identified where major uncertainties in our understanding

remain. First, the role of denitrification for Arctic ozone losses was generally acknowledged and uncertainties in current microphysical schemes are believed to contribute significantly to a general underestimation of the degree of ozone loss in cold Arctic winters. Second, Arctic ozone losses during cold Januaries appear to be larger than can be explained with current models. The January losses do not represent a large fraction of the overall ozone loss over the course of a cold Arctic winter and the impact of these uncertainties on bulk ozone losses is limited. However a full understanding of the processes is required as basis for reliable predictions of future ozone levels in the Arctic stratosphere.

A second area of discussion centred on the current status of coupled chemistry-climate models. The general view was that the impact of increasing greenhouse gas levels on Arctic ozone remains unclear and that a thorough validation of existing models is required to make progress. This should focus on the validation of processes, e.g. by validating the relation of chemical ozone losses to average PSC areas or the relation of Arctic temperatures to mid-latitude wave fluxes, rather than on the validation of bulk quantities like the total ozone column.

Synthesis

The Arctic Ozone Loss Workshop brought together members from different communities to address the uncertainties that limit our ability to "close" the Arctic ozone budget. Several important conclusions were reached by consensus of the group. First, different techniques for quantifying chemical ozone loss in the Arctic vortex are providing a consistent picture of those losses. Second, the measured abundances of ClO and BrO appear to be sufficient to explain ozone losses during the period of most rapid change (late winter and spring). Finally, accurate temperature analyses and realistic microphysical schemes were viewed as being critical to the ability for models to reproduce the observed ozone losses and their interannual variability.

Another important conclusion reached at the Workshop was that ozone losses in mid-winter (i.e. at high solar zenith angles) are real and cannot be fully explained by standard halogen photochemistry. Although these ozone losses are typically small relative to losses later in the season, the fact that

they cannot be explained calls into question our ability to predict future trends in Arctic ozone.

To close out the Workshop, the participants outlined a general strategy for future observations and process studies. It was agreed that continuous observations of O₃, ClO, H₂O, HNO₃, temperature, and polar stratospheric clouds, preferably with large spatial coverage, will be critical for characterising the changes expected as earth's climate changes and as chlorine loading decreases throughout the century. Process studies addressing nucleation of PSC particles and subsequent chlorine activation and denitrification will be crucial to constrain model parameterisations of particle microphysics, necessary for developing a credible predictive capability. New studies of early- and mid-winter ozone losses and the possible role of unknown halogen reactions will be important for reducing the probability of a "surprise"

The group was optimistic that the tools and collective experience are available to address these needs, and that the ability to predict the future evolution of Arctic ozone should be the goal of future research efforts by this community. In particular, research programmes should focus on the response of Arctic ozone to changes in wave driving, source gas abundances (e.g. chlorine, bromine, methane, and H₂O), radiative forcing, and denitrification.

The First Network for the Detection of Stratospheric Change (NDSC) International Symposium

Celebrating 10 years Years of global Global Atmospheric Research
Arcachon, France, 24-27 September, 2001

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On behalf of the NDSC 2001 Symposium Scientific Programme Committee, the Local Organizing Committee, and the NDSC Steering Committee.

The stratosphere plays a critical role in the Earth system. Its composition, chemistry, and circulation are affected by, and at the same time significantly influence, processes in the troposphere below and mesosphere above. Its susceptibility to human-induced change, exemplified by chlorofluorocarbon-induced ozone depletion, makes it imperative that we measure and understand the ongoing changes and their effects on Earth's climate and biosphere. Toward this end, the international Network for the Detection of Stratospheric Change (NDSC) was initiated eleven years ago. A landmark conference has recently recorded the remarkable accomplishments of the first decade of this global network.

At its annual meeting in 2000, the NDSC Steering Committee decided that it was timely to organise the first NDSC scientific symposium after ten years of careful and comprehensive worldwide observations of a large number of atmospheric parameters had been obtained, and when theoretical analyses of these data were yielding exciting new environmental insights. The main objectives of the NDSC 2001 Symposium, held at the Palais des congrès "Le Palatium" in Arcachon, France on 24-27 September 2001, were:

- to assess the current state of activities and data products,
- to evaluate related data analyses in support of global change and climate,
- to emphasize scientific results obtained through the analysis of NDSC data acquired over the past decade, in relation to other data sources such as balloon-borne, aircraft and satellite measurements, and to model computations.

A further goal was to generate discussions and collaborations among the various NDSC working groups as well as among NDSC data producers and external users.

The NDSC began operations in January 1991 to observe ozone, ozone-related chemicals, and meteorological variables primarily at a globally distributed set of ground-based remote sensing stations (Figure 1 p. VIII). The Network includes active lidars; passive ultraviolet, visible, infrared, and microwave instruments for total column and vertical profile measurements; and *in situ* balloon sounding instruments. The NDSC currently involves over 250 scientists from Europe, USA, Canada, Japan, Russia, New Zealand, Australia, and other countries (see <http://www.ndsc.ws> for details). The Symposium included presentations concerning all of the major Network activities.

Approximately 250 participants registered in advance for the Symposium; however, the tragic events of 11 September 2002 in New York and Washington, DC, USA, discouraged or prevented about 30 colleagues from making such a trip less than two weeks after the tragedy.

A special feature of the Symposium was the Poster Session, comprising 200 posters that were displayed for the entire duration of the Symposium in a room that was also used during breaks, allowing attendees to converse frequently on scientific issues with the poster authors. Another special feature was the interactive Plenary Sessions, which enabled all participants to actively discuss key measurements and conclusions.

At the onset of the Symposium, the Scientific Programme Committee and the Local Organizing Committee expressed their gratitude to the various institutions for their generous grants that made the organisation of the NDSC 2001 Symposium possible on a worldwide basis: specifically, the European Commission, ESA, CNES, UNEP, NASA, SPARC/WCRP, Ministère de l'Environnement,

CNRS/INSU, CNRS/PNCA, IPSL, and some local institutions. Thanks were also given for the support of SPARC/WCRP and NASA, which enabled researchers from Egypt, Kenya, and Brazil to attend.

The Symposium was organised into seven complementary sessions:

- 1 - Coupling between Stratospheric Change and Surface UV,
- 2 - Polar Ozone Loss,
- 3 - Global Ozone: Trends and Variability,
- 4 - Ozone-Related Chemical Species: Distribution and Trends,
- 5 - Dynamics and Climate-Related Studies,
- 6 - Satellite Calibration and Validation,
- 7 - Prospects: New Algorithms and Analysis Methods, Instruments, and Sites.

Each session began with a review talk, followed by two or three additional short presentations selected from among the posters to illustrate the session, a long break around the posters related to the scientific theme of the session, and a discussion about the results presented in posters, lead by a chairman, a reviewer, and two discussion leaders, who were also in charge of reviewing and synthesizing the information in the various posters.

The following results highlighted during the sessions bear mentioning:

- Long-term trends of UV radiation in the Northern Hemisphere derived from ground-based measurements and satellite data are in the range of several percent per decade.
- The coupling of stratospheric change and surface UV was discussed for several future climatic scenarios, in both the troposphere and the stratosphere. It is evident that the combination of a warming troposphere and a cooling stratosphere, as expected from increasing greenhouse gases (GHGs), will affect

ozone levels and surface UV fluxes in significant ways.

- Arctic ozone loss was extensively studied by different techniques showing good agreement among them. Satisfactory agreement was also seen in the Antarctic. The roles of polar stratospheric clouds and dynamics were emphasized, and a study of the polar vortex using aerosol and lidar measurements provided estimates of subsidence rates in good agreement with theory.

- Several important aspects of ozone variations were highlighted on time scales ranging from the transient appearance of polar vortex filaments over mid-latitude locations to long-term changes documented by both satellite and ground-based observations. New aircraft and NDSC ground-based observations now better define the ozone distribution all the way from the troposphere to the mesosphere. Atmospheric dynamics was shown to have played a significant role in long-term changes in the lower stratosphere.

- Our understanding of stratospheric ozone has improved remarkably using the detailed knowledge of the free radicals involved in catalytic ozone destruction, as well as their source gases and sinks or reservoir species, obtained from NDSC observations and analyses.

We are now at the point where the impressive NDSC database is being compared with theoretical models to answer fundamental scientific questions. The models generally agree qualitatively with observations, but there are differences that appear due (in part) to inaccuracies in model circulation. Nevertheless, the models whose circulations are based on observed meteorological field are precise enough to interpret specific chemical events. An impressive array of observations of ozone-related chemical species (most of which are NDSC-targeted species) was reported, including ClO, OCIO, ClONO₂, HCl, NO₂, BrO, HNO₃, and N₂O. Our knowledge of stratospheric water vapour is incomplete, despite the fact that it is a key constituent in chemical, dynamical, and radiative processes in both the stratosphere and the upper troposphere. One of the discussion sessions stressed that more priority should be given to measurements of H₂O in all time and altitude ranges, particularly in the free and upper troposphere, as well as in the lower stratosphere. Further study is needed on irreversible processes and their associated implications, such as ozone depletion due to rising GHGs (e.g. N₂O and H₂O). Another issue, which became clear in plenary discussions,

was the need to increase the scope of the NDSC by including more tropospheric measurements. Several examples include the use of global measurement networks:

- for all major GHGs;
- for FTIR total and partial column measurements of tropospheric tracers such as COS, HCN, C₂H₆, and CO;
- for cirrus clouds.

One of the major objectives identified at the inception of the NDSC was the role of ground-based measurements in the validation of satellite observations and, particularly, on the identification of and correction for their possible long-term drift. Many examples of such satellite validation activities using NDSC products were presented relevant to TOMS, ILAS, POAM, MOPITT, SBUV, SBUV/2, GOME, SAGE II, MSX/UVISI, CLAES, and HALOE. Looking to the future, there was a strong request dictated by the new generation of spaceborne instruments to extend NDSC observations towards lower altitudes including the lower stratosphere, upper troposphere, and even the free troposphere. Given the strong diurnal cycle of tropospheric chemical species, most useful tropospheric data for satellite validation would require the measurements to be performed at the precise time of the satellite overpass, which would be possible in some, but certainly not all, circumstances.

Given the importance of the climate issue, it was suggested that the NDSC investigators widen their focus to include measurements that can improve the present-day uncertainties in the role of aerosols and clouds in climate change. For this to succeed, researchers involved in measurements and those involved in climate-change models need to have closer interactions. It was suggested that the NDSC convene a meeting to discuss measurement needs and the rationale for observations that will help answer climate-change questions. The "Prospects" discussion session stressed the need for new instrumentation, and the development of new remote-sensing algorithms with an objective assessment of errors in the retrieved products. The importance of refining publically available datasets and databases, assimilating data into models, and conducting more instrument intercomparisons was emphasized. Finally, as evident from the NDSC sites map, additional stations are needed in the Southern Hemisphere as well as at tropical latitudes to address many outstanding key questions of global relevance to ozone and climate-change research.

The presentations clearly demonstrated that the NDSC, in its first decade, has made major steps toward achieving its founding goals. It has made challenging observations through which key changes in the stratosphere have been determined and understood in a timely way. It has established key links between changes in stratospheric ozone, tropospheric chemistry, surface UV, and climate. The Network has provided independent calibrations of space-based instruments, and has produced accurate publically available data sets for testing and improving atmospheric models. While much still remains to be done, the accomplishments of the first decade bode well for future successes.

Based on the opinions of a large majority of the participants, the NDSC Steering Committee has concluded that the NDSC Symposium was a "tremendous success as a celebration of the first ten years of scientific operations of NDSC. It provided a unique opportunity for the attendees to report and discuss scientific results obtained through the analysis of NDSC data in relation with other sources such as aircraft-balloon- and satellite-borne measurements, and model computations. Through the oral and poster presentations and extensive discussion periods, the goal of fostering new collaborations among and with the various NDSC Working Groups was certainly advanced. Participants also contributed to discussions aimed at identifying new opportunities and directions for the Network's activities during the next decade."

Reports on the EGS'02 General Assembly

Nice, France, April 21-26, 2002

Session A20 - Tropospheric Chemistry and Aerosols

Convenor: Christian George,
CNRS-LACE, France
(Christian.George@univ-lyon1.fr)
Co-Conveners: M. Ammann,
T. Hoffmann, T. Koop,
and F. Dentener

In an overview lecture on the aerosol formation in the free troposphere by **F. Arnold**, special attention was given to aircraft and laboratory measurements of ionic and gaseous aerosol precursors for which our current understanding is poor. Following talks dealt also with aerosol formation and covered a large range of conditions through field observations (i.e., from aircraft exhausts to nucleation over forest or oceans) or laboratory experiments (e.g., oxidation of toluene) or modelling.

Also of interest were the properties of particles such as hygroscopicity, deliquescence and efflorescence points as well as the thermodynamics of the associated changes. For example, the thermodynamic behaviour of single suspended $\text{H}_2\text{SO}_4/\text{NH}_3/\text{H}_2\text{O}$ -particles was presented for different stoichiometries at different temperatures and relative humidities suggesting that a new, hitherto unknown phase is observed during the experiments (then identified as ammonium bisulfate monohydrate).

E. Vignati showed that an efficient and accurate representation of aerosol size distributions and microphysical processes is required to make physically consistent calculations of the direct and indirect radiative effects of aerosols and their impact on climate. This was made through an overview of recent developments of aerosol modelling (global and regional), outlining the advantages and disadvantages of the various techniques for such large scales, which were also highlighted in following talks.

M. Canagaratna then started an overview on the use of aerosol mass spectrometry (AMS), which provides real-time information on size resolved aerosol mass loading for volatile and semi-volatile molecular components. Such an AMS has now been deployed in field studies in 10 locations worldwide, recording aerosol size and com-

position with time resolution of minutes, showing for example that inorganic (sulfate) loading tends to dominate large "accumulation" mode loading while "organics" dominate smaller (100-200nm) particles. The following studies dealt with chemistry on aerosols (liquid or solid) highlighting the complementary between such an approach and field chemical analysis of particles, which underlines, among other the role of organics.

J. Donaldson (invited) studied the uptake of water onto organic films containing oxidised functional groups. In fact, surface oxidation of atmospheric particles containing significant mass fractions of organic compounds is expected to alter the hydrophobic nature of an organic surface layer, and thus perhaps facilitate the particle's ability to act as a cloud condensation nucleus. He highlighted some results for the room-temperature condensation of water onto films composed of aliphatic hydrocarbons, mono- and di-alcohols and mono- and di-acids. Surface oxidation, through radicals, was also highlighted in another presentation where it was studied directly by means of time resolved the diffuse reflectance coupled to flash laser photolysis. A set of presentations showed different modelling studies of the chemistry in aqueous droplets or on mineral aerosols during ACE campaigns.

In a lively poster session, all of the above mentioned topics were again highlighted by many high quality contributions.

Session ST3 - Open Session on the Middle Atmosphere: Dynamics and Chemistry

Convenor: Martin Juckes,
SSTD Oxfordshire, UK
(M.N.Juckes@rl.ac.uk)
Co-Conveners: E. Manzini,
and R. Müller

M. Chipperfield opened the session with an invited talk on 3-D modelling of stratospheric chemistry. His model was able to capture trends and variability well, and attributed most of the mid-latitude ozone trend of around -5%/decade to halogens. **L. Callis** concluded from a 2-D isentropic model that variations in transport associated with

variations in temperature around the stratopause level were responsible for ozone variability in the 1980s. An analysis of the data record for the temperature variability was presented by **F. Schmidlin**. **H.-M. Steinhof** analysed the effect of mixing between air parcels in a Lagrangian chemical model. **Th. Reddman** looked at the effect of combining a prognostic dynamical model in the upper stratosphere with ERA 15 analyses in the lower stratosphere to obtain dynamical fields with greater consistency to drive a chemical model. This approach improved the performance of the chemical model.

M. Giorgetta (invited review) noted that modelled QBOs tend to be less robust than the atmospheric phenomenon. The effects of varying vertical and horizontal resolutions and varying convection parameterisations were discussed.

T. Roeckmann described balloon measurements of the anomalous oxygen isotope ratio in stratospheric carbon dioxide, which cannot be explained by gravitational fractionation. He proposed a chemical fractionation process involving an ozone reaction with an isotope dependant reaction rate. **S. Griffiths** described how non-linear scale selection might account for the vertical and meridional scales of equatorial inertial instability.

In an invited talk **B. Boville** reviewed work with the NCAR Whole Atmosphere Community Climate Model (from ground to 140 km). Gravity wave (GW) drag becomes dominant above 1 hPa. A correlation between El Niño and stratospheric temperatures was found, but the realism of this was questioned in the light of the model's inability to reproduce the QBO. The response to El Niño begins at the tropical stratopause and then moves polewards and downwards. The mesospheric temperatures are sensitive to details of the GW drag parameterisation.

V. Fomichev from doubled CO_2 experiments with the Canadian Middle Atmosphere Model found a warming of 3K in the troposphere and a 10K cooling in the stratosphere. A 10% increase on stratospheric ozone was found.

A. Kutepov described the development of a heterodyne IR spectrometer to

measure species abundances, kinetic temperature, non-LTE effects and local winds in the middle atmosphere. The method relies on the ability to resolve individual spectral line shapes.

S. Kirkwood analysed the relation between noctilucent cloud occurrence (at 85 km) and wave activity (stationary and 5 days) extrapolated from 55km UKMO analyses. It was concluded that meridional advection associated with the waves was a significant factor in the formation of the clouds.

J. Scinocca described an accurate spectral non-orographic GW drag parameterisation: an adaption of the Warner-McIntyre scheme, with efficiency gains achieved by integrating over the intrinsic frequency. This makes the scheme efficient enough for use in a GCM. **K. Stebel** presented a climatology of GW propagation from 5 years of MST radar (ESRAD) data. In the troposphere there was equipartition between kinetic and potential energy, and also between upward and downward propagating waves. In the stratosphere, kinetic energy was 40% greater than potential energy, and upward propagation was dominant. **R. Plougonven** described GW generation near jets in the FASTEX campaign using, inter alia, data from high resolution radiosoundings. Large amplitude wave events generally coincided either with a jet maximum or a jet break.

In an invited talk **K. Kodera** found that the dynamical response of the stratosphere to the solar cycle was more than direct thermal forcing can explain. He suggested that modulation of internal variability associated with planetary wave propagation might be a factor. A model intercomparison produced variable response to fluctuations in solar forcing.

B. Christiansen gave an invited talk on the downward propagation of the Arctic Oscillation. He proposed a QBO style model, based on a Holton and Mass formulation, to explain the observed downwards phase propagation.

R. Müller described a generalisation of Lait's potential vorticity (itself a modification of Ertel's potential vorticity with reduced density dependence) aimed to facilitate intercomparison of PV maps at different heights.

S. Sparrow described some idealised experiments investigating the link between equatorial winds and polar stratospheric warmings. A clear modulation of the warming frequency was found, though there was substantial

internal variability when the imposed equatorial winds were weak. The warmings tended to start at the subtropical stratopause and then move polewards and downwards. Travelling anticyclones appear to play a role in the lead up to the warmings. **H. Heinrich** investigated the non-linear forcing of stratospheric planetary waves using a Duffing equation and CEOF analyses of ERA15 data. The stratosphere was found to lag the troposphere by 4.5 days. **T. Halenka** used NCEP reanalyses to investigate the relation between solar activity and global circulation patterns. **M. Sigmond** investigated correlations between meridional wind in the stratosphere and zonal wind in the troposphere. He found the stratosphere leading the troposphere by about one day.

S. Yoden presented results from a 3-D mechanistic model of the troposphere and stratosphere, forced with 1 km zonal wavenumber 1 orography. Stratospheric warmings were found to occur randomly in time, matching a Poisson process. A 1K cooling of the polar troposphere during easterly phases of the QBO was found.

In the Poster Session, **P. Braesicke** described the ASAD chemistry package developed for use with the UK Met Office Unified Model. **B. Naujokat** intercompared 6 operational meteorological analyses; the differences are large enough to have a significant influence on chemical models they may be used to drive.

I. Fedulina analysed travelling planetary waves using UKMO assimilated stratospheric data. Differences between the hemispheres were consistent with the stronger westerly vortex in the southern winter. **C. Cagnazzo** studied equatorial waves using TOVS temperatures.

C. Piani documented the way in which winds in the polar middle atmosphere lock into solid body rotation in early June every year. **M. Juckes** described the diabatic circulation associated with the disturbed winter polar stratospheric vortex, and the apparent diabatic ascent diagnosed from ERA15 data. **Ch. Jacobi** found from radar data, that a mesospheric wind reversal accompanied the stratospheric warming in February 2001.

C.-F. Enell used ground-based photographs to study PSCs. Interesting new results concerning the intrinsic frequency spectra of stratospheric air motions were obtained by **A. Hertzog** from constant density balloons.

B. Deuber described a new instrument for ground-based measurement of middle atmospheric water vapour. **T. Schroder** used GPS occultation measurements to retrieve temperature and water vapour profiles.

Session ST4 - Atmospheric Ozone (co-sponsored by OA Section)

Converner: Peter Fabian,
University of Munich, Germany
(fabian@met.forst.uni-muenchen.de)
Co-Converner: M. M. Hirschberg.

This year's subsession on Global Ozone comprised 11 oral and 11 poster presentations.

Highlights were water vapour and ozone fields computed with ERA-40 as compared with MOZAIC results (**E.K. Oikonomou** and **A. O'Neill**), ozone and temperature fields derived from CHRISTA measurements (**I. Galkina**, **G. Kruchenitsky** and **S. Perov**) and 3 exciting new Umkehr applications presented in the poster session by **O.V. Postyliakov et al.**, **B. Rajewska-Wiech** and **M. Degorska**.

P. Braesicke and **J.A. Pyle** showed interesting applications of the Cambridge Unified Model, **M. Bourqui** and **K.P. Shine** of the Reading Intermediate GCM, both investigating ozone loss, **B.M. Sinnhuber et al.** elucidated the role of bromine in stratospheric ozone depletion, and **H.P. Haase et al.** discussed the variability of various trace gases based on balloon and satellite data.

It should be noted that while the tropospheric ozone issues belong to OA, the stratosphere is part of the ST Section. This structure has now been changed, and both the troposphere and the middle atmosphere are embedded in the new Atmospheric Section; it is already implemented and will be effective for the 2003 Assembly.

Session ST8 - Chemistry-Climate Interaction

Convener: Martin Dameris,
Institute of Atmospheric Physics,
Wessling, Germany
(martin.dameris@dlr.de)

This session had only 9 contributions (6 oral presentations), but the interest for the session was very high. More than 120 visitors listened to the oral presentations and it would have been even more if the meeting room would have been larger.

C. Schnadt gave an invited talk discussing the main results of an inter-comparison project, where currently

available chemistry-climate models have been evaluated with observations and analyses. The results of specific diagnostics were analysed to examine the differences amongst individual models and observations, to assess the consistency of model predictions, with a particular focus on polar ozone. Many models indicate a clear cold bias in high latitudes, in particular in the Southern Hemisphere during winter and spring. It seems that the problem can be reduced with the use of non-orographic gravity wave drag schemes. The model results were also compared to assess the possible future behaviour of ozone. The different models indicate that ozone depletion may worsen but thereafter give a range of results concerning timing and extent of ozone recovery. The Antarctic ozone recovery could begin any year within the range 2001 to 2008. Due to larger uncertainties, which originate in the dynamic variability of the Northern Hemisphere, for the Arctic the recovery is expected within the range 2004 to 2019.

M. Dameris pointed out that there are indications from some (chemistry-)climate model simulations that the future polar stratosphere in the Northern Hemisphere will be warmer during late winter and early spring than in recent times. Combined with decreasing chlorine concentrations in the stratosphere this would yield an accelerated recovery of the ozone layer to values observed in the 1980s within less than two decades. However, other models show the expected general cooling of the lower stratosphere in all seasons, which is caused by the radiative feedback of enhanced greenhouse gas concentrations and its intensification by ozone depletion in the spring

season. It is still an open question whether the warming of the northern polar lower stratosphere is an artefact of specific models or if it could be a possible behaviour of the future stratosphere due to mutual effects. In his presentation analyses of ECHAM4.L39(DLR)/CHEM model simulations were presented and discussed with respect to dynamic processes, which yield the simulated warming in this coupled chemistry-climate model. It turned out that an increase of the stationary wave activity is responsible for this model behaviour. The activity of the transient waves did not change in the distinct model scenarios.

Results of a Middle Atmosphere version of ECHAM/CHEM were presented by **C. Brühl**. He discussed multi-year model simulations with fixed boundary conditions for past, current and future conditions. Calculated changes in chemical and dynamical values seem to be in fair agreement with observations, for example results from the HALOE instrument.

G. Pitari employed a low-resolution chemistry-climate model, which considers an on-line inclusion of a microphysical code for aerosol formation and growth. Therefore, volcanic perturbations of stratospheric aerosol can be taken into account. First preliminary results were presented of long-term runs, which were compared with TOMS and SAGE data.

Results of the NCAR CCM climate model were presented by **I. Isaksen**, where they have included atmospheric chemical processes. He pointed out that the distribution and changes of active greenhouse gases (ozone and

methane) and secondary particles (sulphate) in the troposphere are strongly affected by atmospheric oxidation involving precursors like NO_x and CO, NMHC and oxidants like O_3 , OH, and H_2O_2 . In order to obtain a realistic representation of the chemistry-climate interaction in coupled models, the global emissions and distribution of the precursors and the formation and distribution of the secondary key gases need to be accurately represented in the models.

Employing the Unified Model, the cause and effect of mid-latitude ozone loss and associated changes in dynamics have been analysed by **J. Pyle** and co-workers. Therefore, the model has been run in conjunction with a simplified chemistry module. Based on a series of simulations he concluded that about 50% of the mid-latitude ozone changes originate from dynamics.

In general, it was an exciting session. Investigations with respect to mutual effects of dynamical, physical and chemical effect will significantly increase in near future. Questions about future changes of chemical composition of the atmosphere and its effect on climate and *vice versa* are raised in nearly all current announcements of atmospheric programmes. Not only the timing of the recovery of the ozone layer is of common interest. Therefore, it is planned to continue with this session during the following EGS meetings.

For further information check the web site :

<http://www.copernicus.org/EGS/egsga/nice02/nice02.htm>



Report on the Heraeus Seminar on Trends in the Upper Atmosphere

Kühlungsborn, Germany, 13-16 May, 2002

Franz-Josef Lübken, Universität Rostock, Germany (luebken@iap-kborn.de)

From May 13-16, 2002, a seminar on trends in the upper atmosphere took place at the Leibniz Institute of Atmospheric Physics (IAP) in Kühlungsborn, Germany. The seminar was supported by the German private foundation "Heraeus-Stiftung" and by SCOSTEP. Over 60 scientists from 10 countries presented experi-

mental and theoretical results regarding long-term variations in the thermal, dynamical and compositional structure of the upper atmosphere (10-150 km). Measurements at these altitudes from satellites, rockets, and ground-based instruments are comparatively sparse due to the complicated experimental conditions. Still, some

of the data records are long enough to allow for a study of long-term variations, including solar cycle modulations and decadal trends. The main advantage of the upper atmosphere is the fact that, generally speaking, trends are considerably larger in magnitude compared to the troposphere.

In the stratosphere there is a general negative temperature trend on the order of $-(0.5-2)$ K/dec, which is in agreement with model predictions based on greenhouse gas increase (mainly carbon dioxide) and decrease of solar heating due to ozone depletion.

Furthermore, a strong increase of water vapour of up to 1.5 ppmv/dec is observed which is approximately twice as much, compared to the expectations based on the increase of methane concentration (methane is photochemically converted to water vapour in the upper atmosphere). It is speculated that part of the water vapour increase is caused by dynamical effects in the lower atmosphere but no consistent picture is currently available.

Very large negative temperature trends of up to $-(3-5)$ K/dec are reported in the mesosphere at middle and equatorial latitudes. Hydroxyl measurements in the upper mesosphere suggest that the trend is smaller in summer as compared to winter. Surprisingly, a comparison of "historical" rocket soundings

from the 1960s with recent measurements revealed the absence of a significant temperature trend in the entire summer mesosphere at polar latitudes. This contradicts the speculation that a cooling of the upper mesosphere could be the reason for the observed increase of noctilucent cloud (NLC) occurrence frequency (NLC consist of ice particles, which nucleate and grow to visible size in the very cold summer mesopause region). At the seminar, model results were presented regarding the influence of temperature, water vapour, and solar variability on NLC occurrence frequency and brightness. The experimental significance of NLC increase and the potential influence of weather conditions and observers network were critically discussed. The observed time lag of approximately 1.5 years between NLC occurrence maximum and solar cycle minimum is confirmed by satellite-based observations of polar mesosphere clouds (PMC), but no satisfactory explanation for this finding is yet available.

Most of the leading scientists in the field of upper atmosphere trends were present at the seminar in Kühlungsborn. An international report on the status of experimental and model results regarding trends in the mesosphere was further discussed during the meeting and will soon be submitted for publication in Review of Geophysics. The participants enjoyed the exciting presentations, the fruitful discussions, and the beautiful surroundings of the sea resort town Kühlungsborn at the Baltic sea. The financial support from the Heraeus foundation and from SCOSTEP was greatly appreciated. There was general consensus that a similar meeting on trends in the upper atmosphere should soon be repeated.



Dear colleagues,

A few days ago I learnt the sad news that Dr. Petra Udelhofen, responsible now for your Data Center, has died suddenly. I was her doctoral advisor in the early nineties at the GKSS Research Center in Geesthacht, Germany, and was always impressed about her positive and quite relaxed attitude towards life. She was extremely smart in rational scientific thinking and made successfully her way from Germany to the US, Australia and later back to the US, where she finally had a chance to settle. Our scientific interest was always quite close; a few weeks ago we had some discussion about her latest work on the relation between cloudiness and "cosmic influences", a hot issue in the climate debate. I had also several chances to meet her at different scientific meetings.

I am sure, that Petra left very many friends behind who will keep Petra in their memory with best thoughts. SPARC lost an active person in its infrastructure and scientific work.

*Yours Sincerely
Professor Ehrhard Raschke*

In Memory of Petra Udelhofen

It is with great sadness that I tell you that the SPARC Data Center Scientist, Dr. Petra Udelhofen suddenly passed away on Friday evening, May 17, 2002, after being taken to the hospital in septic shock. Petra was in charge of operations at the SPARC Data Center for about 3 years, since its beginning. She also worked with Bob Cess on climate and atmospheric radiation research at Stony Brook during this time. Petra received her Ph.D. from the University of Cologne and previously had held positions at the University of Washington, at the University of Georgia, and in Melbourne, Australia. Her parents, a brother, and a sister in Germany survive her. Her colleagues, relatives, friends, and the entire SPARC community will sorely miss her. Petra would have had her 42nd birthday on Tuesday, May 21.

Given the remarkable personal resources that Petra put into the SPARC Data Center, few could appreciate the modest material resources that were behind the Data Center. The SPARC community will miss Petra a great deal. We have all benefited greatly by her efforts. I know you all join me in expressing condolences to her family and others who knew and loved Petra.

A memorial fund is being set up in Petra's name at Stony Brook to benefit undergraduate students majoring in Atmospheric Sciences and Environmental Studies. Petra taught courses in both courses of study. Those who wish to donate to this fund can contact me about details.

Marvin A. Geller
SPARC Co-chair

The SPARC Office received many messages expressing their emotion in reaction to this dramatic news, among them one from her doctoral advisor Pr. Ehrhard Raschke is reproduced here.

Future SPARC and SPARC-related Meetings

- 10-19 October 2002: 34th COSPAR Scientific Assembly and The 2nd World Space Congress**, Houston, Tx, USA. (<http://www.copernicus.org/COSPAR/COSPAR.html>). Chair: S. S. Holt.
- A1.1/C2.7:** Climate Change Processes in the Stratosphere and at the Tropopause. Convener: J. Gille (gille@ncar.ucar.edu)
- C2.3:** Long-term Trends in Stratosphere-Mesosphere-Thermosphere Coupling. Convener: D.K. Chakrabarty (chakra@prl.ernet.in)
- D2.3/E3.3:** Solar Variability and Climate Changes. Convener: J.M. Pap (papj@marta.gsfc.nasa.gov)
- 04-08 November 2002: American Meteorological Society's 12th Conference on the Middle Atmosphere**, Riverwalk, San Antonio, TX, USA. Sponsored by the American Meteorological Society and organised by the AMS Committee. (<http://www.ametsoc.org/AMS/meet/fainst/12middleadmos2002.html>). Program Chairperson: D.W. Waugh (waugh@jhu.edu)
- 12-15 November 2002: International Symposium on Stratospheric Variations and Climate**, Kyushu University, Fukuoka, Japan. (<http://fx.geo.kyushu-u.ac.jp/IntSympo/3rd.html>). Chair: S. Yoden (yoden@kugi.kyoto-u.ac.jp)
- 18-21 November 2002: 10th Session of the SPARC Scientific Steering Group**, Kyoto, Japan. Convener: S. Yoden (yoden@kugi.kyoto-u.ac.jp)
- 03-05 December 2002: DAWEX (Darwin Area Wave Experiment) Workshop**, Honolulu, USA. Convener: K. Hamilton (kph@soest.hawaii.edu)
- 09-13 February 2003: 83rd Annual Meeting of the American Meteorological Society**, Long Beach Convention Center, Long Beach, California, USA. (<http://www.ametsoc.org/AMS/meet/83rdannual/index.html>) Chair: D. Seidel (dian.seidel@noaa.gov). The broad theme of the annual meeting and many of the associated conferences and symposia will be water cycle variability and impacts.
- 17-21 March 2003: 24th Session of the Joint Scientific Committee for the World Climate Research Programme**, University of Reading, UK. (<http://www.wmo.ch/web/wcrp/jsc.htm>). Chair: P. Lemke (plemke@awi-bremerhaven.de), Vice-Chair: B. Hoskins (hoskins@met.rdg.ac.uk)
- 06-11 April 2003: EGS-AGU-EUG Joint Assembly**, Nice, France. (<http://www.copernicus.org/egsagueug/>)
January 15, 2003: deadline for abstract submission
March 07, 2003: deadline for pre-registration
- 30 June-11 July 2003: IUGG General Assembly**, Japan Marine Science and Technology Center, Sapporo, Japan. (<http://www.jamstec.go.jp/jamstec-e/iugg/>).
- 15-18 September 2003: 3rd IAGA Workshop "Solar Forcing of the Middle Atmosphere"**, IAP, Prague, Czechoslovakia. Chair: J. Lastovicka (jla@ufa.cas.cz)

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