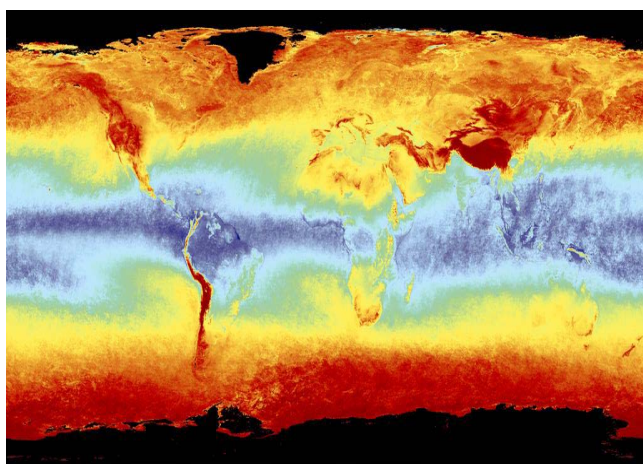


Molecular Spectroscopy Facility

NERC Annual Report

1 April 2007 – 31 March 2008



Front cover figure captions:

Top left: The mean global distribution of atmospheric water vapour during 2006 as measured by the MERIS instrument on Envisat. Water vapour is the most effective greenhouse gas in the atmosphere. It affects weather and climate and is responsible for cloud development, precipitation, and modulates the atmospheric radiative energy transfer. Water vapour influences the energy balance of the Earth and, in turn, also affects the temperature and circulation of the Earth-atmosphere system. The CAVIAR consortium project led by the University of Reading is investigating absorption of infrared radiation in the atmosphere by water vapour. There is still much uncertainty surrounding water vapour spectra, and studies at the MSF are intended to improve our knowledge of absorption from both resolved spectral lines and continuum features.

Top right: Poor air quality in urban environments. Understanding atmospheric chemistry is essential for the accurate forecasting of air quality in highly populated areas. The University of Reading are working at the MSF to detect the Criegee intermediate, a species produced during reactions of ozone with hydrocarbons (alkenes). These reactive intermediates have never been detected in the gas phase, but doing so would enable a much greater understanding of an important atmospheric process.

Bottom left: Aerosol pollution observed over Northern India and Bangladesh. Aerosols play a crucial role in atmospheric chemical reactions and radiative transfer. It is important to understand their properties and behaviour to better understand the behaviour of the Earth's atmosphere. During 2007/8 the University of Oxford studied two such important aerosols at the MSF; ammonium sulphate and ammonium nitrate. These act as cloud condensation nuclei and provide a significant anthropogenic cooling contribution to global radiative forcing.

Bottom right: The ESA Envisat satellite. The MSF continues to provide high-quality spectroscopic reference data for interpretation of satellite observations. Ethane is an important organic compound in the troposphere, providing a tracer of dynamics and information on OH. During 2007/8 the University of Leicester made measurements on ethane that will be used to retrieve atmospheric concentrations from the MIPAS instrument on Envisat.

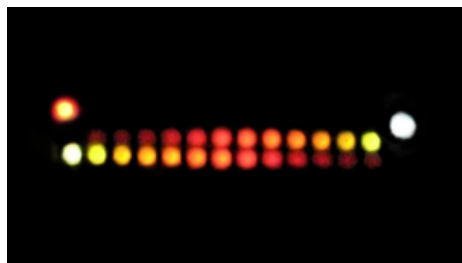
SERVICES & FACILITIES ANNUAL REPORT - FY April 2007 to March 2008

SERVICE Molecular Spectroscopy Facility	FUNDING Block	AGREEMENT SLA	ESTABLISHED as S&F 1997	TERM 5 years
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TYPE OF SERVICE PROVIDED:

The Molecular Spectroscopy Facility (MSF) provides world-class central laboratories, scientific equipment, training, scientific/technical support, and high-quality data for the UK environmental science community in support of a wide range of interdisciplinary research across the spectrum of the NERC remit and SPAs. Infrared, visible, and ultraviolet spectroscopic data are increasingly important for studying the important chemical, physical, biological, and geological processes occurring in the natural environment. The MSF provides essential inputs to many key NERC science and technology areas, in particular Earth observation of the atmosphere and surface using optical remote sensing techniques, atmospheric chemistry, and climate research.

Through the MSF, broadband, high spectral resolution Fourier transform and fibre-optic spectrometers are provided to NERC researchers for measuring the absorption, emission, and scattering properties of solid, liquid, gas/vapour, and aerosol samples contained in a range of spectroscopic cells. High-quality spectroscopic data over the entire spectral range from wavelengths (wavenumbers) of 1 mm (10 cm⁻¹) in the far-infrared/sub-millimetre range to 180 nm (55,000 cm⁻¹) in the far ultraviolet are generated at spectral resolving powers of up to 1 part in a million and time resolutions as high as 5 μs. Customised sample cells are available for specific temperature-dependent measurements over the range 77 to 350 K at optical path-lengths from 1 mm to over 1 km using multi-pass optical systems. For atmospheric chemistry studies, the chemical synthesis area and laser-safe laboratories permit a wide range of projects to be supported. Further details can be found on the MSF Web site (www.msf.rl.ac.uk).



Multiple reflections within the long path absorption cell during the CAVIAR water vapour measurements. The long path (512 m) of the LPAC was required to measure weak continuum-like absorption thought to be from water dimer.



The new short path absorption cell with the outer vacuum jackets removed showing the copper strip heaters that will allow the cell to reach 470 K for high-pressure water vapour measurements as part of CAVIAR.



Quantum cascade laser systems are being developed through other activities at RAL. This benefits the MSF through the availability of state-of-the-art equipment such as this in-house room-temperature continuous-wave QC laser head.

ANNUAL TARGETS AND PROGRESS TOWARDS THEM

This year has been one of both renewal of life-expired equipment and expansion of services. The capacity, flexibility and reliability of the MSF have been increased by the provision of a second high-resolution spectrometer and spectroscopy laboratory. This development has been funded through a combination of an advance of allocation from the NERC and a grant from the STFC knowledge exchange enterprise, CLIK. Work has been completed on the new short path absorption cell and substantial upgrades to vacuum systems are in progress. Both of these developments will have major benefits to a number of projects in 2008/9 and beyond, in particular the £2M 4-year NERC/EPSCRC CAVIAR consortium project.

SCORES AT LAST REVIEW (each out of 5)			Date of Last Review: January 2004	
Need 5.0	Uniqueness 5.0	Quality of Service 5.0	Quality of Science & Training 5.0	Average 5.0

CAPACITY of HOST ENTITY FUNDED by S&F 85 %	Staff & Status Head of Facility 8.5% established Scientist / Manager 85% established Technician 85% established	Next Review (January) 2009	Contract Ends (31 March) 2010
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FINANCIAL DETAILS: CURRENT FY									
Total Resource Allocation £k 203.8	Unit Cost £k						Capital Expend £k 50	Income £k 0	Full Cash Cost £k 269.59
	Unit 1 Entire MSF 2.06	Unit 2 IFS 125HR 1.36	Unit 3 IFS 66v/S 0.68						
FINANCIAL COMMITMENT (by year until end of current agreement) £k									
2007-08	203.8	2008-09	208.6	2009-10	215	2010-11	-	2011-2012	-



STEERING COMMITTEE	Independent Members	Meetings per annum	Other S&F Overseen
MSF	5	2	None

APPLICATIONS: DISTRIBUTION OF GRADES (Current FY — 2007/08)								
	$\alpha 5$	$\alpha 4$	$\alpha 3$	$\alpha 2$	$\alpha 1$	β	R*/Pilot	Reject
NERC Grant projects	2	1	1	0	0	0	0	0
Other academic	0	2	0	0	0	0	2	0
Students	0	0	0	0	0	0	0	0
Pilot	0	0	0	0	0	0	3	0
TOTAL	2	3	1	0	0	0	5	0

APPLICATIONS: DISTRIBUTION OF GRADES (per annum average previous 3 years —2004/2005, 2005/2006 & 2006/2007)								
	$\alpha 5$	$\alpha 4$	$\alpha 3$	$\alpha 2$	$\alpha 1$	β	R*/Pilot	Reject
NERC Grant projects	0.67	1.67	0.33	0.00	0.00	0.00	0.33	0.00
Other Academic	0.67	2.00	0.67	0.00	0.00	0.00	1.00	0.67
Students	0.33	0.67	0.00	0.00	0.00	0.00	0.00	0.00
Pilot	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	1.67	5.33	1.00	0.00	0.00	0.00	1.33	0.67

PROJECTS COMPLETED (Current FY)								
	$\alpha 5$	$\alpha 4$	$\alpha 3$	$\alpha 2$	$\alpha 1$	β	R*/Pilot	
NERC Grant projects	0	1	0	0	0	0	0	0
Other Academic	0	0	0	0	0	0	0	0
Students	0	0	0	0	0	0	0	0
Pilot	0	0	0	0	0	0	0	1

USER PROFILE (current FY)											<i>*Combined non-Directed and Directed</i>
Grand Total	Infrastructure					PAYG					
	Supplement to NERC Grant *	Student		NERC C/S	Other	NERC Grant*	Student		NERC C/S	Other	
	NERC	Other				NERC	Other				
4	1	2	2	0	1	0	0	0	0	0	

USER PROFILE (per annum average previous 3 years)											<i>*Combined non-Directed and Directed</i>
Grand Total	Infrastructure					PAYG					
	Supplement to NERC Grant *	Student		NERC C/S	Other	NERC Grant*	Student		NERC C/S	Other	
	NERC	Other				NERC	Other				
14.33	4.33	7.33	4.67	0.00	2.67	0	0	0	0	0	

USER PROFILE (current FY)				
Academic	Centre/Survey	NERC Fellows	PhD	Commercial
2	0	0	2	0

USER PROFILE (per annum average previous 3 years)				
Academic	Centre/Survey	NERC Fellows	PhD	Commercial
7.00	0.33	0.00	7.00	0.00

OUTPUT & PERFORMANCE MEASURES (current FY)										
Publications (by science area & type)										
SBA	ES	MS	AS	TFS	EO	Polar	Grand Total	Refereed	Non-Ref/ Conf Proc	PhD Theses
0	0	0	7	0	7	0	14	6	7	1

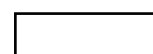
Distribution of Projects (by science areas)						
SBA	ES	MS	AS	TFS	EO	Polar
0	0	0	75%	0	25%	0

OUTPUT & PERFORMANCE MEASURES (per annum average previous 3 years)										
Publications (by science area & type)										
SBA	ES	MS	AS	TFS	EO	Polar	Grand Total	Refereed	Non-Ref/ Conf Proc	PhD Theses
0	0	0	5	0	3	0	9	4	5	1

Distribution of Projects (by science areas)						
SBA	ES	MS	AS	TFS	EO	Polar
1%	0	2%	54%	2%	40%	1%

Distribution of Projects (by old NERC strategic priority) (as whole or part of whole number NOT as a %)				
Earth's life support systems	Climate Change	Sustainable Economies	Underpinning Science	Specific Research
0	3	0	1	0

Distribution of Projects (by new NERC strategic priority) (as whole or part of whole number NOT as a %)						
Climate System	Biodiversity	Earth System Science	Sustainable Use of Natural Resources	Natural Hazards	Environment, Pollution & Human Health	Technologies
3	0	0	0	0	1	0



OVERVIEW & ACTIVITIES IN FINANCIAL YEAR (2007/08): The MSF has continued to provide high-quality data to diverse research projects within the NERC-science remit. There have been continued efforts to develop the Facility to meet NERC customer requirements and improve the service. The following are examples of enhancements that have been made during the reporting year:

Second high-resolution spectrometer

In response to increasing demands on Facility capacity a second state-of-the-art Fourier transform spectrometer will be available from the end of 2007/8. This refurbished instrument will provide increased capacity for academic and non-academic research, and therefore contribute to **knowledge exchange activities** involving the Facility. Potential customers in the near-term include ESA, STFC, DSTL and other agencies connected with homeland security. An important area of work within the NERC remit will be the spectral characterization of the flight-spare AATSR focal plane assembly, which is needed to correct errors in the original calibration. The spectrometer has been fitted with the latest electronic systems by Bruker Optics at their factory in Germany. The laboratory has been fitted out with funds from CLIK, the STFC knowledge exchange enterprise. *Right: The refurbished IFS 120HR spectrometer and new air-conditioned spectroscopy laboratory.*



New short path absorption cell (SPAC)

A much improved version of the previous SPAC has been completed during 2007/8. The SPAC now offers the widest temperature range of any of the MSF gas cells, operating between 77 and 470 K. This multi-pass cell benefits from mirror adjusters that allow optimisation of the optical alignment during operation. It is anticipated that this one feature alone will dramatically improve ease and efficiency of operation as well as enhance the quality of spectroscopic data. The first use of the new cell will be in support of the **£2M 4-year NERC/EPSC CAVIAR consortium project**, with an allocation of 250 days of MSF capacity this is one of the largest projects supported by the Facility. *Right: The SPAC (left hand side) and temperature control unit (right hand side) in position above the spectrometer transfer optics.*



Optical systems

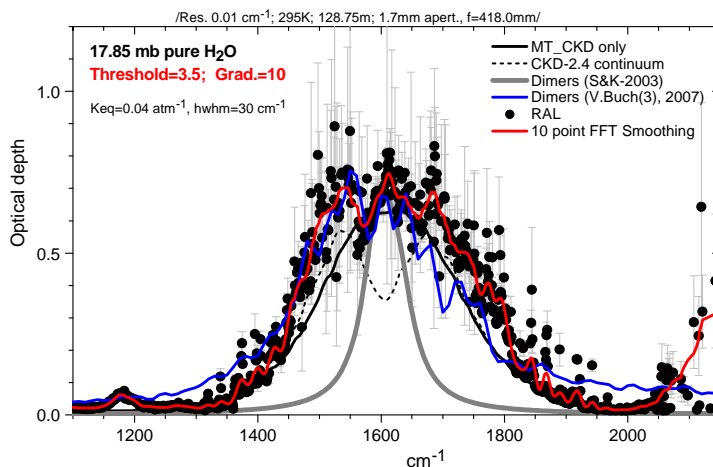
2007/8 has seen new facilities for optical systems become available to users. A new air-damped optical table has been provided for preparation of systems prior to integration with the spectrometers. This table can also be used for instrument calibration-validation activities and laser spectroscopy.

Further developments in the area of quantum cascade lasers (QCLs) have been achieved. New laser heads are now available for use with room-temperature continuous wave QCLs. These compliment the previous pulsed operation laser systems. A new astigmatic Herriot cell with a path length of 200 m is now available for high-resolution trace gas measurements. *Right: The new multi-pass gas cell for use with laser systems. This view shows one end of the glass and stainless steel cell, with one of the astigmatic mirrors visible.*

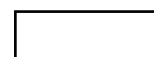


SCIENCE HIGHLIGHTS: Spectroscopic measurements in 2007/8 have been dominated by studies on water vapour for the **£2M NERC/EPSC Continuum Absorption in the Visible and Infrared and its Atmospheric Relevance (CAVIAR) project**.

CAVIAR has made extensive use of the high-resolution spectrometer and the long path absorption cell. Water vapour is the most important radiatively active gas in the Earth's atmosphere. It is responsible for about 55% of the natural greenhouse effect and solar radiation absorbed by the atmosphere. Despite its relatively low atmospheric abundance, water vapour's high importance in the radiation balance results from its strong and complex absorption spectrum. There is still much uncertainty surrounding water vapour spectra, and this work is intended to better characterize the absorption from both resolved spectral lines and continuum features through a series of new measurements that will also investigate pressure and temperature dependencies. Work has progressed on two main fronts: high-resolution spectroscopic measurements using the long path absorption cell (LPAC) and the design, manufacture and construction of a new short path absorption cell (SPAC) as described above. Long-path measurements have so far been made in the mid and shortwave infrared at room temperature. A set of short-path low-pressure measurements have also been made to obtain line parameters in certain spectral regions where the HITRAN database caused problems during analysis of the continuum.

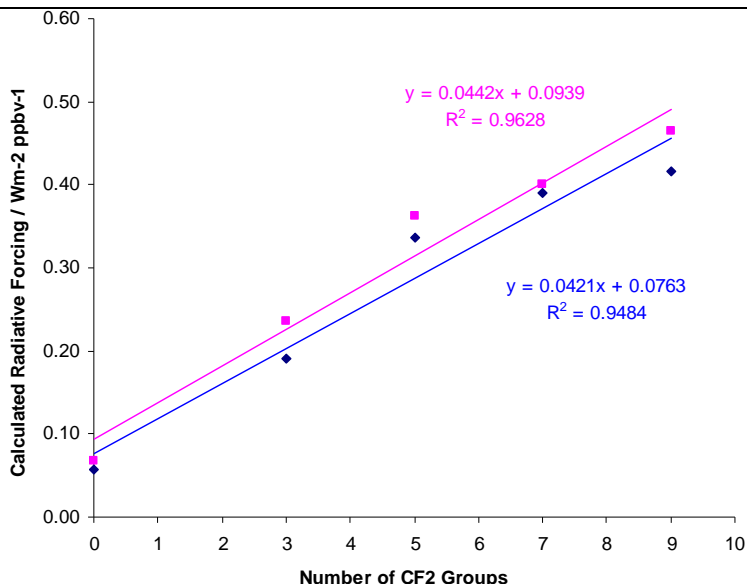


Above: Preliminary results generated by the University of Reading from the initial set of LPAC measurements. This plot shows observed – calculated residuals (black points and smoothed red curve) compared with the latest dimer calculation (blue curve), an older dimer calculation (grey curve) and calculated continua (black curve and black dashed curve).



Perfluorocarbon Measurements

The perfluorocarbons (PFCs) are a family of gases with strong infrared absorption bands and long atmospheric lifetimes. They have been used in aluminum manufacture, as tracers of air motion and in the semi-conductor industry. The emissions of many PFCs are regulated under the Kyoto Protocol to the UN Framework Convention on Climate Change. After 2012, if a protocol similar to Kyoto is put in place, it might be expected that updated data for an extended range of gases would be required. The Global Warming Potential (GWP) is used to assess the impact of each gas relative to CO₂. The calculation of GWP requires the radiative efficiency of the gas and hence detailed knowledge of the infrared absorption cross-section of the molecule. Such cross-sections are generally derived from laboratory measurements, although it is becoming increasingly possible to compute them to reasonable accuracy using ab initio calculations. This project aims to develop a method for modelling the radiative forcing for any given PFC using a set of new laboratory measurements to characterize the absorption cross-sections as a function of molecular structure.



Above: The relationship between radiative forcing and the number of CF₂ groups contained within the molecule for CF₃(CF₂)_nOCH₃ (blue) and CF₃(CF₂)_nOCH₂CH₃ (pink).

PUBLICATIONS: Four relevant publications appearing during the calendar year 2007:

The work that was the forerunner of the £2M NERC/EPSRC CAVIAR consortium project is described in this paper: 'Pure water vapor continuum measurements between 3100 and 4400 cm⁻¹: Evidence for water dimer absorption in near atmospheric conditions', D J Paynter, I V Ptashnik, K P Shine and K M Smith, *Geophys. Res. Lett.*, Vol. 34, No. 12, 23 June 2007.

A two-part article about the MSF appeared in *Spectroscopy Europe*, which is widely read by academic and industrial researchers: 'High resolution infrared studies at the Rutherford Appleton Laboratory Molecular Spectroscopy Facility', K M Smith, Part 1, *Spectroscopy Europe* 19(1): 17-22, February/March 2007 and Part 2, *Spectroscopy Europe* 19(2): 20-23, April/May 2007.

Three papers appeared related to the laser heterodyne radiometer, which underwent testing in the MSF. The most recent is given here: 'Retrieval of atmospheric ozone vertical profiles from an infrared quantum cascade laser heterodyne radiometer: results and analysis', D Weidmann, W J Reburn and K M Smith, *Applied Optics*, 46 (29), 7162-7171, 2007.

In recent years a large amount of research at the MSF has been conducted into the spectroscopic properties of aerosols, some of this work is described in the Ph.D. Thesis 'Spectroscopic studies of biogenic gases and particulates from the terrestrial troposphere', Elizabeth Uttley, The Open University, 2007.

FUTURE DEVELOPMENTS/STRATEGIC FORWARD LOOK The MSF is committed to the continued support of the NERC/EPSRC CAVIAR consortium project, requiring a total of 250 days of Facility capacity over a 28-month period and significant upgrades in technical capability. Further developments in aerosol spectroscopy are planned in support of a major new study of black carbon aerosol with an allocation of 280 days of Facility time. In addition, new work to characterize satellite instrument focal plane arrays is expected in connection with the European Global Monitoring for Environment and Security (GMES) programme, thus increasing UK capabilities in EO technology and providing direct knowledge transfer of NERC expertise. **Calibration facility for satellite instrument focal plane arrays**

The MSF has been asked to characterize the flight-spares focal plane array (FPA) for the AATSR (Advanced Along Track Scanning Radiometer), to correct calibration errors made prior to launch on ESA's satellite Envisat. There will also be a requirement to calibrate FPAs for the AATSR follow-on instrument SLSTR (Sea and Land Surface Temperature Radiometer) for the first of ESA's GMES Sentinel-3 satellites, and the intention is to incorporate the refurbished IFS 120HR in a new FPA calibration facility at RAL. Work will be necessary to provide an interface between the FPAs and the spectrometer that maintains the clean-room conditions necessary for flight equipment.

External cavity quantum cascade lasers

Quantum cascade lasers available at operating wavelengths from the terahertz region to four microns offer huge potential for high-resolution spectroscopic studies. These devices can provide high output power (in the order of mW) and narrow line widths (down to tens of kHz). Until recently a limitation has been the relatively narrow continuous tuning range of individual laser devices, typically 1% of the central wavelength. Studies using external cavity configurations have shown an increase in this tuning range: the current state-of-the-art is 20% of the central wavelength. It is conceivable that in the not too distant future QCL devices will replace Fourier transform spectrometers in the far and mid-infrared spectral regions, by providing vastly improved sensitivity at high resolution. The opportunity has arisen for the MSF to participate in the development of external cavity QCL spectrometers through collaboration with Princeton University in the USA. Initially this will involve a two-week visit by MSF staff to assess the technology and plan a development project.

Renewal of the long path cell vacuum system

During 2007/8 three large vacuum pumps were procured following a successful £50k bid to NERC Services and Facilities to replace the aging pumps attached to the long path absorption cell. 2008/9 will see the new oil-free pumps installed along with new automatic valves, gauges and control systems.

