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MEASUREMENTS OF STRATOSPHERIC COMPOSITION USING A STAR POINTING SPECTROMETER

Deb J. Fish, Rod L. Jones, Ray A. Freshwater
Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge CB2 1EW, UK

Howard K. Roscoe, Derek J. Oldham
British Antarctic Survey, High Cross, Madingley Rd, Cambridge CB3 0ET, UK

ABSTRACT

Measurements of stratospheric composition have been made with a novel star-pointing spectrometer, as described in a companion paper by Roscoe et. al. (this Symposium). The instrument consists of a telescope that focuses light from stars, planets, or the moon onto a spectrometer and two dimensional CCD array detector. Atmospheric absorptions can be measured, from which atmospheric columns of several gases can be determined. The instrument was deployed in Abisko, 69°N, during the European Arctic Stratospheric Ozone Experiment (EASOE). The instrument has the potential for measuring O_3, $OClO$, NO_2, and NO_3. In this paper, a method for the retrieval of vertical columns is described, and some examples of ozone measurements given.

ANALYSIS METHOD

The stellar spectrum recorded by the instrument consists of the extra-terrestrial spectrum, minus light which has been scattered out of the beam by molecules (Rayleigh scattering), and by aerosol (Mie scattering), or absorbed by atmospheric constituents. In order to retrieve vertical columns, two spectra of the star at different elevations are required (fig. 1). The intensities of light I_1 and I_2, measured at low and high elevation angles can be denoted by:

$$I_1 = FI_0 \exp(-\Sigma \sigma_i c_{i,1})$$

$$I_2 = FI_0 \exp(-\Sigma \sigma_i c_{i,2})$$

where I_0 is the extraterrestrial spectrum, F is the instrument function, σ_i is the absorption cross-section of absorber i, and $c_{i,1}$ and $c_{i,2}$ are the slant columns of absorber i in the two spectra. All are functions of wavelength.
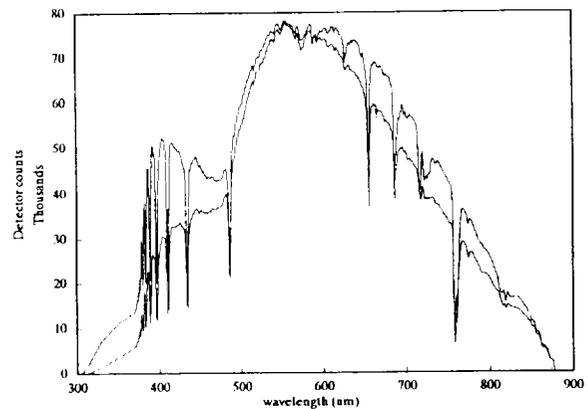

Figure 1. Spectra of Vega at high and low elevation angles. Cubic interpolation is used to place the spectra and absorption cross-sections onto a wavelength grid extending from 270 to 900 nm in 0.5 nm intervals.

If the ratio of the two spectra is taken, the instrument function and extraterrestrial spectrum cancel, so do not need to be measured. The only difference between the two spectra is the length

of atmospheric path that the light traverses. The natural logarithm of this ratio is thus a linear combination of atmospheric absorber cross-sections, the coefficients being the differences in absorber slant column between the two spectra:

$$-\ln(I_1/I_2) = \Sigma \sigma_i(c_{i,1} - c_{i,2})$$

Mie scattering of light by atmospheric aerosol depends on particle size, shape, and composition. Since these are not known, Mie scattering is assumed to be a smoothly varying function of the wavelength of the light. This is a reasonable approximation if the aerosol has a broad size distribution. To remove this unknown, a quadratic polynomial is fitted to $-\ln(I_1/I_2)$. Subtraction of this polynomial from $-\ln(I_1/I_2)$ removes all smoothly varying absorptions, including the unknown Mie scattering, and gives a so called 'differential' spectrum. The same filter is applied to the absolute absorption cross-sections. Analysis involves obtaining the best fit of laboratory differential cross-sections of different gases to the measured differential ratio spectrum (fig. 2).

INITIAL PROCESSING OF STELLAR SPECTRA

For this instrument, the first step in processing the stellar spectra is to subtract dark current, and correct for the difference in responsivity of adjacent pixels in the CCD array (typically 1-2%). Differences in response of individual pixels were measured using light from a quartz halide lamp, with a tungsten filament, scattered from a diffuse reflector, enabling a correction to be made (fig. 3).

Fluctuations in spectrometer temperature cause wavelength calibration to vary. Wavelength calibration is obtained by repeatedly varying shift and stretch and analysing for all constituents, until a minimum residual is found.

RETRIEVAL METHODS

The method of least squares is widely used to solve over constrained problems such as retrieval of absorber slant columns. We are currently investigating this and a second techniques: optimal estimation (Rodgers 1976). Optimal estimation involves the generation of a weighting function matrix, K, to relate the observation, y (a column vector containing values of $\ln(I_1/I_2)$ at each wavelength) to the column vector of absorber slant columns, x:
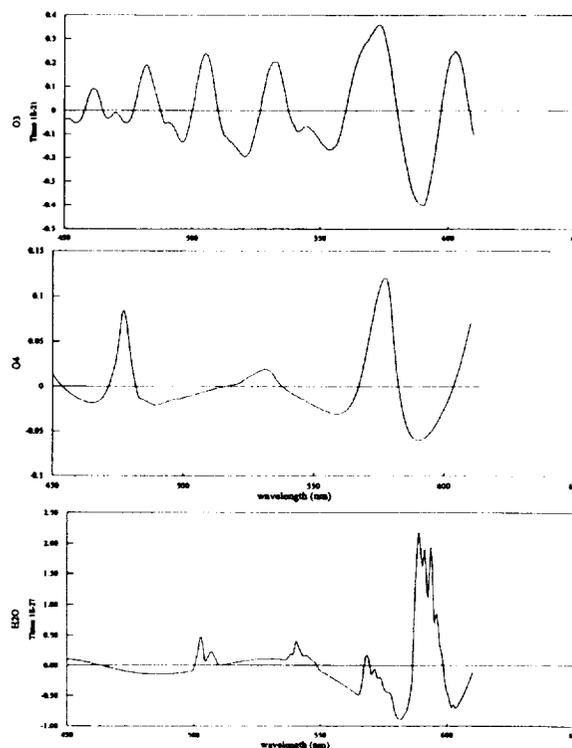

Figure 2. 'Differential' cross-sections used in the 450 - 610 nm region. Differential cross-sections were calculated by fitting a quadratic across the entire analysis region, excluding data within 3 nm of the Balmer line at 486 nm.
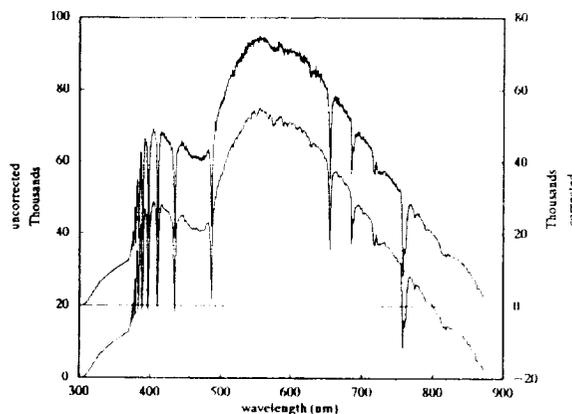

Figure 3. A spectrum of Vega before and after correction for inter-pixel variability.

672

$$y = Kx$$

The weighting function matrix may be calculated using a so called forward model, in which spectra are synthesised with different amounts of each constituent in turn, and the effect on the observation calculated. However, in our case, the weighting function is composed of the differential cross-sections.

One way of calculating absorber slant columns is to take an *a priori* estimate of each slant column, and improve it by inclusion of measurements at each wavelength in turn, inversely weighted by their variances; the technique of sequential estimation. The weighting function for the first wavelength at which we have an observation is used to calculate a value of the observation at that point from the first guess. The first guess is improved, according to the size of the difference between the expected and observed values of y, and the magnitude of the weighting functions for each constituent. The updated value of the first guess is then improved upon by inclusion of the next data point.

The sequential estimation equations for calculation of the absorber slant columns, and their variances, are:

$$x_i = x_{i-1} + S_{i-1}k_i \, (y_i - k_i^T x_{i-1})/(\, k_i^T S_{i-1} k_i + \sigma^2)$$

$$S_i = S_{i-1} - S_{i-1}k_i k_i^T S_{i-1} / (\, k_i^T S_{i-1} k_i + \sigma^2)$$

for $i = 1$ to M, M being the number of wavelengths for which data is available.
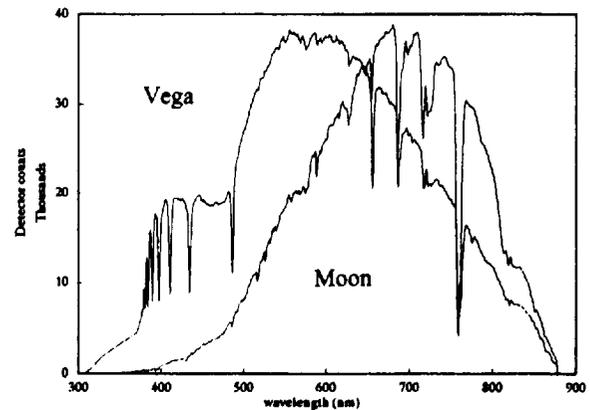
The measurement vector y is treated as series of scalars, y_i. k_i is the ith row of the weighting function matrix, K. σ is the standard deviation of the measurement. S_i is the variance of the solution after inclusion of the ith measurement. The optimal value of x, the matrix of absorber slant columns is that obtained after inclusion of all data points, i.e. x_M, and is independent of the order in which the measurements are combined for a linear problem such as this.

Optimal estimation has certain advantages for measurements with low signal-to-noise ratios, whilst tending towards the same solution as least squares as signal-to-noise ratios increase. Inclusion of an *a priori* value for each slant column steers the system away from any false minima lying outside the region enclosed by the variance of the first guess. The greatest benefits of optimal estimation will be seen when

systematic errors are reduced so that random noise dominates. The photon noise on the measurement varies with wavelength, and sequential estimation can weight measurements accordingly. The propagation of random measurement errors into the retrieved quantities can be calculated.

COMPARISON OF LUNAR AND STELLAR SPECTRA

Provisional retrievals performed on lunar and stellar spectra taken on the same night have been in excellent agreement. On 18/19 January 1992, analyses of two pairs of lunar spectra gave ozone values of 320 and 321 Dobson Units, while analysis of a pair of spectra from Vega gave 328 Dobson Units (figs. 4 and 5).

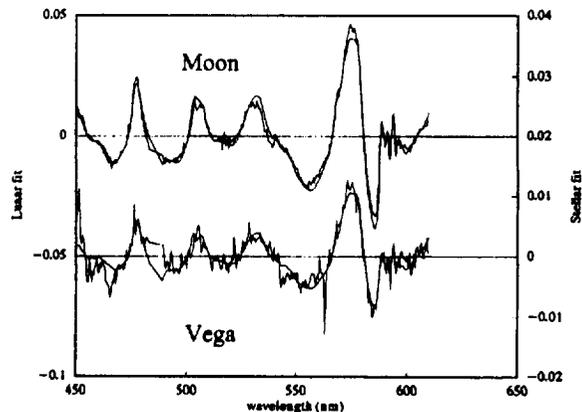4. Spectra of the moon and Vega collected on 18/19 January 1992.

Figure 5. Measured differential ratio spectra, and retrieved fit of differential cross-sections, for the lunar and stellar spectra of fig. 4.

FUTURE DEVELOPMENT

In addition to O_3 columns, we expect to be able to retrieve OClO and possibly NO_3 from stellar spectra, when systematic errors are reduced. We are planning to deploy two star-pointers at different latitudes in the Winter of 1992-3, and also hope to be able to interpret spectra collected with telescopes belonging to the Royal Greenwich Observatory. Columns of NO_2 in the Arctic Winter stratosphere are too low to be measured by this instrument in star pointing mode. However, the instrument can also be used in zenith sky mode, and NO_2 columns should be retrievable given the high stratospheric air mass factors (about 20) attainable from such spectra.

REFERENCES

Rodgers, C.D., Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation, Rev. Geophys. Space Phys. 14, 609-624, 1976

Roscoe, H.K., R.L. Jones, R.A. Freshwater, J.E. Harries, R. Wolfenden, P. Stone, D.J. Fish, A star pointing UV-visible spectrometer for remote sensing of the stratosphere, Proc. Quadrennial Ozone Symposium, Charlottesville, 4-13 June 1992