Research Objectives

A quantitative understanding of photolysis rate coefficients (or "j-values") is essential to determining the photochemical reaction rates that define ozone loss and other crucial processes in the atmosphere. j-Values can be calculated with radiative transfer models, derived from actinic flux observations, or inferred from trace gas measurements. The primary objective of the present effort was the accurate calculation of j-values in the Arctic twilight along NASA DC-8 flight tracks during the second SAGE III Ozone Loss and Validation Experiment (SOLVE II), based in Kiruna, Sweden (68°N, 20°E) during January–February 2003. The JHU/APL radiative transfer model was utilized to produce a large suite of j-values for photolysis processes (over 70 reactions) relevant to the upper troposphere and lower stratosphere. The calculations take into account the actual changes in ozone abundance and apparent albedo of clouds and the Earth surface along the aircraft flight tracks as observed by in situ and remote sensing platforms (e.g., EP-TOMS).

A secondary objective was to analyze solar irradiance data from NCAR’s Direct beam Irradiance Atmospheric Spectrometer (DIAS) on-board the NASA DC-8 and to start the development of a flexible, multi-species spectral fitting technique for the independent retrieval of \( O_3 \), \( O_2-O_2 \), and aerosol optical properties.

Progress and Results

1. Photolysis Rate Coefficient (j-value) Calculations

The SOLVE II j-value calculations were performed using the JHU/APL radiative transfer model, which has been developed over the course of past aircraft missions [Anderson and Meier, 1979; Meier et al., 1982; Anderson, 1983; Anderson and Lloyd, 1990; Anderson et al., 1995; DeMajistre et al., 1995; Swartz et al., 1999; Swartz, 2002]. The version of the model used in SOLVE II is virtually identical to that used for the first SOLVE mission [Swartz, 2002]. The model includes
the effects of refraction (important at large solar zenith angles, SZAs), and extensive comparisons have shown that this technique provides reliable estimates of the radiation field for SZAs of up to 95° [Anderson, 1983; Dahlback and Stamnes, 1991; Gao et al., 2001]. The j-values computed from the model radiation field are based on recent molecular data [DeMore et al., 1997; Sander et al., 2000].

A comprehensive ozone/pressure/temperature climatology was adopted as a baseline description of the atmosphere [Swartz, 2002]. Earth Probe TOMS satellite data [McPeters et al., 1998] were utilized, as in POLARIS and SOLVE, along with the addition of in situ ozone data. The APL model was used in a number of different “modes” to simulate photolysis rate coefficients along DC-8 flight tracks (denoted APLclim[*] and APLTOMS[*]). The differences between the various j-value modes reflect how different model inputs were utilized. The APLTOMS mode was based on TOMS level 2 data (total column ozone, UV effective reflectivity, and cloud fraction), while the APLclim mode relied wholly on climatological data. The ‘*’ed variants of each model mode, APLclim* and APLTOMS*, also incorporated in situ ozone data from the DC-8 [Swartz, 2002].

A summary plot of the j-value calculations is shown in Figure 1. The values of $j_{NO_2}$ and $j_{O_3}$ are shown as representative j-values, along with the SZA, surface albedo, and overhead ozone (vertical) column—the major determinants of j-values [Swartz et al., 1999].

2. Multi-Species Spectral Fitting Technique using DIAS Solar Irradiance

The NCAR Direct beam Irradiance Atmospheric Spectrometer (DIAS, PI: Rick Shetter) measured solar irradiance spectra at 290–630 nm during 11 DC-8 flights. We adapted the MSX/UVISI stellar occultation retrieval [Yee et al., 2002; DeMajistre and Yee, 2002], used in the analysis of ozone loss during the first SOLVE mission [Swartz et al., 2002; Swartz, 2002], to provide for the simultaneous, multi-spectral retrieval of slant column O$_3$, O$_2$:O$_2$, and aerosol optical thickness from the DIAS spectra.

Several fitted spectra from the 6 February 2003 flight in Figure 2 show the goodness of the retrieval fit. The transmission spectra at five SZAs are shown, ranging from 78° to 92°. The fits are excellent, even in the near-UV and when the Sun was barely above the horizon, demonstrating the quality of the DIAS irradiance measurements and the robustness of the fits. At 92°, the devia-

1See http://cloud1.arc.nasa.gov/solveII/instrument_files/03.pdf.
Figure 1. SOLVE II DC-8 flight synopsis (see caption on page 2).
Figure 2. Goodness of fits. (a) DIAS transmission spectra at five SZAs, $78^\circ$–$92^\circ$, from the 6 February 2003 DC-8 flight, with fitted spectra overlaid. (b) Relative transmission difference, (DIAS/fitted spectra) −1, with the same SZA color-coding as (a).

Measurements at the shortest wavelengths are possibly due to a combination of factors, including imprecise wavelength registration with the temperature-dependent ozone cross sections, signal-to-noise limitations, and atmospheric scattering into the DIAS field of view. The retrieval technique is weighted by the measurement precision; thus the signal from the diminished-UV region (and its relatively larger error) contributes less to the fit at large SZAs, and the retrieved parameters are determined by the visible part of the spectrum.

A paper, “Column Ozone and Aerosol Optical Properties Retrieved from Direct Solar Irradiance Measurements during SOLVE II,” describing the adaptation of this sophisticated and robust technique and its excellent comparison with the Ames Airborne Tracking Sunphotometer has recently been published in the SOLVE II special issue of *Atmospheric Chemistry and Physics* [Swartz et al., 2005].
Publications (supported by this grant)


References


