Final Report: Summary of Research for NASA ACMAP NAG-1-2270

Photolysis Rate Coefficient Calculations in Support of SOLVE Campaign

Principal Investigator: Steven A. Lloyd

Co-Investigator: William H. Swartz

Organization: Atmospheric and Ionospheric Remote Sensing Group
The Johns Hopkins University Applied Physics Laboratory
11100 Johns Hopkins Road
Laurel, Maryland 20723-6099
240-228-8164
240-228-6670 (fax)
steven.lloyd@jhuapl.edu

Date: November 20, 2001

Research Objectives

The objectives for this SOLVE project were 3-fold. First, we sought to calculate a complete set of photolysis rate coefficients (j-values) for the campaign along the ER-2 and DC-8 flight tracks. En route to this goal, it would be necessary to develop a comprehensive set of input geophysical conditions (e.g., ozone profiles), derived from various climatological, aircraft, and remotely sensed datasets, in order to model the radiative transfer of the atmosphere accurately. These j-values would then need validation by comparison with flux-derived j-value measurements. The second objective was to analyze chemistry along back trajectories using the NASA/Goddard chemistry trajectory model initialized with measurements of trace atmospheric constituents. This modeling effort would provide insight into the completeness of current measurements and the chemistry of Arctic wintertime ozone loss. Finally, we sought to coordinate stellar occultation measurements of ozone (and thus ozone loss) during SOLVE using the MSX/UVISI satellite instrument. Such measurements would determine ozone loss during the Arctic polar night and represent the first significant science application of space-based stellar occultation in the Earth’s atmosphere.

Summary of Progress and Results

Photolysis Rate Coefficients during SOLVE

The model calculation of j-values plays a vital role in the photochemical analysis of the chemistry of ozone production and loss in the SOLVE campaign. Building upon our j-value modeling success in POLARIS [Swartz et al., 1999], the sophistication of the input of geophysical data to the APL radiative transfer model was increased in order to cope with the high−solar zenith angle (SZA) conditions found in polar winter. A comprehensive ozone/pressure/temperature climatology
was adopted as a baseline description of the atmosphere. Earth Probe Total Ozone Mapping Spectrometer (TOMS) satellite and Composition and Photodissociative Flux Measurement (CPFM) spectroradiometer [McElroy, 1995] data were utilized, as in POLARIS, along with the addition of remote sensing data from the Polar Ozone and Aerosol Measurement (POAM) III satellite instrument and in situ ozone data. The model inputs have been compared and the impact on j-value calculations examined along the ER-2 and DC-8 flight tracks.

The DC-8 j-values were also compared with the Scanning Actinic Flux Spectroradiometer (SAFS) [Shetter and Müller, 1999], which measured the 4π actinic flux on board the DC-8, for the first time. The overall model–measurement agreement for the DC-8 was excellent, within ~5% for \( j_{NO_2} \) (\( NO_2 \rightarrow NO + O(3P) \)) and ~10% for \( j_{O_3} \) (\( O_3 \rightarrow O_2 + O(1D) \)). This extensive comparison also revealed a curious bias in \( j_{NO_2} \) that is consistent with the attenuation of light by polar stratospheric clouds (PSCs). In Figure 1, model calculations utilizing TOMS (APLToMS) and climatological (APLclim) data are compared with SAFS measurements. In the 20000123, 20000125, and 20000308 flights, where PSCs were particularly prevalent, model–measurement agreement deviates significantly from the average. During these high-PSC flights, the measured j-values were lower than the model calculations. The effect is most noticeable at high SZAs (Figure 1b), when Sunlight would have passed nearly horizontally through the putative cloud layers.

**NASA/Goddard Chemistry Trajectory Modeling of SOLVE in situ Measurements**

The NASA/Goddard trajectory chemistry model, initialized with ER-2 data, has been used to evaluate heterogeneous processing and radical photochemistry within the winter 1999–2000 Arctic polar vortex. From this preliminary look, we have found that the model reproduces midlatitude and polar extravortex chemistry with a level of model–measurement agreement comparable to that found during POLARIS [Pierson et al., 2000]. Within the vortex, however, there are inconsistencies that warrant further study.

**HO\(_x\) partitioning.** Similar to POLARIS, the model under-predicts extravortex OH and HO\(_2\) individually by about 20% and OH/HO\(_2\) by approximately 5% on average. The model over-predicts OH/HO\(_2\) by more than 50% within the vortex, using JPL97 cross sections/quantum yields and kinetics, with the addition of more recent OH+NO\(_x\) data. The use of JPL00 j-data leads to better agreement in HO\(_2\) outside the vortex (see Figure 2, for example), with OH/HO\(_2\) still matching well. Using JPL00 k-data and j-data increases HO\(_2\) outside the vortex (now over-predicting HO\(_2\)) and worsens the OH/HO\(_2\) agreement. OH/HO\(_2\) (when the Sun is up) is dominated by HO\(_2\)+ClO, OH+O\(_3\), and OH+ClO (HOCl+hv is often marginally rate-limiting). OH+ClO must be included in the steady-state HO\(_x\) equation inside the vortex. Steady-state calculations based on model concentrations agree well with modeled values (good approximation of important HO\(_x\) chemistry). Extravortex HO\(_x\) steady-state calculations using measured NO, O\(_3\), CO, and ClO are lower than measured OH/HO\(_2\) and about 50% high within vortex. This is slightly improved by substituting the HO\(_2\)+ClO term with \( j_{HOCl}/HO_2\), dependent on the choice of measured or modeled [HO\(_2\)]. HO\(_x\) within the vortex is improved further by using Cl\(_y\) (below).

**HCl measurements.** During many of the SOLVE vortex survey flights, the model over-predicts HCl destruction (even with heterogeneous processing disabled). This disagreement disappears in
Figure 1. Comparison of (a) APL_TOMS and SAFS (measured; SZA < 85°) and (b) APL_clim and SAFS (measured; SZA ≥ 85°) $j_{\text{NO}_2}$ along the DC-8 flight tracks during SOLVE. Each science flight is identified by a unique symbol, as keyed at right.
Figure 2. Inside–outside polar vortex comparison of in situ measured trace gases with modeled chemistry along trajectories for the March 11, 2000 SOLVE ER-2 flight. Measured quantities (solid lines) are shown, along with calculations made with the Goddard trajectory chemistry model along 10-day trajectories (+) using DAO meteorological fields. The chemical model was initialized with measured NOx, NOy, ClO, ClONO2, HCl, Cly, Bry, HOx, H2O, in situ O3 (fixed), overhead O3 column, aerosols, and surface albedo. The shaded area indicates the extra-vortex segment of the flight. The accuracy of modeling of the HOx budget outside the vortex is comparable (or better) to that found during POLARIS. Significant discrepancies are found within the vortex, however.
March as the vortex warmed and weakened. Temperatures must be increased uniformly by 2–5 K to keep prevent HCl from being destroyed. HCl measurements are not correlated with solar zenith angle, latitude, N₂O, temperature, or altitude (but there is greater HCl variability at around 20 km).

\textit{Cl\textsubscript{y} partitioning.} Cl\textsubscript{y} is in good agreement with the N₂O correlations of R. J. Salawitch. There is too much Cl activation (ClO, ClONO\textsubscript{2}) within the vortex. Using JPL00 data provides no ClO\textsubscript{x} improvement. Use of Cl\textsubscript{y}* = measured HCl+ClONO\textsubscript{2}+ClO+2ClOOCI/non-(HOCI+2Cl\textsubscript{2}) fraction of modeled Cl\textsubscript{y} reduces Cl activation. Cl\textsubscript{y}* , however, does not equal Cl\textsubscript{y}, even outside the vortex, so there is likely a problem with the measured Cl\textsubscript{y} budget.

\textbf{Photochemical Ozone Loss Determined by MSX/UVISI Stellar Occultation}

The combined SOLVE campaign sought, in part, to quantify ozone loss within the Arctic polar vortex using a variety of aircraft-, balloon-, ground-, and space-based instrument platforms. The Midcourse Space Experiment (MSX)/Ultraviolet and Visible Imagers and Spectrographic Imagers (UVISI) suite of instruments performed 31 stellar occultation observations from January 23 through March 4, 2000, in and near the Arctic polar vortex. Using a newly developed, combined extinctive–refractive algorithm \cite{Yee et al., 2001}, ozone mixing ratio profiles, along with profiles of total density, pressure, and temperature, were retrieved. Retrieved temperature and ozone profiles were shown to agree well with other measurements. Diabatic trajectory calculations were used to remove the effects of subsidence within the vortex, allowing photochemical ozone loss to be inferred from these occultation measurements. A maximum ozone loss of about 1 ppmv was found at 400–500 K (\textsim 16–21 km), as shown in Figure 3, during the 41-day period for which occultation data are available, in agreement with several other ozone loss analyses of the campaign \cite{Newman et al., 2001}. This corresponds to an average daily loss rate of \textsim 0.024 ppmv/day. If we assume an average loss rate of 0.05 ppmv/day for the second week in March, a total loss of 1.4 ppmv for 1/20–3/12/2000 is inferred, corresponding to the comparison reported by Newman \textit{et al.} \cite{2001}. The combined extinctive–refractive stellar occultation technique has now been demonstrated to accurately measure stratospheric ozone loss during polar winter \cite{Swartz et al., 2001}. 
Figure 3. Profiles of the average daily rates of ozone change and total ozone destruction, from January 23 to March 4, 2000. The results from three different but related methods, utilizing average vortex descent rates and two analyses using individual diabatic trajectory calculations, are shown. The data have been averaged over 25-K layers, and the lined region contains the average 1-σ uncertainties of the linear fits of the ozone measurements (and thus the rates of ozone change) on the individual diabatic surfaces within each layer.
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References


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