Final report for Theoretical Investigations of Clouds and Aerosols in the Stratosphere and Upper Troposphere (NAG5-11243)

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Abstract of Research Objectives

During the past few years my group has completed a number of projects under the support of the Atmospheric Chemistry Modeling and Data Analysis Program. We investigated a wide variety of issues involving ambient stratospheric aerosols, polar stratospheric clouds or heterogeneous chemistry, analysis of laboratory data, and particles in the upper troposphere. The papers resulting from these studies are listed below. In addition, I participated in the 1999-2000 SOLVE mission as one of the project scientists and in the 2002 CRYSTAL field mission as one of the project scientists. Several CU graduate students and research associates also participated in these mission, under support from the ACMAP program, and worked to interpret data.

A. Summary of Progress and Results

As outlined in the references below we have worked on a number of issues. We previously used a two dimensional model to show that downward transport of sulfur dioxide in the polar night could lead to the formation of new particles during polar spring as observed. For this to happen sulfuric acid must photolyse. However, lab data of Burkholder, Mills and McKeen (2000) shows that sulfuric acid does not easily photolyse in the uv. These lab data causes major problems in understanding SO_2 data as well. During the past year Veronica Vaida and colleagues proposed a new photolysis mechanism by which infrared light allows uv to photolyse sulfuric acid. We have put this new mechanism into our two dimensional model and find we can now get agreement with SO_2 measurements as well as reproduce the polar CN layer. We have now published a paper on this issue (Mills et al., 2005). In addition we have worked on sulfur isotopes following the Pinatubo eruption. Ice core data show mass independent fractionation of the sulfur isotopes following the eruption, which is not expected. Pavlov et al (2005) were able to show that if the fractionation step involves SO_3 photolysis we can understand the data. This work has future applications to understanding atmospheric sulfur chemistry, and understanding oxygen levels on Earth prior to 2 billion years ago.

We have finished a series of papers on the SOLVE and CRYSTAL data sets concerning nitric acid. We published a paper with Y. Kondo concerning the deposition of nitric acid on ice. We find significant amounts of nitric acid are on the ice below 215K, in agreement with lab data obtained in the Tolbert lab (Hudson et al, 2002). However, at warmer temperatures little nitric acid seems to be on the ice. More surprisingly we find more nitric acid on the ice than the lab data suggest. We have two papers submitted by B. Gamblin, a graduate student, in which we show that another NOy constituent is condensing. The various atmospheric data sets disagree strongly on the amount of nitric acid condensing. We find many of these problems are related to the kinetics of nitric acid condensation. Indeed one can use the nitric acid found on ice crystals as a clock to measure the cloud lifetime. During CRYSTAL, data from Gao et al (2004) showed that the supersaturation of water over ice seems to be effected by the nitric acid on the ice. We proposed a mechanism to explain how this might happen and are continuing to explore this data set for further clues.

We published two papers on the MASP PSC particle data from SOLVE I. We find the MASP large particle data correlates very well with the Fahey NO_Y data, but there is an offset in the actual mass. We also produce the first mass/temperature data that clearly shows that these large particles are NAT or NAD. We also show that the lidar data obtained on the NASA ER-2 in PSCs is consistent with the MASP particle sizes. We also participated in writing the SOLVE overview paper (Newman et al. 2002).

We also conducted analyses of laboratory data to find the optical properties of water ice in the far infrared. Water ice is observed in the far infrared via satellite, and existing optical constants were in conflict. We made new measurements and showed how data reduction errors hurt some of the previous data (Rajaram et al., 2005). This work will complete our studies of the optical constants of water ice. A student completed and published a paper on water vapor absorption by clay minerals (Frinak et al., 2005). We find above a certain relative humidity threshold that the clays take up water inside their lattice. This work is likely to lead to some surprising new results about nucleation in the atmosphere in the next year or so.

B. Journal Publications:

<u>Papers about ambient stratospheric aerosols</u>:

1. Burkholder, J., M. Mills, S. McKeen, Upper limit for the UV absorption cross sections of H2SO4, Geophys. Res. Lett., 27, 2493-2496, 2000.
2. Kalashnikova, O., M. Horanyi, G. E. Thomas, and O. B. Toon, Meteoric smoke production in the atmosphere, Geophys. Res. Lett., 27,3293-3296, 2000.
3. Mills, M. J., O. B. Toon, V. Vaida, P. E. Hintze, H. G. Kjaergaard, D. P. Schofield, and T. W. Robinson, Photolysis of sulfuric acid vapor by visible light as a source of the polar stratospheric CN layer, J. Geophys. Res., 110,D08201 doi 10.1029/2004JD005519, 2005.
4. Pavlov, A. A., M. J. Mills, O. B. Toon, Mystery of the volcanic mass-independent sulfur isotope fractionation signature in the Antarctic ice-core, Geophys. Res. Lett., 32, L12816, doi:10.1029/2005GL022784, 2005.

<u>Papers about polar stratospheric clouds or heterogeneous chemistry</u>

1. Toon, O. B., Azadeh Tabazadeh, Edward V. Browell, Joseph Jordan, Analysis of lidar observations of Arctic polar stratospheric clouds during January, 1989, *J. Geophys. Res., 105*, 20589-20616 (2000).
2. Tabazadeh, A., E. J. Jensen, O. B. Toon, K. Drdla, and M. R. Schoeberl, The role of polar freezing belt in stratospheric denitrification , *Science, 291*,2591, 2001.

3. Tolbert, M. A. and Owen B. Toon, Solving the PSC Mystery, *Science, 292*, 61, 2001.
4. Tabazadeh, A., K. Drdla, M. R. Schoeberl, P. Hamill, and O. B. Toon, Arctic "Ozone Hole" in a cold volcanic stratosphere, *Pub. Nat. Acad. Of Science, 99*, 2581-3356, 2002.
5. Paul A. Newman, P. A., Neil R. P. Harris, Alberto Adriani, Georgios Amanatidis, Jim Anderson Geir Braathen, William Brune, Ken Carslaw, Michael Craig, Philip DeCola, Marielle Guirlet, Steve Hipskind, Michael Kurylo, Harry Küllmann, Niels Larsen, Gérard Mégie, Jean-Pierre Pommereau, Lamont Poole, Mark Schoeberl, Fred Stroh, Brian Toon, Chip Trepte, and Michel Van Roozendael, An overview of the SOLVE-THESEO 2000 campaign, *J. Geophys. Res.* 107, 8259,doi10.1029/2001JD001303 (2002).
6. Jensen, E. J., O. B. Toon, A. Tabazadeh and K. Drdla, Impact of polar stratospheric cloud particle composition, number density, and lifetime on denitrification, ,*J. Geophys. Res.*, 107, 2000JD000227 (2002).
7. Brooks, S. D., B. Gandrud, D. Baumgardner,J. E. Dye, M. J. Northway, D. W. Fahey , O. B. Toon and M. A. Tolbert, Multiangle Aerosol Spectrometer Probe (MASP) Measurements of large Polar Stratospheric Particles in the Arctic Polar Vortex, *J. Geophys. Res.,* 108 D20 4652(2003).
8. S D. Brooks, B. Gandrud, D. Baumgardner, E. Browell, H Flentje, O B. Toon, M. A. Tolbert, "Polar stratospheric clouds during SOLVE/THESEO: Comparison of lidar observations with in situ measurements" *J. Geophys. Res.*109 (D2): Art. No. D02212 JAN 30 2004.

<u>Papers concerning analysis of laboratory data</u>

1. Rajaram, B., D. L. Glandorf, D. B. Curtis, M. A. Tolbert, O. B. Toon Temperature dependent optical constants of water ice in the near infrared: New results and critical review of the available measurements, *Appl. Opt. 40*, 44449-4462, 2001.
2. Hudson, P. K., J. E. Shilling, M. A. Tolbert, and Owen B. Toon, Uptake of nitric acid on ice at tropospheric temperatures: Implications for cirrus clouds, *J. Phys. Chem.*, A, 106, 9874-9882, (2002).
3. Rajaram, B. D. B. Curtis, O. B. Toon, and M. A. Tolbert Measurement of the temperature-dependent optical constants of water ice in the 15-200 μm wavelength region, Appl Optics, in press, (2005).
4. Frinak, E., C Mashburn, O. F. Toon and M. Tolbert, Infrared Characterization of Water Uptake by Low Temperature Na-Montmorillonite: Implications for Earth and Mars, J. Geophys. Res. Vol. 110, No. D9, D0930810.1029/2004JD005647, 2005.

<u>Papers about particles in the upper troposphere</u>

1. Jensen, O. B. Toon, S. A. Vay, J. Ovarlez, R. May, and P. Bui, C. Twohy, B. Gandrud, R. Pueschel, and U. Schuman, Prevelance of ice supersaturated regions in the upper troposphere: Implications for optically thin ice cloud formation, *J. Geophys. Res., 106*, 17253-17266, 2001.
2. Pfister, L., H. B. Selkirk, E. Jensen, M. R. Schoeberl, O. B. Toon, E. V. Browell, W. B. Grant, B. Gary, M. J. Mahoney, T. P. Bui, and E. Hintsa, Aircraft observations of thin cirrus clouds near the tropical tropopause, J. Geophys. Res., 106, 9765-9786, 2001.

3. Jensen, E., L. Pfister, A. S. Ackerman, A. Tabazadeh, and O. B. Toon, A conceptual model of the dehydration of air due to freeze-drying by optically thin, laminar cirrus rising slowly across the tropical tropopause, *J. Geophys. Res.*, 106, 17237-17252, 2001.
4. Y. Kondo, O. B. Toon, H. Irie, B. Gamblin, M. Koike, N. Takegawa, M. A. Tolbert, P. K. Hudson, A. A. Viggiano, L. M. Avallone , A. G. Haller, B. E. Anderson, G. W. Sachse, S. Vay, D. E. Hunton, J. O. Ballenthin, and T. M. Miller, Uptake of nitric acid on cirrus cloud particles in the upper troposphere and lowermost stratosphere, Geophys. Res. Lett., 30 (4): Art. No. 1154, (2003).
5. Gao, R. S., P. J. Popp, D. W. Fahey, T. P. Marcy, R. L. Herman, E. M.Weinstock, D. G. Baumgardner, T. J. Garrett, K. H. Rosenlof, T. L. Thompson, P. T. Bui, B. A. Ridley, S. C. Wofsy, O. B. Toon, M. A. Tolbert, B. Kärcher, Th. Peter, P. K. Hudson, A. J. Weinheimer, A. J. Heymsfield. Evidence that Nitric Acid Increases Relative Humidity in Low-Temperature Cirrus Clouds, *Science*303 (5657): 516-520, *2004*.
6. Gamblin,B., O. B. Toon et al.Condensation of nitric acid on ice : I Non-HNO3 constituent of NOy condensing on Low temperature upper Tropospheric Cirrus Cloud Particles, J. Geophys. Res. Submitted, 2005.
7. Gamblin, B., O. B. Toon, M. Tolbert, P. Hudson, et al., Condensation of nitric acid on ice: II kinetic limitations a possible clock for cloud parcel lifetimes, J. Geophys. Res. Submitted, 2005.