

Final Technical Report

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“Solar Effects on Global Climate Due to Cosmic Rays and Solar Energetic Particles”

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Summary of Research

During the period of time covered by this grant, we have studied the properties of naturally occurring atmospheric ions generated by galactic cosmic radiation in relation to their potential for enhancing the formation of condensation nuclei (CN), and contributing to solar-induced climate change.

Introduction: *In situ* measurements have shown evidence of large charged molecular clusters throughout the middle atmosphere [e.g. Arnold et al., 1977; Arnold and Henschen, 1978, 1982; Viggiano and Arnold, 1981; Hauck and Arnold, 1984; Eisele, 1986; 1988; Eichkorn et al., 2002]. The observed species are largely dominated by hydronium water aggregates, as well as nitrate and bisulfate clusters containing water, nitric acid and sulfuric acid ligands, although other ion sequences including organic species have been documented [e.g., Arijs, 1983, Eichkorn et al., 2002]. In the free troposphere and lower stratosphere, atmospheric ions are generated primarily by penetrating galactic cosmic radiation (GCRs). The GCR ionization rate varies with altitude and latitude, as well as with solar activity. This latter dependence potentially links solar variability with short-term climate change.

The modulation of GCR fluxes by solar activity can ultimately perturb the microphysical and optical properties of clouds, particularly in regions where the ionization rate is dominated by solar effects (e.g., in the upper troposphere, but also in the mesosphere where ionization is controlled by direct solar forcing). The optical properties of clouds affect Earth’s radiation balance, and hence the climate. A promising mechanism connecting solar variability to terrestrial climate involves the growth of condensation nuclei (CN) on large atmospheric ionic molecular clusters [Turco et al, 1998; Yu and Turco, 2000]. Some of these CN evolve into cloud condensation nuclei (CCN), which determine the microphysical and radiative properties of clouds [Yu and Turco, 2001]. Modulation of CN and CCN production rates can have an amplified impact on global climate forcing. Accordingly, causes of systematic changes in CN properties must be identified if the origin of climate variability is to be ascertained. Likewise, to properly discriminate man-made from natural contributions to global change requires a quantitative understanding of underlying natural variability.

Satellite observations have been interpreted to suggest that variations in global cloud cover are correlated with changes in the eleven-year solar cycle modulation of galactic cosmic rays entering the atmosphere [e.g., Svensmark and Friis-Christensen, 1997; Svensmark, 1998]. Svensmark and Friis-Christensen [1997; also Svensmark, 1998] have suggested that cloud

coverage varies by up to 3–4% corresponding to changes in galactic cosmic ray intensities of up to 20–25% over the 11-year cycle. This correlation applies mainly to low-level clouds over the oceans at mid-latitudes (since observations of clouds over land and at high latitudes are more uncertain).

Ion Cluster Model: In the course of this project, the fundamental properties of ionic clusters were studied with the aim of relating GCR ionization rates to aerosol (CN and CCN) production rates. In particular, we: i) identified and quantified a physical mechanism through which variations in GCRs can influence atmospheric opacity via the formation of CN from growing ion clusters; ii) developed a detailed kinetic model that simulates the processes controlling the formation and growth of charged molecular aggregates; iii) calculated and compiled basic thermodynamic and chemical kinetic parameters relative to ion cluster dynamics for families having atmospheric relevance; and iv) carried out preliminary model simulations for key ion sequences, and analyzed the results in relation to specific atmospheric phenomena. The work is discussed in detail in a series of papers supported under this grant [D'Auria, 2005; D'Auria and Turco, 2001a,b, 2004; D'Auria et al., 2004]. A synopsis of the findings is given below.

The time-dependent ion kinetic model developed under this grant predicts the rates of formation and concentrations of charged molecular aggregates, and follows their evolution toward macroscopic droplets [D'Auria and Turco, 2001a,b]. The model treats forward and reverse clustering reactions, as well as ion sources and sinks. Basic thermodynamic data used to determine equilibrium constants and rate coefficients (see below) were obtained by surveying the literature on existing experimental and computational results, but also by applying advanced quantum mechanical techniques to calculate cluster properties from first principles. Hence, in this work, a body of new information critical to the understanding of the physics of aerosol formation has been generated.

A computational approach provides detailed descriptions of the molecular structures and energetics that determine clustering mechanisms and pathways. We have now demonstrated that virtually all cluster species of atmospheric interest can be studied at an unprecedented level of detail using “hybrid” datasets such as those constructed under this project. The hybrid databases combine existing measurements (from the literature) with new and existing computational results, including predictions derived from “classical” physics models (e.g., the Thomson model for small charged “droplets”). These unique hybrid datasets allows cluster behavior to be extrapolated from microscopic, or molecular, scales to the macroscopic regime of aerosol microphysics, without the need for ad hoc assumptions about physical properties.

The key to the implementation of our model lies in the determination of thermochemical properties that apply to charged aggregates across their entire size range. At the scale of small clusters, where the classical Thomson model breaks down, the required data can be found in published data in certain cases. Alternatively, modern computational approaches are very successful in determining cluster properties in this regime [e.g., D'Auria, 2005]. By using high-level quantum mechanical calculations to quantify cluster equilibrium geometries and energies, we have been able to fill gaps in experimental measurements for small clusters. Moreover, such simulations provide significant guidance on, and validation of, the level of theory needed to achieve sufficient accuracy for atmospheric applications.

At larger cluster sizes, thermodynamic properties are asymptotically constrained by the macroscopic properties of the corresponding condensates (including the enthalpies and entropies of vaporization, heats of solvation, and so on). Typically, the systems studied show convergence between microscopic simulations and macroscopic observations—the latter represented by an appropriate form of the Thomson model—at cluster sizes of ~10-20 ligand molecules [Castleman et al., 1978; D'Auria and Turco, 2001b; D'Auria et al., 2004]. That is, for example, the enthalpy change upon adding or removing a single ligand from a cluster of a given size tends to converge toward the expected value for the bulk phase (e.g., the enthalpy of condensation/evaporation). We observe that the enthalpy change converges more decisively than the entropy change. Nevertheless, errors associated with the utilization of these data under atmospheric conditions are controlled by the uncertainty in enthalpy rather than entropy. Accordingly, the analytical approach is quite feasible. We have shown that quantum computational techniques are applicable to cluster systems of the appropriate transitional sizes (up to 10+ ligands), although computations of much larger clusters would be very difficult. The convergence of microscopic and macroscopic properties at intermediate cluster sizes is a fundamental characteristic defining the “hybrid” database developed in this project.

Once the thermodynamics of an ion cluster family is determined, the rate constants for specific clustering steps (that describe cluster growth and evaporation) can be calculated. First, note that the equilibrium constant for any clustering step is completely defined by the enthalpy and entropy changes associated with adding (or removing) one ligand to (from) the cluster. The quantum configurational simulations for the cluster family yield these enthalpy and entropy changes (direct measurements, when available, are also used). The forward reaction rate coefficient for each clustering step can be estimated independently using well-established ion-neutral collision theory [e.g., Su and Chesnavich, 1982]. For example, we utilized the COLRATE program for this purpose [Lim, 1994]. Finally, the reverse rate coefficient for the corresponding clustering step is determined by dividing the forward rate coefficient by the equilibrium constant for the process. At this point, the kinetics of each step in the clustering sequence is explicit, and the dynamic evolution of the system can be studied quantitatively for a wide range of environmental conditions.

Application: We specifically employed the computational approach described above to develop hybrid databases for the following ionic systems: hydronium-water clusters (i.e., one of the most important charged components of the middle atmosphere); nitrate anion-water, and nitrate anion-nitric acid clusters [D'Auria and Turco, 2001a,b]; and acetone and sulfuric acid clusters on hydronium and bisulfate core ions [D'Auria, 2005]. For the mixed protonated water and nitric acid system, we also carried out a detailed analysis of the cluster configurations and energy states, and the transitions between favorable molecular configurations (e.g., between nitronium and hydronium based mixed clusters) [D'Auria, 2005; D'Auria et al., 2004].

Our ion cluster model was applied to determine the distributions and activation of hydronium-based and nitrate-core clusters in the middle atmosphere, including the upper troposphere. This analysis points to the likelihood that an efficient ion-mediated nucleation mechanism operates in the upper troposphere, and also near the mesopause [D'Auria, 2005; D'Auria and Turco, 2004]. The ion families consisting of pure ligand shells (i.e., pure hydronium ions, and nitrate ions

clustered with either water or nitric acid) do not undergo nucleation under typical atmospheric conditions. An exception appears to be hydronium-water clusters at the very low temperatures encountered in the vicinity of the mesopause, where noctilucent clouds are observed. Importantly, the mixed ionic clusters containing very stable combinations of water and nitric acid offer very favorable sites for the nucleation of aerosols, particularly in the lower stratosphere [D'Auria and Turco, 2001a].

Under this grant, we also characterized more complex mixed clusters consisting of water, sulfuric acid, acetone and ammonia [D'Auria, 2005]. Massive clusters having such compositions have been detected through *in situ* measurements in the upper troposphere [e.g., Eichkorn et al., 2002]. Hence, these species will be included in kinetic studies of atmospheric aerosol formation as an extension of the work reported here. Our detailed results are described in the references listed below.

Conclusion: Although the work reported here does not directly connect solar variability with global climate change, this research establishes a plausible quantitative causative link between observed solar activity and apparently correlated variations in terrestrial climate parameters. Specifically, we have demonstrated that ion-mediated nucleation of atmospheric particles is a likely, and likely widespread, phenomenon that relates solar variability to changes in the microphysical properties of clouds. To investigate this relationship, we have constructed and applied a new model describing the formation and evolution of ionic clusters under a range of atmospheric conditions throughout the lower atmosphere. The activation of large ionic clusters into cloud nuclei is predicted to be favorable in the upper troposphere and mesosphere, and possibly in the lower stratosphere. The model developed under this grant needs to be extended to include additional cluster families, and should be incorporated into microphysical models to further test the cause-and-effect linkages that may ultimately explain key aspects of the connections between solar variability and climate.

No patents or inventions resulted from this project.

Grant-related Publications

- D'Auria, R., and R. P. Turco: Ionic clusters in the polar winter stratosphere. *Geophys. Res. Lett.*, 28, 3871–3874, 2001a.
- D'Auria, R., and R. P. Turco: A thermodynamic-kinetic model for ionic cluster formation, growth and nucleation. *Proc. Workshop on Ion-Aerosol-Cloud Interactions*, J. Kirkby, Ed., CERN, Geneva, CERN 2001-007, 2001b.
- D'Auria, R., R. P. Turco and K. Houk: Effects of hydration on the properties of protonated-water-nitric acid clusters. *J. Phys. Chem. A*, 108, 3756–3765, 2004.
- D'Auria, R., and R. P. Turco: Preliminary study on tropospheric ion-induced nucleation. *Proc. 14-th International Conference on Clouds and Precipitation*, Bologna, Italy, 19-23 July, 2004, Vol. 1, pp 55–58, 2004.
- D'Auria, R.: *A study of ionic clusters in the lower atmosphere and their role in aerosol formation*. PhD Dissertation, University of California, Los Angeles, 2005.

References

- Arnold, F., and G. Henschen: First mass analysis of stratosphere negative ions. *Nature*, 299, 134–137, 1978.
- Arnold, F., and G. Henschen: Positive ion composition measurements in the upper stratosphere—evidence for an unknown aerosol component. *Planet. Space Sci.*, 30, 101–108, 1982.
- Arnold, F., D. Krankowsky, and K. H. Marien: First mass spectrometric measurements of positive ions in the stratosphere. *Nature*, 267, 30–32, 1977.
- Arijs, E.: Positive and negative ions in the stratosphere. *Annales Geophysicae*, 1, 149–160, 1983.
- Castleman, A. W., Jr., P. M. Holland and R. G. Keese: The properties of ion clusters and their relationship to heteromolecular nucleation, *J. Chem. Phys.*, 68, 1760–1767, 1978.
- D'Auria, R.: *A study of ionic clusters in the lower atmosphere and their role in aerosol formation*. PhD Dissertation, University of California, Los Angeles, 2005.
- D'Auria, R., and R. P. Turco: Preliminary study on tropospheric ion-induced nucleation. Proc. 14-th International Conference on Clouds and Precipitation, Bologna, Italy, 19–23 July, 2004, Vol. 1, pp 55–58, 2004.
- D'Auria, R., and R. P. Turco: Ionic clusters in the polar winter stratosphere. *Geophys. Res. Lett.*, 28, 3871–3874, 2001a.
- D'Auria, R., and R. P. Turco: A thermodynamic-kinetic model for ionic cluster formation, growth and nucleation. Proc. Workshop on Ion-Aerosol-Cloud Interactions, J. Kirkby, Ed., CERN, Geneva, CERN 2001-007, 2001b.
- D'Auria, R., R. P. Turco and K. Houk: Effects of hydration on the properties of protonated-water-nitric acid clusters. *J. Phys. Chem. A*, 108, 3756–3765, 2004.
- Eisele, F. L.: Identification of tropospheric ions. *J. Geophys. Res.*, 91, 7897–7906, 1986.
- Eisele, F. L.: First tandem mass spectrometric measurement of tropospheric ions. *J. Geophys. Res.*, 93, 716–724, 1988.
- Eichkorn, S., S. Wilhelm, H. Aufmhoff, K. H. Wohlfrom and F. Arnold: Cosmic ray-induced aerosol-formation: First observational evidence from aircraft-based ion mass spectrometer measurements in the upper troposphere. *Geophys. Res. Lett.*, 29, 43-1–43-4, 2002.
- Hauck, G., and F. Arnold: Improved positive ion composition measurements in the upper troposphere and lower stratosphere and the detection of acetone. *Nature*, 311, 547–550, 1984.
- Lim, K. F.: Program COLRATE. QCPE 643: Calculation of gas-kinetic collision rate coefficients. *Quantum Chemistry Program Exchange*, 14 (1), 3, 1994.
- Su, T., and W. J. Chesnavich: Parameterization of the ion-polar molecule collision rate-constant by trajectory calculations. *J. Chem. Phys.*, 76, 5183–5185, 1982.
- Svensmark, H., and E. Friis-Christensen: Variation of cosmic ray flux and global coverage—A missing link in solar-climate relationship. *J. Atmos. Sol.-Terr. Phys.*, 59, 1225–1232, 1997.
- Turco, R. P., F. Yu and J.-X. Zhao: A new source of tropospheric aerosols: Ion-ion recombination. *Geophys. Res. Lett.*, 25, 635–638, 1998.
- Viggiano, A. A., and F. Arnold: The first height measurement of the negative ion composition of the stratosphere. *Planet. Space Sci.*, 29, 895–906, 1981.
- Yu, F., and R. P. Turco: Ultrafine aerosol formation via ion-mediated nucleation. *Geophys. Res. Lett.*, 27, 883–886, 2000.
- Yu, F., and R. P. Turco: From molecular clusters to nanoparticles: The role of ambient ionization in tropospheric aerosol formation. *J. Geophys. Res.*, 106, 4797–4814, 2001.