

Final Report: " Growth Rates of Freshly Nucleated Particles"  
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## Overview of achievements.

Our proposal for this project identified the following objectives. Our accomplishments are summarized along with the enumerated objectives.

(1) TDCIMS Instrumentation Development. We will replace the existing  $^{210}\text{Po}$  alpha source with a corona source for the ions used in the unipolar nanoparticle charger. We will also explore methods to eliminate ion-induced nucleation in  $^{210}\text{Po}$  bipolar chargers.

*Achievements (including papers on improved instrumentation for measuring sub-10 nm particles):* McMurry et al. (2009), Iida et al (2008a), Kuang et al. (2012b). Stolzenburg and McMurry (2008), McMurry et al (2011), Held et al (2008), Smith et al. (2008)

(2) Atmospheric Field Observations during the DOE “clear air” intensive field campaign. We will measure nanoparticle physical properties (size distributions with SMPS), physical/chemical properties (volatility and hygroscopicity nano-TDMA), cloud condensation nuclei (CCN) concentrations (DMT continuous flow CCN counter) and chemical composition (TDCIMS). We will aim to understand chemical processes responsible for nanoparticle growth rates and to quantify the impact of NPF on cloud condensation nuclei concentrations.

*Achievements (including work on improved models for atmospheric growth rates):* Iida et al. (2006), Iida et al. (2008b), Jiang et a. (2011 abc), Kuang et al. (2009), Kuang et al. (2010), Kuang et al. (2012a), Mikkonen et al. (2011a), Mikkonen et al. (2011b), Smith et al. (2007), Smith et al. (2010), Hamed et al (2011)

(3) Laboratory Studies. Laboratory studies aimed at elucidating the chemical mechanisms that contribute to high nanoparticle growth rates will be carried out. These studies include:

- (i) Uptake and gas/particle partitioning of aliphatic amines onto seed particles of varying acidities;
- (ii) Uptake and gas/particle partitioning of mono and di-carboxylic acids onto seed particles of varying acidities;
- (iii) Uptake and gas/particle partitioning of organonitrates onto seed particles of varying acidities;
- (iv) Measurement of the TDCIMS response to peroxy compounds; nitric, sulfuric, and carboxylic acid esters; and organonitrates;
- (v) The formation of organosulfates from pinonaldehyde.

*Achievements:* Grose et al. (2006), Smith et al. (2010), Hao et al. (2009), Hao et al. (2011), Zhao et al. (2011)

(4) Thermodynamic Model for Nanoparticle Composition. A model for nanoparticle growth rates is needed. Before this can be done, we need to understand factors that influence their equilibrium composition. Based on TDCIMS measurements we believe that organic acids and bases are major constituents of nanoparticles. We plan to study the thermodynamic properties of organic ions and salts formed from such compounds. The modeling work will be done in parallel with and supported by experimental studies of vapor pressures and particle composition.

Achievements: Barsanti et al (2009), Barsanti et al. (2011)

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Barsanti, K. C., P. H. McMurry, J. N. Smith, 2009, "The potential contribution of organic salts to new particle growth," *Atmospheric Chemistry and Physics* 8, 2949-2957.

Barsanti, K. C., J. N. Smith, and J. F. Pankow, 2011: Application of the np plus mP modeling approach for simulating secondary organic particulate matter formation from alpha-pinene oxidation. *Atmospheric Environment*, **45**, 6812-6819.

Grose, M., H. Sakurai, J. Savstrom, M. Stolzenburg, D. Kittelson, P. H. McMurry, 2006, "Physical properties of ultrafine diesel exhaust particles sampled downstream of a catalytic trap," *Environ. Sci. Technol.*, doi:10.1021/es052267+; Published on line 7/21/06.

Hamed, A., H. Korhonen, S. Sihto, J. Joutsensaari, H. Jarvinen, T. Petaja, F. Arnold, T. Nieminen, M. Kulmala, J. Smith, K. Lehtinen, and A. Laaksonen, 2011: The role of relative humidity in continental new particle formation. *Journal of Geophysical Research-Atmospheres*, **116**.

Held, A., G. Rathbone, and J. Smith, 2009: A Thermal Desorption Chemical Ionization Ion Trap Mass Spectrometer for the Chemical Characterization of Ultrafine Aerosol Particles. *Aerosol Science and Technology*, **43**, 264-272.

Hao, L., P. Yli-Pirila, P. Tiitta, S. Romakkaniemi, P. Vaattovaara, M. Kajos, J. Rinne, J. Heijari, A. Kortelainen, P. Miettinen, J. Kroll, J. Holopainen, J. Smith, J. Joutsensaari, M. Kulmala, D. Worsnop, and A. Laaksonen, 2009: New particle formation from the oxidation of direct emissions of pine seedlings. *Atmospheric Chemistry and Physics*, 8121-8137.

Hao, L., S. Romakkaniemi, P. Yli-Pirila, J. Joutsensaari, A. Kortelainen, J. Kroll, P. Miettinen, P. Vaattovaara, P. Tiitta, A. Jaatinen, M. Kajos, J. Holopainen, J. Heijari, J. Rinne, M. Kulmala, D. Worsnop, J. Smith, and A. Laaksonen, 2011: Mass yields of secondary organic aerosols from the oxidation of alpha-pinene and real plant emissions. *Atmospheric Chemistry and Physics*, **11**, 1367-1378.

Iida, K., M. Stolzenburg, P. H. McMurry, M. Dunn, J. Smith, F. L. Eisele, 2006, "Contribution of ion-induced nucleation to new particle formation: Methodology and its application to atmospheric observations in Boulder, CO," *J. Geophys. Res.* **111**, D23201.

Iida, K., M. R. Stolzenburg, P. H. McMurry, J. N. Smith, F. R. Quant, D. R. Obereit, P. B. Keady, G. Lewis, S. V. Hering, 2008a, "An ultrafine, water-based condensation particle counter and its evaluation under field conditions," *Aerosol Sci. Technol.* 42(10): 862-871. doi: 10.1080/02786820802339579.

Iida, K., M. R. Stolzenburg, P. H. McMurry, and J. N. Smith, 2008b, Estimating nanoparticle growth rates from size-dependent charged fractions: Analysis of new

particle formation events in Mexico City, J. Geophys. Res., **113**, D05207, doi:10.1029/2007JD009260.

Jiang J., J. Zhao, M. Chen, J. Scheckman, B. J. Williams, F. L. Eisele, P. H. McMurry, 2011a, "First Measurements of Neutral Atmospheric Cluster and 1-2 nm Particle Number Distributions During Nucleation Events," Aerosol science and Technology (Aerosol Research Letter). 45:ii-v. doi: 10.1080/02786826.2010.546817.

Jiang, J, Attoui, M., Heim, M., Brunelli, N. A., McMurry, P. H., Kasper, G., Flagan, R. C., Giapis, K., and Mouret, G., 2011b, "Transfer Functions and Penetrations of Five Differential Mobility Analyzers for Sub-2 nm Particle Classification," Aerosol Sci. Technol. **45**:480-492 doi: 10.1080/02786826.2010.546819.

Jiang, J. Chen, M., Kuang, C., Attoui, M., and McMurry, P. H., 2011c, "Electrical Mobility Spectrometer Using a Diethylene Glycol Condensation Particle Counter for Measurement of Aerosol Size Distributions Down to 1 nm," Aerosol Sci. Technol., 45:510-521. doi: 10.1080/02786826.2010.547538.

Kuang, C., P. H. McMurry, A. McCormick, 2009, "The Production of Cloud Condensation Nuclei from New Particle Formation Events," Geophysical Research Letters, 36:L09822, doi: 10.1029/2009GL037584.

Kuang, C. , Riipinen, I., S.-L. Sihto, M. Kulmala, A. V. McCormick, and P. H. McMurry, 2010, "An improved criterion for new particle formation in diverse atmospheric environments," Atmospheric Chemistry and Physics., **10**. doi: 10.5194/acp-10-1-2010

Kuang, C., M. Chen, J. Zhao, J. Smith, P. H. McMurry, J. Wang, 2012a, "Size and time-resolved growth rate measurements of 1 to 5 nm freshly formed atmospheric nuclei," Atmospheric Chemistry Physics, **12**: 3573-3589, doi: 10.5194/ 10.5194/acp-12-3573-2012.

Kuang, C., M. Chen, P. H. McMurry, J. Wang, 2012b, "Modification of Laminar Flow Ultrafine Condensation Particle Counters for the Enhanced Detection of 1 nm Condensation Nuclei," Aerosol Science & Technology **46**(3) 309-315 doi: 10.1080/02786826.2011.626815.

McMurry, P. H., A. Ghimire, K.-H. Ahn, H. Sakurai, M. Stolzenburg, and J. N. Smith, 2009, "Sampling Nanoparticles for Chemical Analysis by Low Resolution Electrical Mobility Classification," Environmental Science and Technology 43(13):4653-4658, doi: 10.1021/es8029335.

Mikkonen, S., S. Romakkaniemi, J. N. Smith, H. Korhonen, T. Petäjä, C. Plass-Duelmer, M. Boy, P. H. McMurry, K. E. J. Lehtinen, J. Joutsensaari, A. Hamed, R. L. Mauldin III, W. Birmili, F. Arnold, M. Kulmala, and A. Laaksonen, 2011a, "A statistical proxy for sulphuric acid concentration," Atmospheric Chemistry Physics, **11**: 11319-11334. doi: 10.5194/acp-11-11319-2011.

Mikkonen, S., H. Korhonen, S. Romakkaniemi, J. N. Smith, J. Joutsensaari, K. E. J. Lehtinen, A. Hamed, T. J. Breider, W. Birmili, G. Spindler, C. Plass-Duelmer, M. C. Facchini, and A. Laaksonen, 2011b: Meteorological and trace gas factors affecting the number concentration of atmospheric Aitken (D(p)=50 nm) particles in the continental

boundary layer: parameterization using a multivariate mixed effects model. *Geoscientific Model Development*, **4**, 1-13.

Smith, J. N., M. J. Dunn, T. M. VanReken, K. Iida, M. R. Stolzenburg, P. H. McMurry, G. Huey, 2007, "The chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth," *Geophysical Research Letters* **35**:L04808, doi:10.1029/2007GL0325237.

Smith, J. N., K. C. Barsanti, H. R. Friedli, M. Ehn, M. Kulmala, D. R. Collins, J. H. Scheckman, B. J. Williams, and P. H. McMurry, 2010, "Observations of aminium salts in atmospheric nanoparticles and possible climatic implications," *Proceedings of the National Academy of Sciences*, **107** (15), 6634-6639. doi: 10.1073/pnas.0912127107. (invited article).

Smith, J., and G. Rathbone, 2008: Carboxylic acid characterization in nanoparticles by thermal desorption chemical ionization mass spectrometry. *International Journal of Mass Spectrometry*, **274**, 8-13.

Stolzenburg, M. R., P. H. McMurry, 2008, "Equations governing single and tandem DMA configurations and a new lognormal approximation to the transfer function," *Aerosol Sci. Technol.* **42**(06):421-432, DOI: 10.1080/02786820802157823.

Zhao, J., J. N. Smith, F. L. Eisele, M. Chen, C. Kuang, and P. H. McMurry, 2011: Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements. *Atmospheric Chemistry and Physics*, **11**, 10823-10836.

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McMurry, P.H., C. Kuang, J. N. Smith, J. Zhao, and F. Eisele, 2011, "Atmospheric New Particle Formation: Physical and Chemical Measurements," Chapter 31, pp 681-696, in *Aerosol Measurement: Principles, Techniques, and Applications*. Editors: Kulkarni P., Baron P. A., Willeke K., John Wiley & Sons, New York.