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The Characterization of Atmospheric Aerosols: Application to Heterogeneous Gas-Particle Reactions

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The Characterization of Atmospheric Aerosols: Application to Heterogeneous Gas-Particle Reactions

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The objective of this collaborative research project is the measurement and modeling of atmospheric aerosols and heterogeneous (gas/aerosol) chemical reactions. The two major accomplishments are single particle characterization of tropospheric particles and experimental investigation of simulated stratospheric particles and reactions thereon. Using aerosol time-of-flight mass spectrometry, real-time size and composition measurements of single particles are performed on ambient aerosol samples. This technique allows particle size distributions for chemically distinct particle types to be described. The thermodynamics and chemical reactivity of polar stratospheric clouds are examined using vapor desposited thin ice films. Employing nonlinear optical methods, as well as other techniques, phase transitions on both water and acid ices are monitored as a function of temperature or the addition of gases.

Background and Research Objectives

Aerosol particles play a unique role in the physics and chemistry of our atmosphere and, as a result, are receiving increasing attention from the scientific community. Many atmospheric processes cannot be accurately described by only gas phase chemistry. Therefore, some other contributors, such as atmospheric particles, must be influencing or catalyzing atmospheric chemical reactions. The heterogeneous chemical reactions occurring on polar stratospheric cloud (PSC) particles contributing to ozone depletion in the Antarctic are a famous example. In the troposphere, aerosol particles participate in photochemical reactions related to urban air pollution. In addition, ambient particle concentration levels are known to affect human health. Although the effects of some of these processes have

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been recognized for over a decade, in many cases exact compositions of atmospheric particles are still not known. Therefore, the goal of this project is the characterization of atmospheric aerosol particles and heterogeneous (gas-particle) chemical reactions on aerosol surfaces.

Atmospheric aerosol measurements are carried out primarily at the University of California, Riverside (UCR). This research has included the development and instrumental calibration of a unique analytical method for aerosol characterization—aerosol time-of-flight mass spectrometry (ATOFMS). ATOFMS is employed for the real-time measurement of the size and composition of individual aerosol particles in polydisperse atmospheric samples. At Los Alamos National Laboratory (LANL), heterogeneous chemical reactions are studied on thin ice films that simulate PSC particles. The gas/ice interface is monitored using nonlinear laser spectroscopy. Complementary mass spectrometric analysis of the gas phase reagents and water vapor pressure allows us to investigate the phase diagram of PSC particles under stratospheric conditions.

Importance to LANL's Science and Technology Base and National R & D Needs

This work is one of the components of the new Atmospheric Science Initiative at LANL. The information obtained in the joint studies between UCR and LANL will be an invaluable contribution to existing atmospheric models that currently do not include processes involving aerosol particles. Most models can only account for processes involving atmospheric gas phase components. Part of the problem in developing an understanding of aerosols has been the lack of analytical instrumentation that probes the particles at the required level. Aerosols are much more difficult to study than gas phase species due to their complex and typically unstable nature. The ATOFMS system, by examining each particle in real time, will allow more accurate information to be obtained directly. Once the system is completely developed, the portable system can be transported to different parts of the world to obtain regional information on aerosols that can then be added to global models. In addition, this instrument can be used to directly

characterize many sources of aerosols, something which is essential to the development of adequate government regulations on aerosol particles.

One of the Laboratory tactical goals that this work supports is nonproliferation. The portable ATOFMS represents an advanced aerosol detection technology that we would like to test on chemical weapons surrogates in the near future. The results of the heterogeneous chemistry reaction studies will enhance our understanding of the effects of aerosols in the atmosphere. Because our methods are based on real time monitoring, a key advancement, errors associated with current methods of sampling and bulk analysis will be avoided. Kinetic data for heterogeneous reactions as a function of temperature and pressure may be expected to have significant impact on the scientific study of these atmospheric systems.

The compilation of data by the World Meteorological Organization is critical to the formation of international policies such as the U.N. Framework Convention on Climate Change and the Montreal Protocols. The data provided by the work proposed here could be expected to contribute directly to these concerns by providing accurate measures of the relative importance of heterogeneous reactions to ozone depletion mechanisms. Potential users for the data and/or a portable ATOFMS include EPA, NASA, DOE, and DoD.

Scientific Approach and Accomplishments

Tropospheric Aerosols. Work at UCR has focused on developing both a laboratory-based instrument and two field-portable instruments [1-4]. A schematic diagram of the laboratory-based ATOFMS system is shown in Figure 1. All ATOFMS systems combine the techniques of two-laser aerodynamic particle sizing with time-of-flight mass spectrometry. For the field portable instruments, dual polarity ion extraction into two separate mass analyzers is employed for bipolar ion detection. Though other rapid single-particle mass spectrometry methods can determine the composition of single particles, ATOFMS is currently the only method that allows for the real-time measurement of the size

and composition of single particles in a polydisperse aerosol sample. This is of importance because particle size is related to particle mobility and reactivity while composition determines the reactions in which a particle may participate.

As a demonstration of the capabilities of ATOFMS, a detailed study of ambient tropospheric particles was performed in spring 1995 at Riverside, CA [5,6]. Particles are sorted into chemically specific categories based on their mass spectra. Examples of several particle classes are shown in Figure 2. Based on the ion peaks that are present in the mass spectra and the measured particle size, possible aerosol sources can be identified. In Figure 2a, a spectrum of an organic particle is shown. Particles that provide similar mass spectra typically fall in the ~0.4-2.0 μm range. These particles are thought to be the byproducts of combustion processes (due to the carbon and hydrocarbon peaks) with potentially some secondary heterogeneous reactions with gas phase ammonia and nitric acid. An example of the inorganic/organic particle class is shown in Figure 2b. The size range in which this particle type is most often found is ~0.5-2.5 μm. This particle type is similar to the organic class, in that it contains carbon and hydrocarbon ions. However, it also contains peaks due to metal cations such as Na^+, V^+, Cr^+ and Fe^+. It is speculated that these particles are also produced by combustion. Figure 2c shows an example spectrum of the inorganic oxide particle class, which typically falls in the ~1.5-4.5 μm size range. Particles of this type mainly contain compounds of soil origin, such as Na, Mg, Al and Si, and are thought to be dust or soil particles that have been suspended in the atmosphere by wind.

Because the corresponding particle size is measured for each particle, size distributions of chemically specific classes can be plotted. In Figure 3, the size distribution of organic particles is plotted with the total particle size distribution. During this sampling period, there are two prominent modes, one centered at ~0.6 μm and the second centered at ~1 μm. The organic particles during this period are mainly associated with the smaller size mode while the larger mode is due to other particle classes.

Another project that has been recently started at UCR is the characterization of particles from known emission sources. To date, the general focus has been analyzing particles produced by combustion, including portable diesel engines, automobiles and brush fires. For the automobile particulate emissions study, various vehicle models and ages are of interest. Notable differences are apparent in particle size distribution and composition from vehicle to vehicle. One observable trend in the vehicles tested is that the older vehicles tend to emit larger particles than the newer vehicles. Also, due to the amount of wildfires in Southern California over each summer, initial investigations are being performed on the emissions from various samples of local vegetation. These particles

emission sources have been chosen for characterization because the results are expected to assist in determining the percent contribution of specific sources to the total ambient aerosol concentration.

Other research conducted at UCR includes the design and development of two field-deployable ATOFMS systems, which will allow for real-time aerosol sampling at remote locations. Also, a comparison has been made between ATOFMS and laser microprobe mass spectrometry (LMMS) for single particle analysis of inorganic salt particles [7].

Stratospheric Aerosols. At LANL, the nonlinear optical technique second harmonic generation (SHG) is used to probe the surface of the laboratory grown porous ice films which simulate PSCs [8-11]. The second harmonic light is generated in reflection from the solid/vapor interface of pores, arising from the transparency of the ices to the laser (ω) and second harmonic (2ω) frequencies. This is shown schematically for scattering from a single pore in Figure 4. Due to the random orientation of these interfaces relative to the input laser polarization, the reflected second harmonic light is unpolarized, making this type of experiment distinct from SHG polarization anisotropy studies. The information content of the experiments reported here depends instead on the total surface second harmonic efficiency, which is an orientational average of the second harmonic response from all chemical components comprising the interface.

The ice films were condensed from vapor onto a temperature-controlled brass support in an optically accessible vacuum chamber. The experimental apparatus is shown in Figure 5. The samples were illuminated by 532-nm light from a Q-switched, mode-locked Nd:YAG laser delivering approximately 100 μJ, 100 psec pulses, at 10 Hz. The second harmonic light was collected near the specular reflection angle, with a detection solid angle of 0.05 steradians, passed through a 0.25m or 1.0m monochromator, detected by a phototube, and integrated.

Second harmonic generation was used to study the solid/vapor interface of porous ice films of HNO_3 with H_2O [9]. This binary system forms solid hydrates, which figure prominently in ozone depletion, at temperatures and pressures characteristic of the polar stratosphere. The second harmonic intensity was collected in reflection from porous, polycrystalline films of H_2O ice and $HNO_3(H_2O)_n$ hydrate ices of calibrated total surface area and porosity. Measurements of the second harmonic intensity as a function of the amount of H_2O adsorbed on $HNO_3(H_2O)_n$ hydrate ices indicate that generation of the harmonic light is localized to the solid/vapor interface of pores throughout the ice film.

Measurements of the reflected second harmonic intensity as a function of temperature reveal a strong dependence on the thermodynamic phase of the molecular interface. We have correlated several signatures in the temperature-dependent, second-harmonic response with known bulk phase transitions in the HNO_3/H_2O system. We have also identified a surface localized transition that we have assigned to roughening. This work demonstrates the utility of nonlinear light scattering as a direct probe of the structure and chemical composition of the solid/vapor ice interface.

We have demonstrated that SHG can be used to monitor adsorption on model ice films [8]. We have developed a formalism that relates the second harmonic signal directly to the surface coverage of the adsorbate [10]. The formalism is based on multilayer physical adsorption theory (Brunnauer-Emmett-Teller or BET) and the modification that allows for lateral adsorbate-adsorbate interactions, the Bragg-Williams theory (BET-BW). We have applied this analysis to our measurements of the adsorption of a large organic molecule on water ice [10], water on nitric acid hydrate ice [12], and HCl adsorption on water ice [11]. The HCl/H_2O system is very complex and is particularly important in polar stratospheric chemistry. Stable trihydrate, $HCl(H_2O)_3$, and hexahydrate, $HCl(H_2O)_6$, crystalline phases are thought to be formed at stratospheric temperatures. Figure 6 shows an adsorption spectrum for HCl on water ice. The coincidence of the rapid increase in SH signal at nonzero coverage with the abrupt increase in HCl vapor pressure measured by mass spectroscopy suggests that a phase transition occurs. The presence of a quasi-liquid layer has been proposed by others. Because it is a surface sensitive probe, second harmonic generation, coupled with mass spectrometric measurements of vapor pressure, is a promising method to resolve this issue.

Publications

1. Fergenson, D. F., Liu, D.-Y., Silva, P. J. and Prather, K. A., "SpectraSort: A Data Analysis Program for Real-Time Aerosol Analysis by Aerosol Time-of-Flight Mass Spectrometry," *J. Chemom. Intell. Lab. Syst.*, submitted for publication.

2. Henson, B. F. and Robinson, J. M., "Surface Probes of Porous Toluene/Water Ices: Adsorption Kinetics and Annealing Spectra Measured by Second Harmonic Generation," *Proc. SPIE—Int. Soc. Opt. Eng.*, **2125**, 140-149 (1994).

3. Henson, B. F., Wilson, K. R. and Robinson, J. M., "A Physical Adsorption Model of the Dependence of $ClONO_2$ Heterogeneous Reactions on Relative Humidity," *Geophys. Res. Lett.*, **23**, 1021-1024 (1996).

4. Henson, B. F., Wilson, K. R., and Robinson, J. M., "Porous $HNO_3(H_2O)_n$ Ice Films: Adsorption and Surface Thermodynamics Measured by Second Harmonic Generation," *J. Phys. Chem.* (submitted).

5. Henson, B. F., Wilson, K. R., and Robinson, J. M., "Quantitative Measurements of Multilayer Physical Adsorption on Heterogeneous Surfaces Measured by Second Harmonic Generation," *Phys. Rev. Lett.* (submitted).

6. Noble, C. A. and Prather, K. A., "Aerosol Time-of-Flight Mass Spectrometry: A New Method for Performing Real-Time Characterization of Aerosol Particles," *Appl. Occup. and Environ. Hyg.*, submitted for publication.

7. Noble, C. A. and Prather, K. A., "Real-Time Measurement of Correlated Size and Composition Profiles of Individual Atmospheric Aerosol," *Environ. Sci. Technol.*, **30**, 2667-2680 (1996).

8. Noble, C. A., Nordmeyer, T., Salt, K., Morrical, B. and Prather K. A., "Aerosol Characterization Using Mass Spectrometry," *TRAC—Trends Anal. Chem.*, **13**, 218-222 (1994).

9. Nordmeyer, T., Prather, K. A., "Real-Time Measurement Capabilities Using Aerosol Time-of-Flight Mass Spectrometry," *Anal. Chem.*, **66**, 3540-3542 (1994).

10. Prather, K. A., Nordmeyer, T., Salt, K., "Real-Time Characterization of Individual Aerosol Particles Using Aerosol Time-of-Flight Mass Spectrometry," *Anal. Chem.*, **66**, 1403-1407 (1994).

11. Salt, K., Noble, C. A. and Prather K. A., "Aerodynamic Particle Sizing Versus Light Scattering Intensity Measurement as Methods for Real-Time Particle Sizing Coupled with Time-of-Flight Mass Spectrometry," *Anal. Chem.*, **68**, 230-234 (1996).

12. Salt, K. and Prather, K. A., "Comparison of Aerosol Time-of-Flight Mass Spectrometry and Laser Microprobe Mass Spectrometry as Methods for the Analysis of Sulfur-Containing Aerosol Particles," *J. Am. Soc. Mass Spectrom.*, accepted for publication.

References

1. Noble, C. A., Nordmeyer, T., Salt, K., Morrical, B. and Prather K. A., "Aerosol Characterization Using Mass Spectrometry," *TRAC—Trends Anal. Chem.*, **13**, 218-222 (1994).
2. Nordmeyer, T., Prather, K. A., "Real-Time Measurement Capabilities Using Aerosol Time-of-Flight Mass Spectrometry," *Anal. Chem.*, **66**, 3540-3542 (1994).
3. Prather, K. A., Nordmeyer, T., Salt, K., "Real-Time Characterization of Individual Aerosol Particles Using Aerosol Time-of-Flight Mass Spectrometry," *Anal. Chem.*, **66**, 1403-1407 (1994).
4. Salt, K., Noble, C. A. and Prather K. A., "Aerodynamic Particle Sizing Versus Light Scattering Intensity Measurement as Methods for Real-Time Particle Sizing Coupled with Time-of-Flight Mass Spectrometry," *Anal. Chem.*, **68**, 230-234 (1996).
5. Noble, C. A. and Prather, K. A., "Aerosol Time-of-Flight Mass Spectrometry: A New Method for Performing Real-Time Characterization of Aerosol Particles," *Appl. Occup. and Environ. Hyg.*, submitted for publication.
6. Noble, C. A. and Prather, K. A., "Real-Time Measurement of Correlated Size and Composition Profiles of Individual Atmospheric Aerosol," *Environ. Sci. Technol.*, **30**, 2667-2680 (1996).
7. Salt, K. and Prather, K. A., "Comparison of Aerosol Time-of-Flight Mass Spectrometry and Laser Microprobe Mass Spectrometry as Methods for the Analysis of Sulfur-Containing Aerosol Particles," *J. Am. Soc. Mass Spectrom.*, accepted for publication.
8. Henson, B. F. and Robinson, J. M., "Surface Probes of Porous Toluene/Water Ices: Adsorption Kinetics and Annealing Spectra Measured by Second Harmonic Generation," *Proc. SPIE—Int. Soc. Opt. Eng.*, **2125**, 140-149 (1994).
9. Henson, B. F., Wilson, K. R., and Robinson, J. M., "Porous $HNO_3(H_2O)_n$ Ice Films: Adsorption and Surface Thermodynamics Measured by Second Harmonic Generation," *J. Phys. Chem.* (submitted).
10. Henson, B. F., Wilson, K. R., and Robinson, J. M., "Quantitative Measurements of Multilayer Physical Adsorption on Heterogeneous Surfaces Measured by Second Harmonic Generation," *Phys. Rev. Lett.* (submitted).
11. Henson, B. F., Wilson, K. R., Noble, C. A., Worsnop, D. R., and Robinson, J. M., Los Alamos National Laboratory, Private communication of unpublished data (1996).
12. Henson, B. F., Wilson, K. R. and Robinson, J. M., "A Physical Adsorption Model of the Dependence of $ClONO_2$ Heterogeneous Reactions on Relative Humidity," *Geophys. Res. Lett.*, **23**, 1021-1024 (1996).

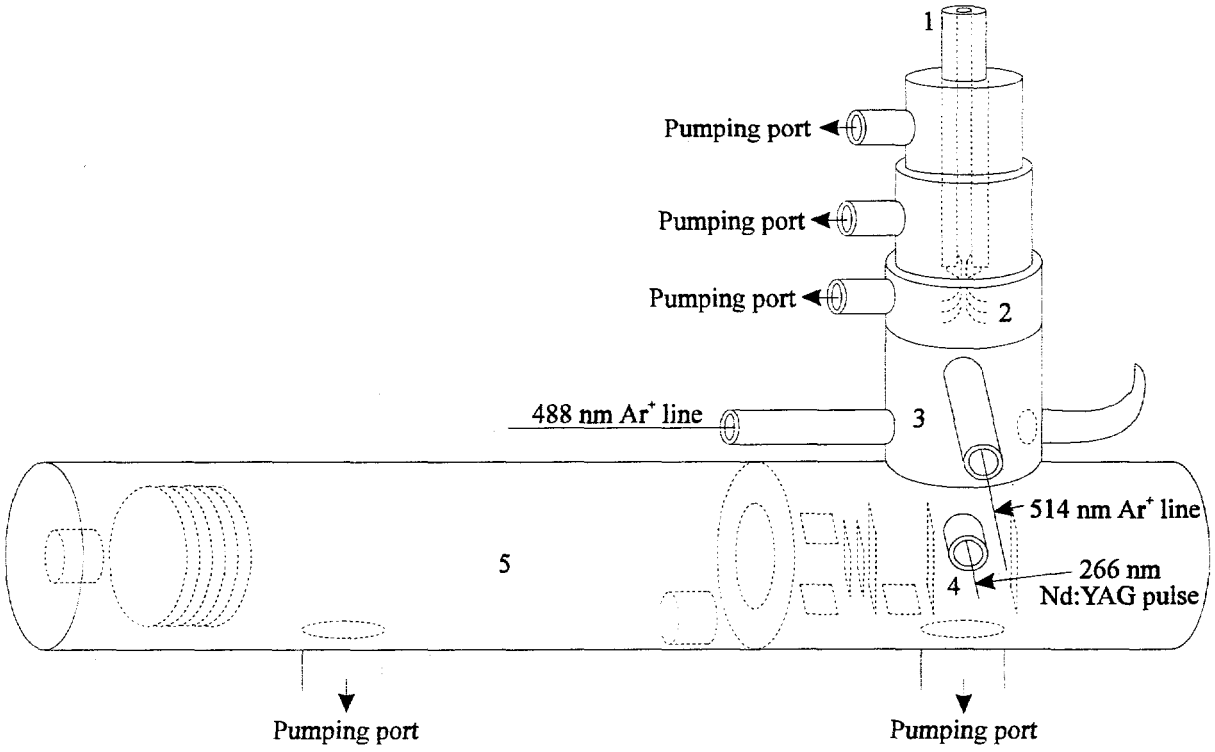

Figure 1. Schematic diagram of aerosol time-of-flight mass spectrometry system: 1-particle inlet, 2-differential pumping region, 3-aerodynamic particle sizing region, 4-ion source, and 5-TOF mass analyzer.

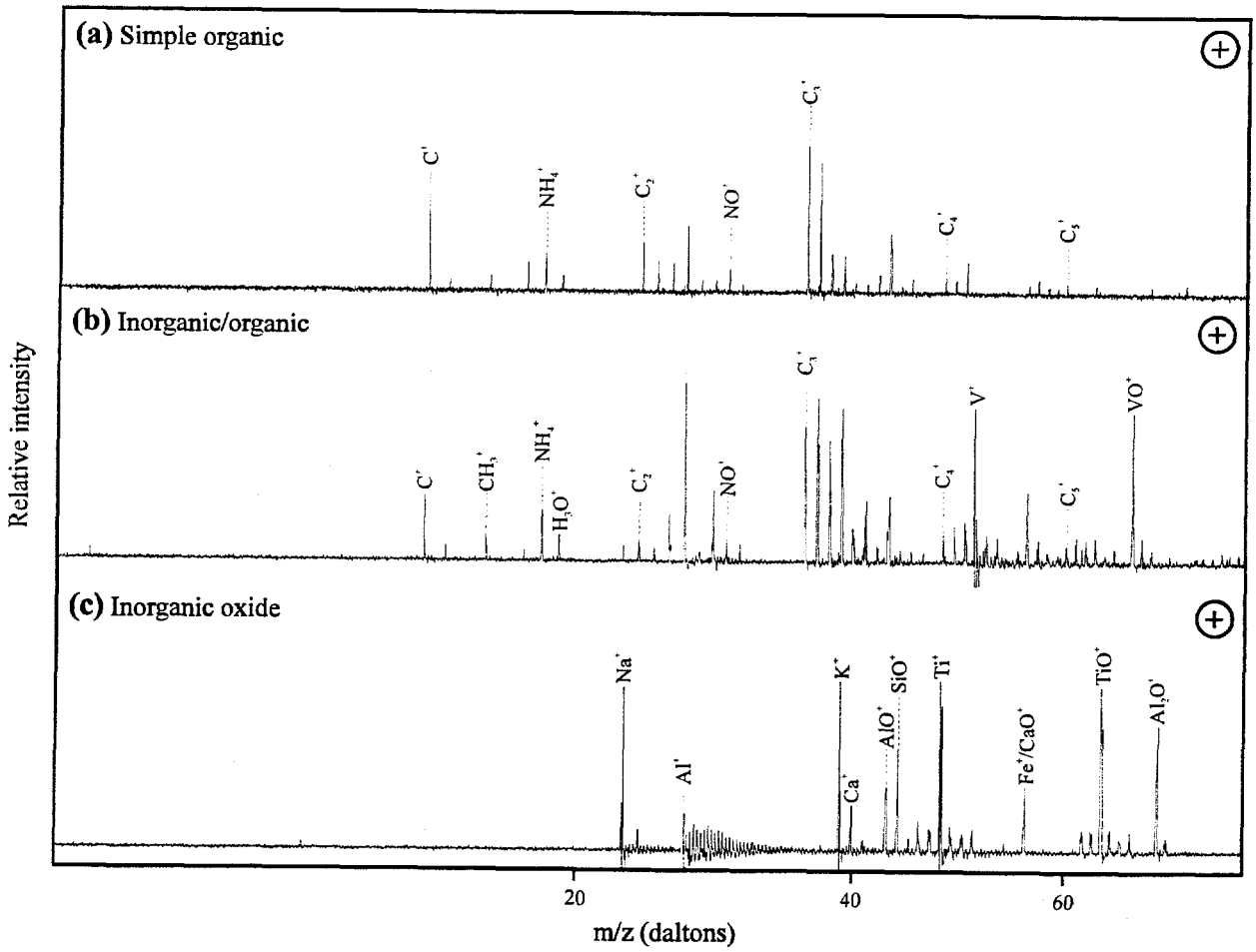

Figure 2. Laser desorption/ionization positive ion mass spectra of single ambient aerosol particles. (a) Simple organic particle mass spectrum. (b) Inorganic/organic particle mass spectrum. (c) Inorganic oxide particle mass spectrum.

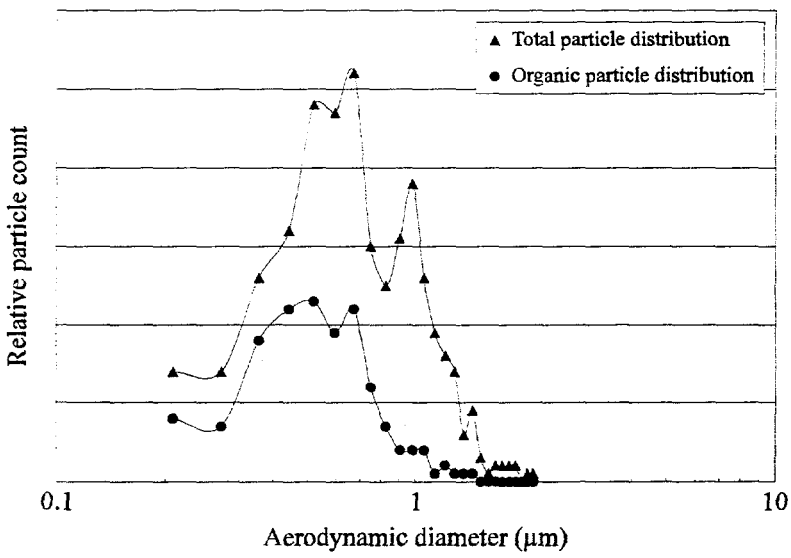

Figure 3. Total particle size distribution and organic particle size distribution from ambient sampling.

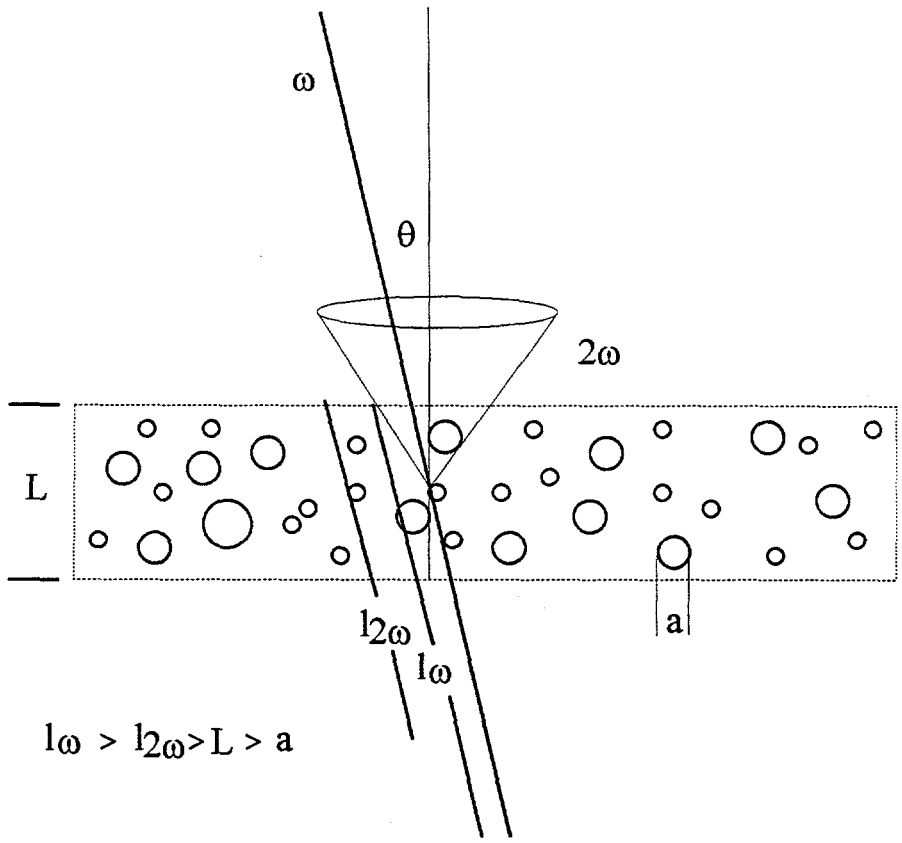

Figure 4. Schematic diagram of ice films with length scales defined. The dashed border identifies the macroscopic boundary of the film and the geometric surface area; the internal pores are represented by circles, which form an interconnected network in the film. The ray labeled ω is the input fundamental laser and the second harmonic light at frequency 2ω is shown scattered into a cone. The detection angle is θ. L is the film thickness, and a is the scattering diameter of a pore. The Rayleigh lengths l_ω and $l_{2\omega}$ are are not shown to scale but are longer than L for films in these experiments.

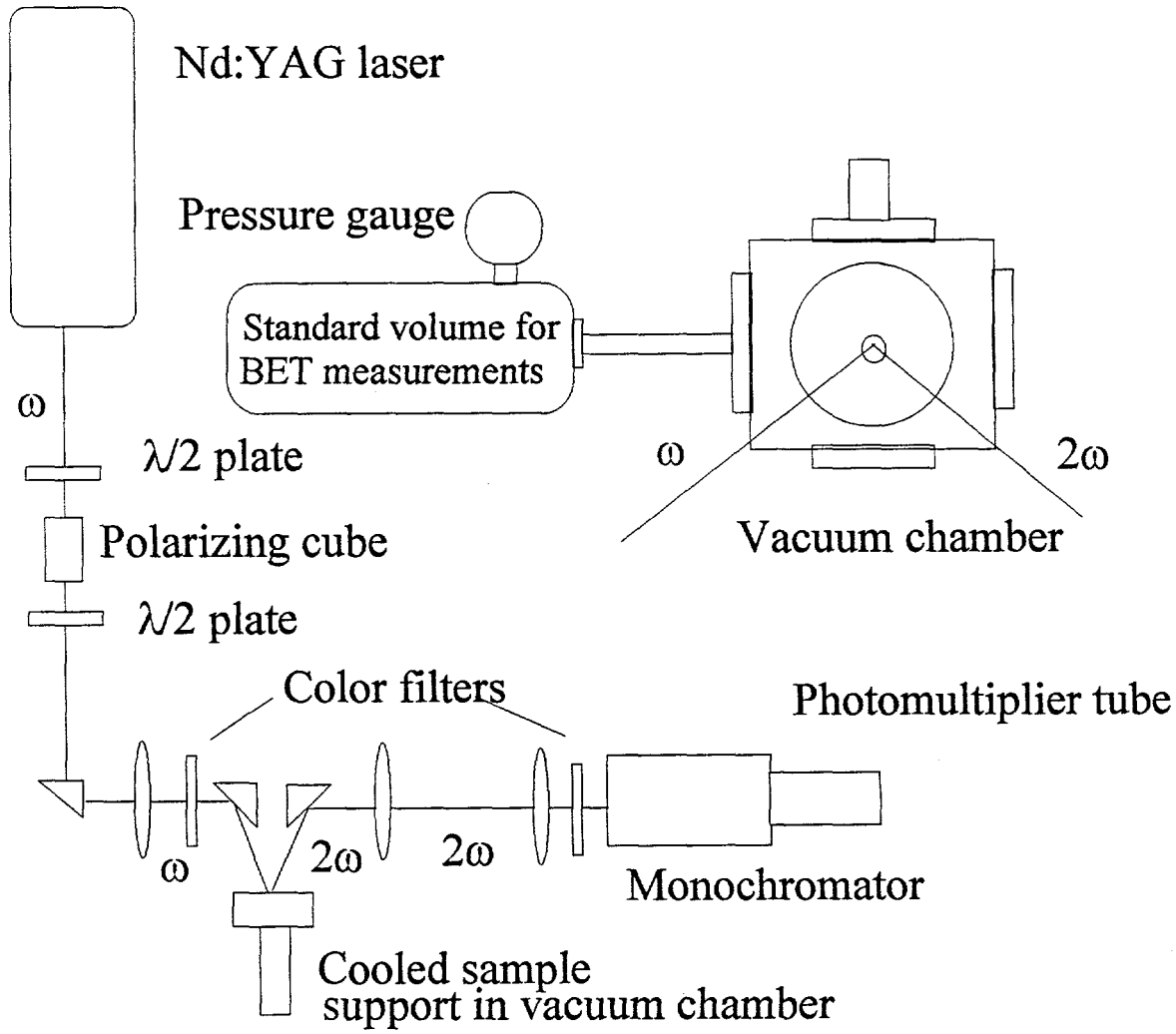

Figure 5. Schematic diagram of the vacuum apparatus and optical train. The 532-nm fundamental light is focused mildly to a 3-mm spot. The second harmonic light at 266 nm is detected through a monochromator with a solar blind phototube. A standard volume is coupled to the chamber to conduct physical adsorption measurements and calibrate the area and morphology of ice films grown identically to those used for the optical measurements.

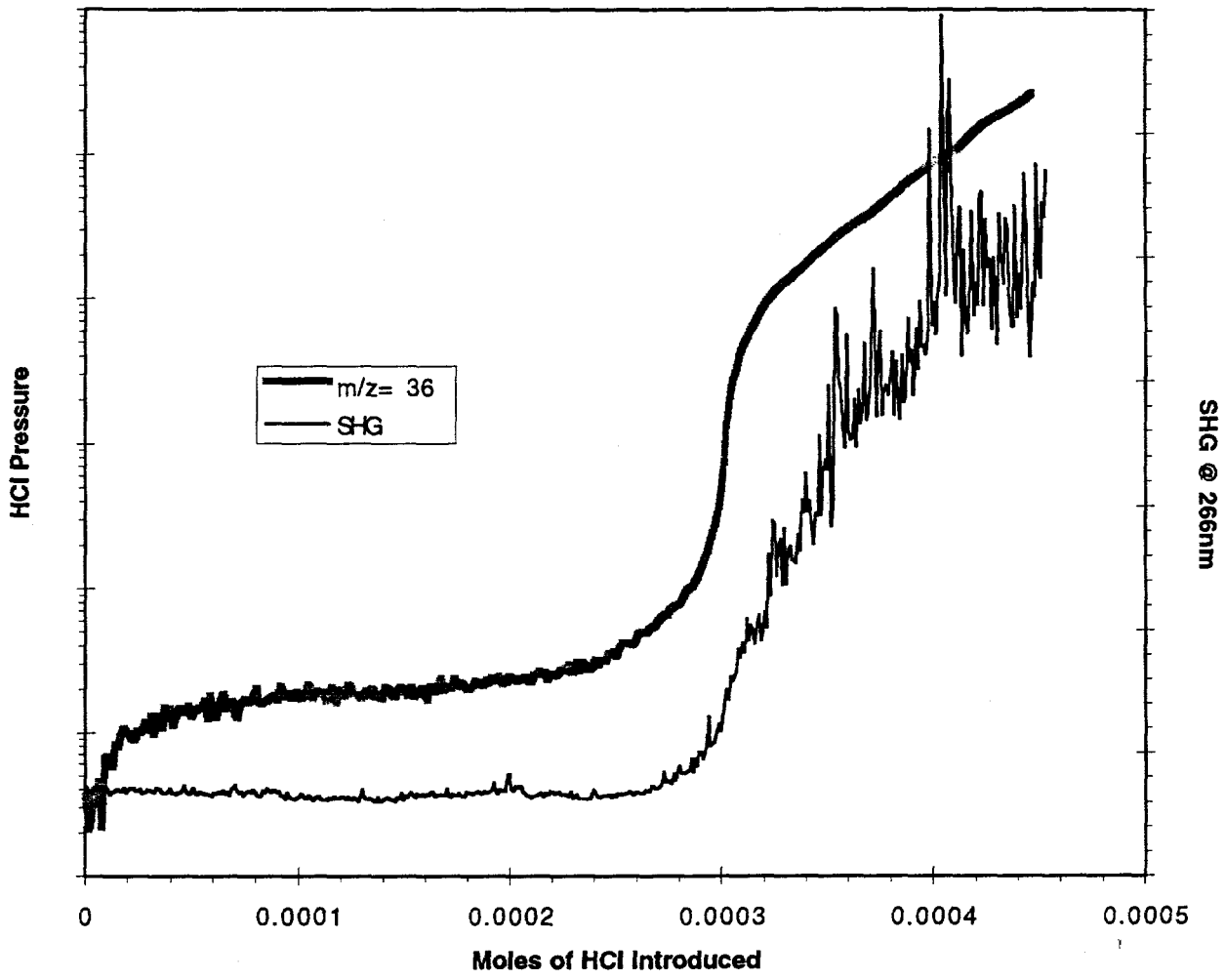

Figure 6. Adsorption spectra and HCl vapor pressure at 180K. The second harmonic intensity and HCl vapor pressure were measured concurrently as HCl was introduced over an ice film of known surface area at a fixed temperature.