Chemical Compositions of Black Carbon Particle Cores and Coatings via Soot Particle Aerosol Mass Spectrometry with Photoionization and Electron Ionization

1. INTRODUCTION

Atmospheric aerosol particles are known to have detrimental effects on human health and climate. Black carbon plays a significant role in the global climate radiation budget through direct and indirect forcings that are still poorly understood.[1−3] Black carbon has also been shown to have a negative impact on human health.[4] Respirable black carbon containing particles are

typically directly emitted into the atmosphere through incomplete combustion of fossil fuels, biofuels, and biomass.[5] Once emitted into the atmosphere, they can be coated with organic and inorganic species that are produced by secondary gas-to-particle conversion processes. Measurement methods that can directly detect, quantify, and chemically characterize black carbon particle cores and coatings are needed in order to better apportion and understand the sources, transformation processes, and ultimate effects of these particles.

Online refractory carbon particle measurements have been made possible by the advent of aerosol mass spectrometers.[6−9] Aerosol mass spectrometers are typically classified according to whether they characterize particles on an individual single particle basis or on an ensemble (bulk) basis. Single particle characterization is achieved with pulsed laser vaporization/ionization schemes, while ensemble particle measurements are usually obtained with continuous two-step thermal vaporization and ionization schemes. The soot particle aerosol mass spectrometer (SP-AMS) discussed here provides ensemble aerosol measurements and is based on the widely used Aerodyne aerosol mass spectrometer (AMS).[9,10] In the AMS, aerosols are continuously vaporized on a heated (200−600 °C) tungsten surface and subsequently detected by 70 eV electron ionization (EI) mass spectrometry. A key advantage of the AMS is its ability to quantify total nonrefractory OA mass. A disadvantage is its inability to measure refractory carbon species. In the SP-AMS, an intracavity CW Nd:YAG laser module (operating at 1064 nm) is used as an alternative or additional vaporizer to the heated tungsten vaporizer. Refractory particulate species that absorb the 1064 nm light (black carbon and metals) cause the particles to heat up, resulting in quantitative vaporization of both coating and core materials. Thus, this module allows the SP-AMS to detect nonrefractory (organic) and refractory (i.e., elemental carbon) species.[11]

The SP vaporization technique was first developed for the single particle soot photometer (SP2) by Droplet Measurement Technologies (DMT, Boulder, CO). The SP2 uses incandescence signals from single black carbon particles to quantify black carbon mass loadings, particle number concentrations, and size distributions, but it does not provide chemical composition information about the black carbon containing particles.[12−14] Unlike pulsed laser ablation instruments, the SP2 and the SP-AMS use a CW 1064 nm laser operating below the power density required for plasma formation and/or multiphoton ionization. This allows for linear and gentle continuous vaporization of the particles. Moreover, since adsorbed species evaporate as soon as they attain their respective vaporization temperatures, on the time scale of a few microseconds, many undergo minimal thermal decomposition.[11] One of the goals of this work is to investigate the degree to which the softness of the SP vaporization scheme allows enhanced chemical characterization of both core and coating materials in ensemble aerosol mass spectrometer measurements. In order to limit ion fragmentation due to the 70 eV ionization process used in standard SP-AMS systems, a soft single photon VUV ionization is used to measure the gas phase species that result from SP vaporization. The information obtained from these measurements is then used to interpret and understand chemical signatures produced by the standard 70 eV EI SP-AMS instrument.

Soft single photon ionization of organic aerosol species has been demonstrated using Nd:YAG lasers that produce ultraviolet light at 10.5 eV (118 nm),[15−17] tunable (7.4−10.2 eV) four-wave difference-mixing pulsed laser methods,[18] and VUV lamps.[19−21] The soft ionization method used for the experiments described in this manuscript, however, must be capable of ionizing not only the organic coating species but also the carbon clusters generated from vaporization of the refractory carbon core of the particle. SP vaporization of refractory carbon particle constituents takes place at temperatures of ∼4000 K. Previous studies have shown that small neutral carbon clusters with less than 10 atoms are the dominant products of black carbon vaporization at these temperatures.[22] The ionization energies of small carbon clusters are in the 9−13 eV energy range. The photon energy in the VUV sources mentioned above is not high enough to ionize smaller clusters like C, C_2, and C_3 in a single-photon process.[23] Multiphoton ionization schemes using 355 nm (3.49 eV) or 193 nm (6.42 eV), on the other hand, provide too much energy in excess of the ionization energy and result in fragmentation of the carbon cluster ions.[22] Synchrotrons produce tunable, continuous VUV photons in the desired energy range and have been previously used to obtain detailed chemical information about organic aerosol species.[24,25] The tunable VUV light also allows for monitoring appearance energies of ions, allowing direct photoionization processes to be distinguished from fragmentation. Thus, synchotron-generated tunable VUV light was chosen as the soft ionization source for these experiments.

The first part of this work is focused on investigating whether the carbon cluster mass spectra that result from SP vaporization contain any spectral signatures that reflect underlying physical and chemical differences in the evaporated carbon core. Carbon samples from different sources can differ in nanostructure (graphitic, fullerenic, or amorphous) and carbon bonding (extent of sp^2 and sp^3 bonding). Distinctive spectral signatures within SP-AMS carbon cluster mass spectra that correlate with these properties could provide useful source-specific information for multivariate analyses of combined (coating and core) SP-AMS mass spectra from mixed ambient environments.[26,27]

Previous single particle measurements have shown differences in the mass spectral ratios between total organic carbon ion signal and elemental carbon ion signal (OC/EC)[28] or the total carbon content and elemental carbon signal (TC/EC)[29] for different carbon and soot sources. SP-AMS mass spectra (with 70 eV EI) have been obtained from several different types of carbon sources (e.g., on-road vehicle emissions,[26,30,31] ship emissions,[32,33] flares,[34] and aircraft[35]). The SP-AMS spectra of most of the sources are dominated by small carbon cluster ion signals (C_n^+, $n < 6$). Corbin et al. (2014) have shown that the C^+/C_3^+ and C_4^+/C_3^+ ratios in SP-AMS spectra vary between different types of refractory carbon. Larger carbon clusters (C_n^+, $n > 6$)[35] and fullerene ions such as C_{60}^+ have also been observed in SP-AMS spectra of some sources.[11,34]

The degree to which the carbon cluster distributions measured with 70 eV EI reflect the neutral clusters generated from SP vaporization is unknown. Carbon cluster distributions produced by laser vaporization of black carbon samples have been studied by mass spectrometric methods for many years.[22] Two broad groups of clusters have been identified based on cluster structures. Clusters with greater than 30 carbons have three-dimensional shapes. Clusters with less than 30 carbon atoms have two-dimensional linear, cyclic, or polycyclic structures; clusters such as C_3 and C_{60} are particularly stable.[22] Much of the previous work in this area has focused on the use

of pulsed laser vaporization of graphite and other types of black carbon to generate plasmas that are supersonically cooled to allow for growth of larger carbon cluster species. This study differs from previous studies in that it seeks to directly characterize the nascent carbon cluster distribution formed by the 4000 K CW SP vaporization process without collisional cooling and cluster growth.

The second part of this work is focused on investigating the capability of SP vaporization to provide improved chemical characterization of organic coatings on absorbing refractory carbon or metallic cores. Soft vaporization has been used extensively in single particle aerosol mass spectrometer applications to decrease the degree of fragmentation and increase the level of chemical information obtained for organic compounds.[36,37] Typically, in these instruments soft vaporization of semivolatile aerosol organic species has been achieved with a two-step desorption/ionization scheme in which an IR laser pulse (usually a pulsed CO_2 laser operating at 10.6 μm) is used for the desorption step.[36,38] The surface plasmon resonance of gold and silver nanoparticles has also been utilized to demonstrate an alternative pulsed soft vaporization scheme for detection of small peptides in single particle mass spectrometers.[39] The SP vaporization scheme discussed here offers an analogous, new means of achieving soft vaporization for aerosol mass spectrometers that provide ensemble measurements. Since these instruments typically use continuously heated surfaces rather than pulsed lasers, soft vaporization is usually achieved by operating the vaporizer surfaces at reduced temperatures. Thermal denuder measurements have shown that ambient oxidized OA particles must be heated to a temperature ~225 °C for several seconds in order to achieve quantitative vaporization.[40] Recent measurements indicate, however, that thermal decomposition of oxidized organic molecules with acid and alcohol functionalities occurs efficiently even at 200 °C [41] and may inherently limit the level of chemical composition information that can be obtained with this method. In this study the performance of the SP vaporization scheme is evaluated by comparing the degree of fragmentation observed in SP-AMS organic mass spectra with those obtained using a continuous heater operating at a lower limit temperature of 200 °C. Organic coating spectra are obtained for particles containing both refractory carbon and metal cores.

2. EXPERIMENTAL METHODS

2.1. VUV-SP-AMS. The standard SP-AMS has been previously described.[11] Briefly, in the standard SP-AMS, particles are sampled through an aerodynamic lens and the resulting particle beam is intersected with a 1064 nm CW YAG laser. Particles that absorb the 1064 nm radiation (i.e., black carbon and metallic cores) heat up and vaporize. This allows for detection of the absorbing refractory species as well as adsorbed nonrefractory species in the particles. While the refractory carbon components are heated to around 4000 K during the SP vaporization process, adsorbed organic coatings are vaporized as soon as they attain their respective vaporization temperatures. During standard SP-AMS operation, vaporized species are ionized with 70 eV EI and detected with high-resolution time-of-flight aerosol mass spectrometry. Thus, in this manuscript the term SP-AMS is used to refer to standard operation with 70 eV EI.

In this experiment the SP-AMS was modified to allow for ionization using tunable VUV light from the Chemical Dynamics beamline (9.0.2) of the Advanced Light Source

(ALS) at Lawrence Berkeley National Laboratory.[25] The term VUV-SP-AMS will be used to refer to the combined use of SP vaporization and VUV ionization. These measurements required aligning three distinct beams (the particle beam, the 1064 nm YAG laser beam, and the synchotron VUV beam). The overlap of these three beams was achieved within a large AMS ionizer cage. The AMS thermal vaporizer, which is often retained in the SP-AMS to enable alternation between SP and thermal vaporization schemes, was removed from the SP-AMS to allow the VUV beam to enter through a custom flange in the back of the AMS. A 20° angle was used between the YAG laser beam and the particle beam to prevent the particle beam from entering the vacuum system of the beamline. Previous AMS work has shown that VUV spectra are typically less complex and have reduced ion fragmentation compared to 70 eV EI spectra.[9,19] For example, molecular ions observed in AMS-VUV spectra of unoxidized and slightly oxidized squalane have been successfully used to obtain chemical and mechanistic insight into the squalane oxidation reaction.[42]

During the experiment the SP laser driver voltage was alternated between two different settings. Preliminary tests with Regal Black samples were used to identify a high voltage setting (1.28 V) that allowed for vaporization and detection of all the refractory carbon core and a low voltage setting (0.31 V) that allowed for vaporization of only organic coatings and minimal signal from the refractory core. The high voltage setting was used when examining carbon core compositions, and the low voltage setting was used when examining VUV-SP-AMS spectra of organic species adsorbed on refractory carbon and metallic particles. It is important to note that the absolute values of the SP driver voltage settings used in these experiments are not directly transferable between instruments, since the actual laser fluence in the vaporization region will depend on additional factors such as pump laser performance, coupling of the pump laser to the Nd:YAG crystal, and cavity alignment. While measurements of the laser power would have provided more direct information about the laser fluence, these measurements were not available for these studies. Thus, the voltage values are simply used here to refer to the operating settings at which two different extremes of SP operation were observed (i.e., vaporization of core and coating versus vaporization of only coating). Spectra of the carbon samples are reported at 12 eV VUV, since all carbon clusters, including $C-C_3$, are ionized at this VUV energy. Since most organic species have ionization energies less than 10.5 eV, this energy allows for near-threshold ionization spectra of adsorbed organic species. The energy of the VUV beam was also scanned in order to obtain VUV photoionization efficiency curves from several of the samples. The scans were typically in the range from 8 to 12 eV with step sizes of 0.25 eV.

The ToF-AMS Analysis Toolkit (version 1.55) and the ToF-AMS HR Analysis (version 1.14) were used to analyze both sets of data.[43] For the VUV-SP-AMS measurements, unit mass resolution data are available up to m/z 2290, but high-resolution analysis is only performed by identifying and fitting high-resolution ions until m/z 340. The m/z calibration for the data set was performed using known polyaromatic hydrocarbon ions and organic ions from oxidized organic standard molecules used in this study. For the unit mass resolution spectra the accuracy of the m/z calibration at high m/z was checked with known fullerene peaks.

2.2. Materials. Commercially available carbon samples examined in this work include Regal Black (Cabot Corpo-

ration), fullerene black (nano-C), and fullerene C_{60} (Materials and Electrochemical Research, MER, 99.9% purity). The Regal Black and fullerene black samples were atomized in water (TSI constant-output atomizer), and the resulting polydisperse aerosol particles were sampled after passing through a Dri-Rite diffusion dryer. Atomization was performed under argon in order to reduce interference from air signals CO_2, CO, and H_2O. The C_{60} particles were milled under nitrogen and dry dispersed from a pillow bag by flowing argon through the bag.[44]

Carbon samples generated from laboratory flames were also studied here. Ethylene flame soot particles were generated using a premixed flat burner flame as described in detail elsewhere.[45,46] Collected soot was transferred into a vial and ground to a fine powder using a ball mill (Spex Certriprep Mixer/Mill 5100) to facilitate subsequent dry dispersion of soot particles with argon. Methane flame soot samples were generated from methane fuel using an inverted diffusion flame.[47] The methane flame soot samples were collected on filters, atomized directly in water, passed through the diffusion drier, and sampled into the SP-AMS. Filters containing hydrophilic methane flame soot particles (produced by exposing the methane flame soot samples to high concentrations of ozone[48]) were also analyzed in a similar way.

VUV-SP-AMS and SP-AMS spectra of oxidized organic coatings were obtained by atomizing the oxidized organics with gold, silver, or platinum nanoparticles (Sigma-Aldrich). Since the SP-AMS vaporization process is selective for the absorbing refractory carbon or metal core, only signals from oxidized organics adsorbed on the absorbing cores were detected in the SP-AMS or the VUV-SP-AMS spectra.