

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

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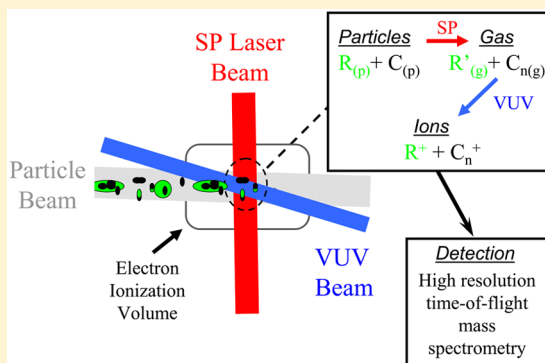
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S Supporting Information

ABSTRACT: Black carbon is an important constituent of atmospheric aerosol particle matter (PM) with significant effects on the global radiation budget and on human health. The soot particle aerosol mass spectrometer (SP-AMS) has been developed and deployed for real-time ambient measurements of refractory carbon particles. In the SP-AMS, black carbon or metallic particles are vaporized through absorption of 1064 nm light from a CW Nd:YAG laser. This scheme allows for continuous “soft” vaporization of both core and coating materials. The main focus of this work is to characterize the extent to which this vaporization scheme provides enhanced chemical composition information about aerosol particles. This information is difficult to extract from standard SP-AMS mass spectra because they are complicated by extensive fragmentation from the harsh 70 eV EI ionization scheme that is typically used in these instruments. Thus, in this work synchrotron-generated vacuum ultraviolet (VUV) light in the 8–14 eV range is used to measure VUV-SP-AMS spectra with minimal fragmentation. VUV-SP-AMS spectra of commercially available carbon black, fullerene black, and laboratory generated flame soots were obtained. Small carbon cluster cations ($C^+ - C_5^+$) were found to dominate the VUV-SP-AMS spectra of all the samples, indicating that the corresponding neutral clusters are key products of the SP vaporization process. Intercomparisons of carbon cluster ratios observed in VUV-SP-AMS and SP-AMS spectra are used to confirm spectral features that could be used to distinguish between different types of refractory carbon particles. VUV-SP-AMS spectra of oxidized organic species adsorbed on absorbing cores are also examined and found to display less thermally induced decomposition and fragmentation than spectra obtained with thermal vaporization at 200 °C (the minimum temperature needed to quantitatively vaporize ambient oxidized organic aerosol with a continuously heated surface). The particle cores tested in these studies include black carbon, silver, gold, and platinum nanoparticles. These results demonstrate that SP vaporization is capable of providing enhanced organic chemical composition information for a wide range of organic coating materials and IR absorbing particle cores. The potential of using this technique to study organic species of interest in seeded laboratory chamber or flow reactor studies is discussed.



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

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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, C₂, and C₃ 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, synchrotron-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 sp² and sp³ 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 aircraft³⁵). 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⁺/C₃⁺ and C₄⁺/C₃⁺ 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 C₆₀⁺ 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 C₃ and C₆₀ 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 CO₂ 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 °C⁴¹ 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 synchrotron 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–C₃, 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 Certiprep 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 ozone⁴⁸) 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.

3. RESULTS AND DISCUSSION

3.1. Chemical Characterization of Carbon Cores.

3.1.1. VUV-SP-AMS Spectra. Figure 1 shows an overview of

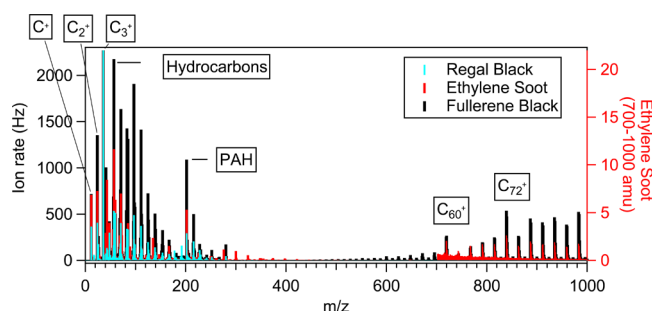


Figure 1. Overview of the VUV-SP-AMS unit mass resolution spectra obtained for Regal Black, ethylene flame soot, and fullerene black. The spectra were obtained with the VUV laser set at 12 eV and the SP laser operating at its highest power setting. The m/z 700–1000 region of the ethylene soot mass spectrum is expanded and shown on the right-hand axis to highlight the presence of weak spectral peaks in the fullerene cluster ion region.

12 eV VUV-SP-AMS unit mass resolution spectra obtained for three different types of carbon particles (Regal Black, ethylene flame soot, and fullerene black). Regal Black, which is used for calibration of the SP-AMS,¹¹ contains negligible fullerene content while the fullerene black has a high fullerene content. Ethylene flame soot is a complex carbon core that could contain a variable amount of fullerene. Since C_3^+ is the dominant ion in all three spectra, the spectra are normalized to the C_3^+ intensity in Figure 1. Expanded unit mass resolution

spectra of each of these species from m/z 0–360 (i.e., $<C_{30}^+$) to m/z 360–2000 are also shown in Figure S1 of Supporting Information. The main features of the spectra in Figure 1 are similar to those previously seen in 70 eV EI SP-AMS mass spectra of the same materials.⁴⁹ All three spectra contain prominent ion signals at small carbon cluster ions (C , C_2^+ , and C_3^+). The three spectra also contain other strong signals at masses less than m/z 300 which are primarily due to the adsorbed organic coatings associated with the different types of refractory carbon. Intense peaks that are part of aliphatic hydrocarbon and polyaromatic hydrocarbon organic series, for example, are identified in Figure 1. The distinguishing feature of the fullerene spectrum is the fullerene ion envelope at masses greater than m/z 420 that contains ion signals separated by 24 u. While the figure only extends to m/z 1000, the fullerene peaks continue to m/z 2000 (corresponding to clusters with over 166 carbon atoms) as shown in Figure S1. The ethylene flame soot spectrum contains some weak fullerene signals at masses greater than m/z 420 and signals between m/z 300 and 398 that are not observed in the other two types of carbon sources.

Since the aerosol sampled in these measurements contain refractory carbon as well as adsorbed organic species, high-resolution mass spectral analysis is used to separate isobaric organic ion and carbon cluster ion signals from each other. Figure 2 shows an example of the high-resolution mass spectral

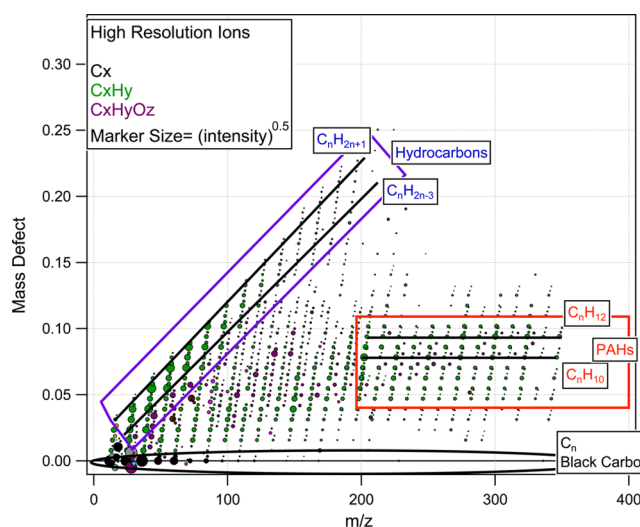


Figure 2. High-resolution VUV-SP-AMS spectrum observed for ethylene flame soot. Mass defects are used to separate isobaric organic species from each other and from carbon cluster species.

separation that is observed for the 12 eV mass spectrum of ethylene flame soot from Figure 1. The vertical axis shows the high-resolution signal intensities observed at each unit mass for different mass defects (i.e., difference from unit mass). Mass defects of zero reflect ions with only carbon atoms, since each C atom has an exact mass that is equal to 12.000. Larger mass defects reflect ions with significant H content, since the exact mass of each H atom (1.007) provides a positive mass defect of 0.007. Different positive mass defects are indicative of different H:C ratios. For example, in Figure 2, the mass defect plot clearly shows the two main groups of organics that belong to aliphatic hydrocarbon series and polyaromatic hydrocarbon (PAH) series. The strong PAH signals observed in these spectra are consistent with previous results from single particle

mass spectrometers which show that VUV photoionization is particularly sensitive to detection of PAH species.^{15,50} In addition to the purely hydrocarbon species, some species that have been previously identified as contaminants from silicone tubing materials⁵¹ are also observed. A few species that contain oxygen atoms are observed as well.

These species, which are identified by their lower mass defects from each oxygen atom (exact mass of 15.9949), account for only a small fraction of the observed coating mass and could reflect either true organic aerosol products of the ethylene flame itself or other contaminants as well. Carbon clusters from C^+ to C_{10}^+ are observed with significant intensity in Figure 2.

Figure 3 shows the carbon cluster cation distributions obtained from high-resolution analysis of the three VUV-SP-

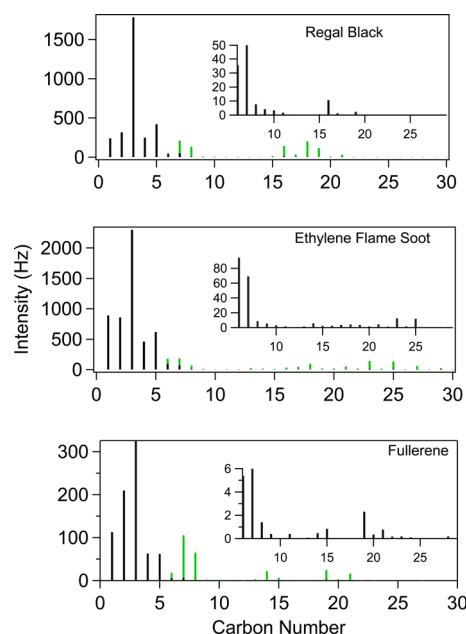


Figure 3. Carbon cluster signals and organic signals (observed at carbon cluster masses in unit mass resolution spectra) in VUV-SP-AMS spectra of Regal Black, ethylene flame soot, and fullerene black. The inset graph in each panel shows an expanded view of carbon cluster signals observed for C_6 – C_{30} in the spectra.

AMS spectra shown in Figure 1. The figure shows the ion intensities of the carbon cluster and organic species observed at the unit mass values of the carbon clusters. The dominant carbon cluster cation signals have five or fewer carbons. The C^+ – C_5^+ carbon clusters also appear to have negligible interference from isobaric organic coating species. The signals of the carbon clusters between C_6^+ and C_{29}^+ (the mid-carbon range) have very low intensities despite the use of a soft VUV ionization scheme, indicating that their neutral counterparts are not produced in significant quantities. Ethylene flame soot shows some C_{25}^+ and C_{23}^+ signal. Regal Black shows C_{16}^+ and C_{19}^+ , and fullerene black shows signal at C_{19}^+ and C_{21}^+ . However, it is important to note that for the carbon clusters larger than C_5^+ , the interference from isobaric organic ions (particularly PAH species) is large. Previous 12 eV VUV studies that utilized pulsed laser ablation of graphite together with supersonic cooling produced mass spectra with mid-carbon signals (C_6^+ , C_7^+ , C_9^+ , C_{10}^+ , C_{12}^+ , and C_{14}^+) that were at least one-third the intensity of the intense C_3^+ signal.⁵² This

indicates that the different vaporization conditions used in these SP-VUV experiments (4000 K CW YAG vaporization and no collisional cooling) favor formation of only the small carbon clusters. The dominance of the small carbon cluster ions in the VUV-SP-AMS spectra is in fact consistent with previous studies that have shown that C^+ , C_2^+ , and C_3^+ are the primary gas phase components in equilibrium with heated graphite.²² The graphite in those studies was heated to temperatures from 2000 to 5000 K; at 2700 K, for example, C_3^+ was found to be the main component of the vapor over graphite (30%) with C_1^+ and C_2^+ accounting for 14% and 15% respectively.^{53–55} Single particle aerosol mass spectrometers using 266 nm pulsed light for vaporization and ionization have also measured small carbon cluster ions from black carbon containing particles.^{28,29}

3.1.2. VUV-SP-AMS Photoionization Efficiency Curves. Figure 3 shows differences in the relative intensities of C^+ and C_2^+ relative to C_3^+ in the VUV mass spectra of Regal Black, ethylene flame soot, and fullerene samples. Before these differences can be investigated as spectral signatures, however, it is useful to understand whether fragmentation of larger ion clusters contributes to the observed intensity variations in the small carbon cluster ions. The 12 eV VUV light used in these experiments was chosen because it allows for near-threshold ionization of the small carbon clusters and limited fragmentation of most carbon cluster cations.⁵² The carbon cluster ionization energy (IE), however, decreases with increasing cluster size. For example, the measured IE of C_{15} is 8.9 eV⁵² and the IE of fullerenes is typically around 7 eV.⁵⁶ Since the dissociation energy for a C–C bond in the small carbon cluster ions is on the order of 4–6 eV,⁵⁷ it is potentially possible for 12 eV ionization to provide enough excess energy for fragmentation of fullerene and large carbon cluster ions.

The appearance energies of ions in photoionization efficiency (PIE) curves (i.e., ion signals as a function of VUV photon energy) were measured to investigate the importance of ion fragmentation in the measured VUV-SP-AMS carbon cluster distributions. In PIE curves appearance energies that match the known IE of the neutral parent molecule are indicative of direct ionization while appearance energies that differ from the known neutral IE values are indicative of other processes including fragmentation. Figure 4 shows PIE curves for the small carbon cluster ions (C_n^+ , $n = 1–5$), fullerene ions (C_{60}^+ and C_{58}^+), and representative organic hydrocarbon ($C_4H_9^+$) and PAH ($C_{16}H_{10}^+$) ions. The PIE curves of the individual traces are scaled to the same background and peak values in order to allow for easier comparisons between their shapes. The dip in all signals just before and after 12 eV is likely due to argon absorption in the beamline gas filter that is used to block harmonics of the VUV light from entering the AMS ionizer. Previously reported IEs for C_{60} vary between 7.57 and 8.1 eV depending on the measurement method.⁵⁶ The appearance of nonzero C_{60}^+ signal at 8 eV in Figure 4 (top) is consistent with this IE. The C_{58}^+ PIE curve is investigated because previous studies have shown that fullerene positive ions primarily fragment through loss of neutral C_2 units.⁵⁸ As shown in Figure S3, C_{58}^+ signal is observed in both 12 eV VUV-SP-AMS and 70 eV SP-AMS spectra. Previous literature measurements indicate that fragmentation of C_{60}^+ to produce C_{58}^+ and C_2 requires anywhere from 20 to 44 eV of energy.⁵⁶ The appearance of nonzero C_{58}^+ ion signal at a significantly lower energy of 8 eV is consistent with the known IE of neutral C_{58} (7.07 eV⁵⁶) and confirms that the C_{58}^+ observed in the 12 eV VUV-SP-AMS measurements is primarily formed by photoionization of

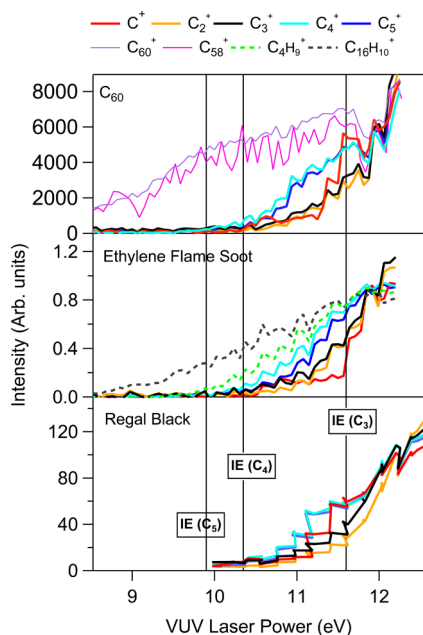


Figure 4. Mass spectral signals observed at selected ions as a function of VUV photon energy. The top panel shows results for C_{60}^+ , while the middle and bottom panels show results for ethylene flame soot and Regal Black, respectively. The VUV photon energy is scanned from 8 to 12 eV with a step size of 0.25 eV. Ionization energies measured in previous VUV studies⁵² are shown for C_5^+ (9.9 eV), C_4^+ (10.35 eV), and C_3^+ (11.6 eV).

neutral C_{58} clusters produced from SP vaporization rather than fragmentation of C_{60}^+ . The fact that the relative intensity of C_{58}^+ is larger in the 70 eV EI SP-AMS measurements (see Figure S3) likely indicates that the harsher ionization scheme provides enough excess energy for the fragmentation pathway to become more important. Known IE values of PAH species are around 8 eV, and those of aliphatic hydrocarbons are around 10.5 eV.⁵⁶ The appearance energies of the PAH and hydrocarbon ions in Figure 4 (middle) are consistent with these values.

The PIE curves of the small carbon cluster ions (C_n^+ , $n = 1-5$) are similar across all samples shown in Figure 4. The appearance energies of these cluster ions are in reasonable agreement with the expected IE values of the corresponding neutral clusters. Previously measured IE values of C_3 (11.6 eV), C_4 (10.35 eV), and C_5 (9.9 eV) are indicated in the figure.⁵² Literature IE values of C_2 and C range from 10.9 to 13 eV and from 10.9 to 12.4 eV, respectively.⁵⁶ The PIE curves of C^+ , C_2^+ , and C_3^+ show some weak signal below the expected IE values, but previous studies indicate that these signals are likely due to ionization from low-lying electronic states that are known to exist for small carbon clusters.⁵² Taken together, this indicates that the main source of the small cluster ions for all three samples, including fullerene, is photoionization of corresponding neutral clusters and not fragmentation of larger carbon cluster ions. The fact that these ions reflect direct products of the SP vaporization process is important, since previous SP-AMS studies indicate that these ions are the most useful spectral features for mass calibration and source identification of carbon sources.^{35,49}

3.1.3. Comparison between VUV-SP-AMS and SP-AMS Spectra. As discussed above, the 12 eV VUV-SP-AMS spectra represent a minimally perturbed measure of neutral products

generated during the SP vaporization process. Thus, it is of interest to investigate the degree to which the excess energy available in SP-AMS measurements distorts the near-threshold cluster distributions observed in VUV-SP-AMS spectra. Figure S2 compares the carbon cluster distributions observed in VUV-SP-AMS and SP-AMS spectra of Regal Black, ethylene flame soot, and fullerene black. The relative intensities of ion signals in VUV-SP-AMS and SP-AMS spectra are not necessarily comparable because of potential variability in the VUV ionization efficiencies of the different carbon clusters, but these qualitative comparisons provide the opportunity to examine the effects of enhanced fragmentation in the SP-AMS spectra. Since the C_3^+ signal is the strongest carbon signal in both the VUV-SP-AMS and SP-AMS spectra, the cluster signals are normalized to C_3^+ in each spectrum. The C^+ – C_5^+ carbon clusters are the dominant features in both types of spectra. The relative intensities of C^+ and C_2^+ relative to C_4^+ and C_5^+ are larger in the SP-AMS spectra compared to VUV-SP-AMS spectra. This suggests that in SP-AMS spectra the C_4^+ and C_5^+ clusters undergo fragmentation to the smaller clusters. This is consistent with previous collision-induced dissociation measurements which indicate that C_2^+ , C_3^+ , and C_4^+ ions dissociate by loss of C or C_3 atoms.^{57,58}

Previous SP-AMS studies have suggested using ratios of carbon cluster intensities as a means of distinguishing between different types of carbon sources.³⁵ Figure 5 examines several

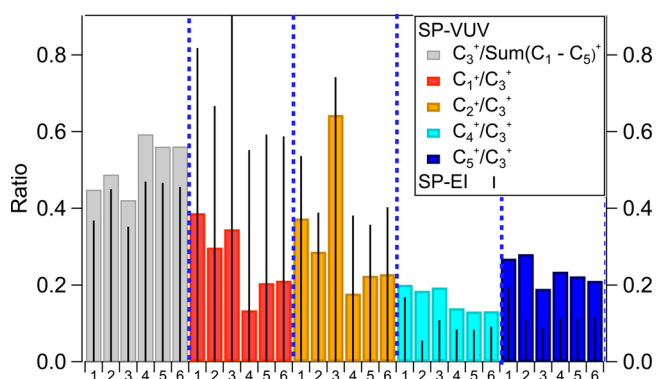


Figure 5. Observed ratios between different carbon cluster ions in the C^+ – C_5^+ range in both VUV-SP-AMS and SP-AMS spectra for the following carbon sources: ethylene flame soot (1), C_{60} (2), fullerene black (3), Regal Black (4), methane flame soot (5), and hydrophilic methane flame soot (6).

ratios (C^+/C_3^+ , C_2^+/C_3^+ , C_4^+/C_3^+ , C_5^+/C_3^+ , and C_3^+/sum (from C_1^+ to C_5^+)) observed in SP-AMS and VUV-SP-AMS spectra across different types of carbon particles. Six different types of carbon particles (ethylene flame soot, C_{60} , fullerene black, Regal Black, methane flame soot, and hydrophilic methane flame soot) are examined. The first three carbon types have higher fullerene content than the latter three. The goal is to identify the ratios that show similar trends in both types of spectra and also appear to show the largest differentiation between different types of carbon. One satisfying feature of Figure 5 is that for any given ratio, the general trend across sources is similar for SP-AMS and VUV-SP-AMS spectra. This indicates that SP-AMS spectra retain source-specific carbon cluster information despite enhanced fragmentation. Previous studies have shown that the C^+/C_3^+ and C_4^+/C_3^+ ratios in SP-AMS EI mass spectra are generally higher for black carbon sources with higher fullerene content.³⁵ The

VUV-SP-AMS spectra in Figure 5 show similar trends for these ratios. These observations provide support for the usefulness of these ratios in differentiating between types of refractory carbon. These variations in the carbon cluster ion distributions could be useful for separation and identification of black carbon containing particles in mixed ambient environments using multivariate analysis of SP-AMS spectra.

It is interesting to note that in Figure 5 the carbon cluster ratios for methane flame soot and hydrophilic methane flame soot are similar. The hydrophilic methane flame soot is generated by exposing the methane flame soot to large concentrations of ozone. Figure 5 shows that this process has no effect on the ratios of the carbon clusters with respect to each other. This lack of oxidation of the black carbon core upon aging is consistent with the heterogeneous oxidation results of Browne et al.⁵⁹ This indicates that carbon cluster ratios can be used to identify sources of black carbon aerosols even after they have been partially oxidized in the atmosphere.

3.2. Chemical Characterization of Organic Coatings.

3.2.1. Demonstration of Less Fragmented Mass Spectra. Most studies using the SP-AMS have focused on its capability to provide information about soot cores; an additional advantage that has received less attention is the capability of the SP vaporizer to provide soft vaporization of the coatings and thus less fragmented spectra. While soft vaporization techniques have been successfully developed for single particle aerosol mass spectrometers,^{36,37} there is still a need for new soft vaporization techniques that can be used to continuously transfer organic species from the particle phase into the gas phase in ensemble aerosol mass spectrometers. Thermal vaporization schemes used in the AMS, for example, have been shown to produce significant decomposition and dehydration of oxidized organic species. Thermal decomposition during vaporization has been observed at vaporizer temperatures down to 200 °C.⁴¹ Fragmentation from excess thermal energy also produces additional ion fragmentation and reduces useful mass spectral information about parent molecular composition.⁴¹

Here we discuss experiments performed to examine the extra chemical information that is obtained when using SP vaporization. For these experiments mixed particles containing Regal Black and an oxidized organic species were generated. Several types of oxidized organic species (polyols, carboxylic acids, multifunctional species) known to undergo thermally induced decomposition and fragmentation were studied in these experiments.⁴¹ VUV-SP-AMS spectra were obtained at a VUV energy of 10.5 eV. The SP laser was also operated at the low voltage setting in order to minimize interferences from refractory carbon signals and to further reduce extra thermal energy. These conditions allow near-threshold ionization of the oxidized organic coatings with minimal ion fragmentation.

Figure 6 shows mass spectra of glutaric acid and citric acid. VUV spectra utilizing two different vaporizers (SP and thermal vaporizer) are compared for each organic species.

VUV spectra obtained with the thermal vaporizer are referred to as VUV-AMS, while those obtained with the SP vaporizer are referred to as VUV-SP-AMS. VUV-AMS spectra are obtained with the AMS vaporizer set at 200 °C (the lowest temperature needed to vaporize most oxidized organic species observed in the atmosphere) or at 600 °C (the default vaporizer temperature of the AMS). Figure 6 indicates that for both molecules the VUV-SP-AMS spectrum is less fragmented than the VUV-AMS spectra. Interestingly, the VUV-SP-AMS

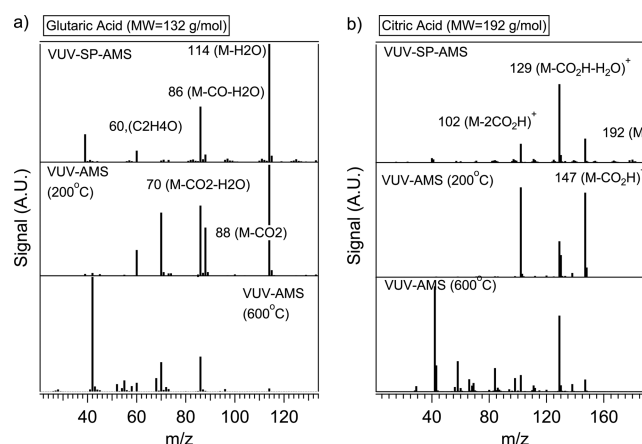


Figure 6. VUV-SP-AMS and VUV-AMS mass spectra of glutaric acid and citric acid coated on Regal Black particles. All spectra were obtained with the VUV light set at 10.5 eV. The VUV-SP AMS spectra were obtained with the SP module operating at the low voltage setting. VUV-AMS spectra were obtained with the thermal vaporizer operating at 200 and 600 °C.

spectrum is not free of fragmentation. The largest ion observed in the glutaric acid VUV-SP-AMS spectrum is not the molecular ion but an ion that is indicative of dehydration. The largest ion observed for citric acid is the molecular ion, but other ions that correspond to net losses of CO₂H and or H₂O during vaporization/ionization are more intense than the molecular ion.

Despite this evidence of fragmentation, the larger molecular mass fragments observed in the VUV-SP-AMS spectrum provide more information about the parent composition than can be obtained from the VUV-AMS 200 °C spectrum. Standard SP-AMS systems utilize 70 eV EI instead of VUV ionization. Thus, Figure 7 shows a similar comparison plot between SP-AMS and AMS spectra obtained for citric acid. The SP-AMS spectrum shown in Figure 7 contains more fragmentation than the corresponding VUV-SP-AMS spectrum shown in Figure 6, but the increased chemical information obtained with SP vaporization instead of thermal vaporization is still clear.

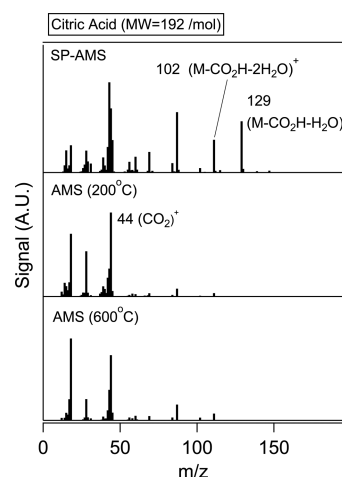


Figure 7. Comparison of SP-AMS and AMS spectra obtained for citric acid. AMS spectra obtained with the thermal vaporizer operating at 200 and 600 °C are shown. For the SP-AMS measurements, the SP laser was operated at the low voltage setting.

The soft vaporization achieved with the SP could be particularly useful for understanding the chemical composition of aerosol particles formed in environmental chamber or flow reactor experiments that involve a limited number of precursors and reaction pathways. SP-AMS spectra could be obtained by condensing the organic species of interest onto seed particles that absorb 1064 nm light. Metal nanoparticles often have less adsorbed organic contaminants than black carbon and could be ideal seeds for these types of studies. Figure 8 shows examples

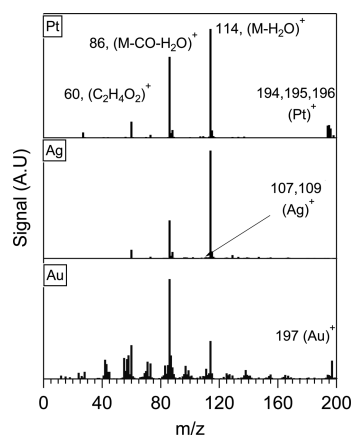


Figure 8. VUV-SP-AMS mass spectra of glutaric acid coated on platinum, silver, and gold nanoparticles. The main glutaric acid peaks and metal peaks are highlighted in the graphs. The platinum and silver spectra were obtained with the low SP laser setting (0.3 V) and 10.5 eV VUV light. The Au spectrum was obtained at the highest SP laser setting (1.28 V) and with 12 eV VUV light.

of glutaric acid VUV-SP-AMS mass spectra obtained on activated platinum, silver, and gold seed particles. The top two spectra in the figure are obtained with a 10.5 eV VUV beam. These spectra are very similar to the glutaric acid spectrum from Regal Black seed particles (see Figure 6). This demonstrates that SP laser vaporization of organic species off metal particles is as effective as vaporization off black carbon particles at minimizing thermal decomposition and fragmentation. The bottom panel of Figure 8 shows VUV-SP-AMS spectra obtained for glutaric acid using 12 eV VUV energy. This spectrum appears more complicated than the platinum and silver spectra because of organic contaminants in the gold nanoparticle sample. The gold seed spectrum also shows increased fragmentation due to the excess energy provided by the operating conditions (high SP laser power and 12 eV VUV energy). Despite these differences, the spectrum still contains glutaric acid fragment ions at m/z 114 and 86 that can be used for chemical identification.

Given the fact that soft vaporization with pulsed CO_2 lasers operating at 10.6 μm has been successfully utilized in single particle mass spectrometers,^{6–8} it is of use to compare its capabilities with those of SP vaporization. One fundamental difference between SP vaporization and pulsed CO_2 vaporization is the fact that the light absorbing species in the former method is the absorbing core and not the vaporized organic species themselves. Both methods, however, produce less fragmented organic mass spectra and are thus useful for measuring the chemical composition of organic aerosol particles.^{36,37} In addition to bulk composition, pulsed CO_2 lasers have been used to provide detailed information about single particle composition as a function of depth within the

particle.^{60,61} These studies have demonstrated layer by layer vaporization of individual particles (depth profiling), allowing for selective characterization of surface and/or bulk compositions. The depth profiling capability is achieved by varying the fluence or the wavelength (when a tunable optical parametric oscillator is used) of the vaporizing laser.^{60,61} The degree to which differential vaporization of organic coating species can be successfully achieved with SP vaporization is not yet known. However, the fact that the SP laser power can be varied between operating conditions that allow for vaporization of only the coating or both coating and core suggests that preferential desorption of coating species may be potentially achieved by varying the SP laser power. It is also useful to point out that bulk and surface effects could still be explored with the SP vaporizer in laboratory experiments by varying the thickness of the organic coatings. The capability of the SP-AMS to detect and characterize a range of organic coating thicknesses from extremely thin coatings (as small as a few nm) to coatings with 10 times the mass of the absorbing core has been previously demonstrated.¹¹

3.2.2. Evaluation of Elemental Ratios Obtained from SP-AMS Spectra. During ambient operation, SP-AMS instruments are often operated while alternating between SP vaporization and thermal vaporization with a 600 °C oven. Thus, it is useful to consider the implications of the observed differences in SP-AMS and AMS organic mass spectral patterns on analyses of combined data sets. Positive matrix factorization of field data with interleaved AMS and SP-AMS mass spectra, for example, is likely to identify the mass spectral differences between these two vaporization sources as different factors. The elemental ratios (O/C and H/C) extracted from the SP-AMS and AMS mass spectra of a given oxidized species are also likely to be different because of differences in the measured mass spectra. Current elemental analysis methods for AMS spectra are based on calibrations with standard organic molecules vaporizing on a 600 °C surface.^{41,62,63} The calibration factors account for differences between the elemental compositions of the detected fragment ions and their parent molecules, e.g., due to the tendency of more electronegative fragments with high O content to end up as neutrals rather than as positive ions during the ion fragmentation process. Since the relative intensities of the ions detected in SP-AMS spectra differ from those observed in AMS spectra, these calibration factors are unlikely to be appropriate for SP vaporization conditions. Figure 9 compares the O/C and H/C ratios calculated for oxidized organic species from AMS (600 °C oven) and SP-AMS (high SP laser driver

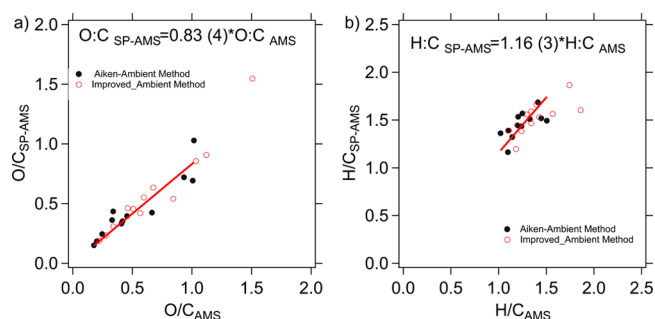


Figure 9. Comparison between O/C ratios (panel a) and H/C ratios (panel b) obtained from SP-AMS and AMS (600 °C) mass spectra using the Aiken-Ambient and Improved-Ambient analysis methods.^{41,63}

voltage) spectra using the Aiken-Ambient and Improved-Ambient methods.^{63,41} The oxidized organics examined in this comparison include C3–C9 diacids (malonic, succinic, glutaric, pimelic, azelaic), multifunctional acids (citric, *cis*-pinonic, tartaric, ketoglutaric, ketopimelic), and alcohols (xylitol, sucrose). The relative differences between the elemental ratios calculated from SP-AMS and AMS spectra are similar for both Aiken-Ambient and Improved-Ambient methods. The fit to the Aiken-Ambient results indicates that the SP-AMS O/C and H/C values differ from their corresponding AMS values by factors of 0.83 and 1.16, respectively.

4. CONCLUSIONS

This study utilizes near-threshold VUV ionization to investigate the degree to which soft SP vaporization can be utilized to obtain enhanced chemical information about aerosol particles. Different types of black carbon particles (ethylene flame soot, C₆₀, fullerene black, Regal Black, methane flame soot, and hydrophilic methane flame soot) were studied. The VUV-SP-AMS spectra of all of these materials are dominated by small carbon cluster cations (C⁺–C₅⁺). The VUV-SP-AMS and SP-AMS spectra display similar trends in carbon cluster ion ratios across different types of black carbon. The observed VUV-SP-AMS ratios are consistent with previous observations that C⁺/C₃⁺ and C₄⁺/C₃⁺ ratios differ between black carbon samples with low and high fullerene content.³⁵ Taken together, these results indicate that the small carbon cluster ion signals in SP-AMS data could provide useful additional information for multivariate analysis of ambient aerosol.

VUV-SP-AMS and SP-AMS spectra of oxidized organic species adsorbed on black carbon and metallic particles (silver, gold, and platinum) were also examined in this study. The purpose of these experiments was to investigate whether the soft SP vaporization scheme provides more chemical information than traditional thermal vaporization methods operating at lower temperatures. Both types of SP-AMS spectra display less fragmentation and thermal decomposition than corresponding AMS spectra obtained with a thermal vaporizer set at 200 °C (the lowest temperature needed to vaporize most oxidized organic species observed in the atmosphere). These measurements suggest that the SP-AMS could be used to provide enhanced chemical information in laboratory experiments that utilize seed particles that absorb 1064 nm light. VUV-SP-AMS spectra of organic coatings adsorbed on metal nanoparticles indicate that they could function as ideal seeds particles for these types of experiments. The differences in mass spectral fragmentation patterns also result in differences in elemental ratios calculated from AMS and SP-AMS spectra. For the oxidized organic species tested here, the O/C and H/C ratios calculated from SP-AMS spectra differ by factors of 0.83 and 1.16, respectively, from those obtained using AMS spectra.

■ ASSOCIATED CONTENT

■ Supporting Information

Figure S1 comparing VUV-SP-AMS mass spectra of Regal Black, ethylene, and fullerene black; Figure S2 showing the carbon cluster relative intensities in VUV-SP-AMS and SP-AMS spectra for the same three species; Figure S3 showing an expanded view of C₆₀ SP-VUV-AMS and SP-AMS spectra around the C₆₀⁺ region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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