Surface-Enhanced Raman Spectroscopy for Environmental Monitoring of Aerosols

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ABSTRACT: Surface-enhanced Raman spectroscopy (SERS) is conducted from single aerosol particles held in a linear electrodynamic quadrupole trap. SERS measurements from two representative types of ambient aerosol particles, semi-liquid and solid aerosols, are demonstrated; aerosol composed of adenine where the metallic nanoparticles (MNPs) are volume distributed throughout the particle and aerosol composed of polystyrene latex (PSL) beads where the MNPs are surface coated. An enhancement factor > 10^6 is demonstrated from 5 μm aerosols containing trace amounts of adenine (0.1% by mass), with a detection limit of 10^-8 M corresponding to 5 × 10^5 molecules (equivalent to 100 ag in mass or a 50 nm diameter sphere), and a ratio of 100 adenine molecules per Ag NP. SERS signal intensities are linear with particle adenine concentration up to a saturation point. Both the linearity and enhancement factor were confirmed by SERS measurements of adenine as bulk suspensions. The SERS spectra of adenine as bulk suspensions were explored as a function of excitation wavelength ranging from 400 to 800 nm. The two main Raman peaks of adenine at 738 and 1336 cm^-1 exhibit SERS maxima for excitation in the 450−500 nm range for commercially available 40 nm spherical Ag nanoparticles (NPs) used in this study, which shifts to longer wavelengths with the addition of NaCl. Shifts in SERS and spontaneous Raman shifts were observed between aqueous and dry adenine, in agreement with the literature, demonstrating the utility of SERS to possibly study water uptake of aerosols. SERS is measured from MNP surface-coated PSL beads with an enhancement factor of 30 for 5 μm PSLs. Theoretical extrapolation demonstrates that the enhancement factor will increase for decreasing particle size with an estimated enhancement factor of 140 for 1 μm PSLs.

1. INTRODUCTION

There is great interest in understanding the chemical composition of natural and anthropogenic aerosols to elucidate their effect on our planet, health, and climate. Atmospheric aerosols, particularly black carbon and other organic aerosols, heat and cool the atmosphere by absorbing and scattering solar radiation, impacting our climate and hydrological cycle. Hydrophilic organic aerosols and/or molecular clustering that lead to new particle formation can act as cloud condensation nuclei or result in secondary organic aerosol formations. The atmospheric conditions and human contributions to these formations are not yet fully understood. The chemical complexity and the large variability of the physical properties of aerosols, often on very short time scales, make studying the physiochemical properties of aerosols incredibly challenging. Simplifying assumptions have been traditionally made about the mixing state of aerosols in most models, leading to large uncertainties in variables relevant to weather, transport, or deposition in human lungs even though considerable progress has been made in recent years. Besides climate impacts, aerosols of biological origin have important human and animal health and agricultural implications. Of timely relevance and utmost interest is the recent spread of Covid-19, where respiratory illnesses are believed to be transmitted from person to person in the form of droplets and aerosols emitted from infected humans through cough, speech, or just breathing.

Despite significant advances in instrumentations and understanding these various complex phenomena, there is room for advancement. Single particle investigations are well suited to contribute and are pursued in fields ranging from environmental sensing to defense applications as they allow us to probe and characterize the individual particles without the added complexity imposed by studying spectra of a population of particles. Furthermore, aerosol mixing state modeling...
Surface enhanced Raman spectroscopy (SERS) is also an attractive technique that can probe single particles as it combines the specificity offered by Raman spectroscopy with the sensitivity needed to study the weak spectra of individual aerosol particles. In recent years, there has been a surge in the number of SERS studies from individual particles, exploiting various properties of aerosols such as chemical composition, reactions, and formation and to probe their environment such as water adsorption and pH. Surface-enhanced Raman spectroscopy (SERS) is an analytical technique that can resolve the molecular compositions of individual aerosol particles. The SERS response can be enhanced either on the surface of the particles or throughout the sample matrix. The study of atmospheric and surrogate aerosols using SERS has encompassed a wide range of techniques. SERS spectral measurements using Raman microscopy has been conducted on atmospheric particles ranging in size from 150 to 800 nm that were collected and deposited on a substrate coated with silver (Ag) NPs. Tip-enhanced Raman spectra were studied from nanometer-sized simulated ambient particles. Electrospray-coated SERS, where the metallic nanoparticles (MNPs) are coated on the surface of collected aerosols to enhance the back-scattered Raman signal in microscopy, was demonstrated by Gen et al. SERS was also demonstrated from 2 m stand-off detection configuration technique that allowed clouds of particles and MNPs to mix and coat to provide Raman enhancement. While all these techniques have their advantages, the interest of the authors is to develop a technique that would lead to an inline SERS measurement technique that samples individual aerosol particles from the ambient air. In our prior paper, we reported the first-time observation and measurement of surface-enhanced resonance Raman spectroscopy (SERRS) signatures from individual micron-sized suspended aerosol particles containing MNPs and 10 enhancement. We note two distinct advantages of performing SERS measurements on suspended aerosols compared to aerosols collected on a substrate. First is the possibility that this technique could lead to in situ measurement capability, where the sampled aerosols from the atmosphere are co-deposited with MNPs inline prior to downstream Raman detection. Second is the increased MNP and analyte interaction due to the higher coverage of the aerosol with MNPs compared to the relatively small overlap between an aerosol particle and a substrate.

In this paper, we explore the SERS response of two types of ambient aerosols; solid and liquid or semi-liquid. When the sampled aerosols are solid, we expect the MNPs to only coat the surface of the aerosol and the measured SERS signal would be representative of the surface properties of the aerosol. However, if the sampled aerosols are in the semi-liquid state, one expects the sprayed MNPs to be able to diffuse into the aerosol, resulting in a volumetric coverage, and the measured SERS would be representative of the volume of the aerosol particle that adsorbed the MNPs. We use adenine (surrogate for liquid/semi-liquid particles), a nucleobase of DNA routinely studied as a biomarker, and polystyrene latex (PSL) beads (surrogate solid particles) which are typically used as calibration standards. We use adenine as a base material for volume-infused aerosols (surrogate for liquid/semi-liquid particles) where the MNPs are distributed throughout the particle and PSL beads are used as surrogate solid particles for the surface-coated aerosol work. We generate single-suspended particles from droplet suspensions containing analyte molecules of interest and MNPs. To validate our technique, we compare our SERS measurements from individual aerosols, with bulk suspensions prepared with the same analytes and colloids of MNPs. Spontaneous Raman spectra of aerosol and bulk suspensions of the same analyte materials are measured for comparison of their spectral features and for quantification of enhancement factors. The effect of addition of water is studied in Raman and SERS spectra, demonstrating an application in aerosol water uptake studies, an important research area. The SERS spectra of the bulk adenine suspension is explored as a function of excitation wavelength in the 400 to 800 nm region with peak enhancements in the 450 to 500 nm region. The effect of the addition of NaCl is predicted and corroborated by measurements. Observation of two new peaks at 1685 and 2140 cm⁻¹, not explored in a prior literature is discussed. SERS spectra of the PSL surface coated with MNPs are explored. Modest enhancement factors are reported, and theoretical extrapolations for more relevant size aerosol particles are discussed. The applicability of SERS to study individual aerosol particles is demonstrated with possibility for future in situ application.

2. RESULTS AND DISCUSSION

2.1. Evaluation of Commercially Available Silver NPs.

We are interested in using commercially available MNPs for...
our SERS study in order to ensure repeatability and ease of use. In a previous SERS paper,19 we used Ag particles from BBI solutions and demonstrated a SERRS enhancement factor of $10^5$ for rhodamine 590 chloride (R6G) as aerosol and aqueous suspension using 532 nm excitation. Here, we use three other commercially available Ag NPs and compare their enhancement factors with the Ag particles used in our prior work.31 40 nm Ag (BBI Solutions) with a particle concentration of $9 \times 10^9$ per mL of water. The three Ag samples are: 40 nm PELCO NanoXact (Ted Pella) with a particle concentration of $5.7 \times 10^9$ per mL of 2 mM citrate/water, 80 nm PELCO NanoXact (Ted Pella) with a particle concentration of $7.1 \times 10^8$ per mL of 2 mM citrate/water, and nanocube (NanoComposix), a cubic-shaped MNP with linear dimensions of 75 nm with a particle concentration of $2.3 \times 10^{11}$ per mL of ethanol. Laser dye, R6G, is used as the analyte for this comparison study whose absorption peak matches the interrogation wavelength of 532 nm. The bulk suspensions are prepared by combining the various MNP suspensions with $10^{-5}$ M NaCl and $10^{-8}$ M R6G. The nanocube suspension was used as received in ethanol since mixing with NaCl greatly reduces the SERS signal. The recorded SERRS spectra from the four bulk suspensions are plotted in Figure 1a. The typical broad fluorescence of R6G is observed along with the prominent Raman peaks at 617, 777, 1367, 1514, and 1657 cm$^{-1}$. The extinction spectra recorded for each of these samples are shown in Figure 1b. Two of the new Ag NPs exhibit higher SERRS response compared to the 40 nm Ag suspension used in our prior study. 40 nm PELCO NanoXact and 75 nm cubes are a factor of 20 and 2 higher, respectively, whereas 80 nm PELCO NanoXact shows a factor of 2 lower signal, averaged for the five Raman bands of R6G stated above. Both 40 nm Ag NPs are spherical in shape, and with suspensions of similar size distributions, but the concentration of 40 nm PELCO NanoXact is six times higher compared to the 40 nm Ag suspension used in the previous study. The higher concentration results in the higher enhancement and extinction observed in Figure 1. The 80 nm PELCO NanoXact suspension with comparable concentration and extinction shows a weaker signal by a factor of two. Even though the 75 nm nanocubes have 26 times higher concentration, the enhancement is only higher by a factor of two. We do not have an explanation for this discrepancy. However, one main difference is in the suspension preparation, the addition of NaCl, which is essential for good enhancement in R6G/Ag suspensions, reduces the SERRS response for the nanocubes; therefore, the suspension with nanocubes was used as is, while NaCl was added to the other three suspensions. Furthermore, as the extinction spectra in Figure 1b demonstrate, the plasmon resonance band is broad for the nanocubes, covering the range of 350–600 nm with the peak near 600 nm. This comparison study demonstrates that 40 nm PELCO NanoXact ($10^{-10}$ M concentration) suspension exhibits the highest SERRS response and was therefore chosen to be used exclusively in the rest of studies included in this report.

2.2. Adenine as Bulk Suspension. Adenine (C$_5$H$_5$N$_5$) is one of the four nucleobases in the nucleic acid of DNA and thus widely used in studies as a biomarker. Adenine was chosen for our SERS study since it is a thoroughly studied SERS material and represents a broad class of biological and organic materials present in the atmosphere. The prominent peaks near 730 and 1330 cm$^{-1}$ are found in the SERS spectra of various bacterial species and have been assigned to adenine or adenine-related compounds like adenosine or ATP.33–35 Adenine and five other purine compounds are shown to be responsible for most of the 785 nm excited SERS peaks from vegetative bacterial cells.33,36 These compounds are present in the outer layer of bacterial cells and in their secretions from nucleotide degradation or DNA denature.33,36 The 730 cm$^{-1}$ band of adenine has been shown to be highly enhanced in SERS analysis of organic compounds and therefore may serve as a sensitive biomarker for aerosolized biological particles.

The SERS spectra of adenine are studied in the bulk suspension and in the aerosol form for comparison study. For bulk measurements, the samples are prepared and placed in standard 3 mm cuvettes for measurement. Adenine solution in water of varying concentrations in the range of $10^{-2}$ to $10^{-9}$ M are combined with $10^{-10}$ M 40 nm Ag NP suspensions in water and $10^{-2}$ M NaCl solution, and their spectra are recorded. As an example, the SERS spectrum for $10^{-6}$ M concentration of adenine is shown in Figure 2 along with the spontaneous Raman spectrum of 10$^{-1}$ M adenine in 10$^{-1}$ M solution of NaOH in water. At such high concentrations, adenine solution is opaque and the addition of NaOH dissolves adenine, resulting in a clear solution making transmission of the laser beam possible.37 Both Raman and SERS spectra are recorded under identical experimental conditions using 100 mW laser (2 kW/cm²) with 100 s of exposure. The Raman spectrum exhibits a red shift, in agreement with the literature and is discussed in Section 2.4. A SERS enhancement of 10$^6$ is demonstrated. The strong peak around 240 cm$^{-1}$ is observed and attributed to the formation of Ag–N or Ag-Cl complexes.

![Figure 2. Raman and SERS spectra of bulk suspensions of adenine.](https://doi.org/10.1021/acsomega.1c00207)

Figure 2. Raman and SERS spectra of bulk suspensions of adenine. The SERS spectrum was recorded from a suspension of $10^{-6}$ M adenine, $10^{-10}$ M 40 nm Ag NPs, and $10^{-2}$ M NaCl in water. The spontaneous Raman spectrum was measured from a solution of $10^{-1}$ M adenine in $10^{-1}$ M solution of NaOH in water. Both spectra are recorded using 100 mW laser (2 kW/cm²) with 100 s of exposure. The SERS spectrum exhibits a red shift, in agreement with the literature and is discussed in Section 2.4. A SERS enhancement of 10$^6$ is demonstrated. The strong peak around 240 cm$^{-1}$ is observed and attributed to the formation of Ag–N or Ag-Cl complexes.
10^{-1} M solution. We observe that the SERS signal is near linear in the 10^{-8} to 10^{-6} M range and exhibits saturation at concentrations higher than 10^{-5} M. The extinction spectra of 10^{-10} M Ag, 10^{-6} M adenine, 10^{-6} M adenine with 10^{-10} M Ag, and 10^{-6} M adenine with 10^{-10} M Ag and 10^{-2} M NaCl are plotted in Figure 3b. The extinction spectrum of adenine exhibits a strong absorption peak around 280 nm, and Ag exhibits the expected primary plasmon resonance peak at 410 nm. The addition of adenine reduces the Ag extinction peak and extends the curve to longer wavelengths, and the addition of NaCl further strengthens this feature by facilitating the agglomeration of Ag that results in a more pronounced secondary peak centered at 700 nm.

The surface area of an adenine molecule is 0.8 nm^2, implying that a maximum of about 4.5 × 10^4 adenine molecules can be in close packing (single layer) contact with each 40 nm MNP. Given the concentration of Ag NPs is 10^{-10} M, this yields an upper bound close contact concentration of 2 × 10^{-6} M. This is in good agreement with the saturation observed in Figure 3a for concentrations of 10^{-5} M and higher, even though NP agglomeration is present in our case, as discussed in Figure 3b, which acts to reduce the close contact concentration. This type of agreement between the observed saturation region and the concentration of close contact molecules was observed in our prior work for a different material, R6G, and implies that almost all the molecules present in the sample are contributing to SERS up to the observed saturation limit. Increasing the concentration of adenine further does not result in additional SERS signal but rather decreases and plateaus for even higher concentration, as demonstrated in Figure 3a. The signal leveling off can occur due to the presence of available silver sites to further enhance the signal, while the decrease in the signal could be due to reabsorption of the emitted SERS photons causing it to quench.

The analytical enhancement factor, the ratio of measured SERS signal to spontaneous Raman signal, can be directly quantified by comparing the SERS signal to the Raman signal normalized by their appropriate concentrations from Figure 3a. The enhancement factor for the 738 cm\(^{-1}\) band ranges from 1.4 × 10^6 to 1.0 × 10^7 and for 1336 cm\(^{-1}\) ranges from 1.1 × 10^6 to 2.4 × 10^8 as the concentration varied from 10^{-6} to 10^{-8} M. Therefore, conservatively, our overall analytical enhancement factor for aqueous adenine can be stated as 10^6.

2.3. SERS of Adenine as a Function of Excitation Wavelength. In order to ascertain the behavior of the SERS signal from adenine as a function of excitation wavelength, an Optical Parametric Oscillator laser is used as the light source and is tuned from 400 to 800 nm in approximately 50 nm intervals to measure the SERS response. The laser is pulsed at 10 Hz with energy varying from 5 to 50 μJ and an exposure time of 100 s. The spectra are corrected for varying laser intensity, transmission of optics and filters, grating, and detector efficiencies. 10^{-7} M adenine is used for this study, mixed with 10^{-10} M MNP's with and without 10^{-2} M NaCl, and their SERS spectra are recorded. The SERS spectra of adenine recorded at the discrete wavelengths of 410, 490, 532, and 610 nm are shown in Figure 4. Notable is the strong peak observed at 1685 cm\(^{-1}\) only for the shortest excitation wavelength of 410 nm. This peak rides on the shoulder of the weak Raman peak of water at 1635 cm\(^{-1}\) due to the OH bending bond observed for the higher excitation wavelengths as well. This peak is prominently present in adenine suspensions with or without NaCl but only for the shortest excitation studied here. Additional studies at lower excitation wavelengths are needed to understand the origin of this peak. To date, we are unaware of discussion about this peak as most researchers are studying the emission in the range of 400–1500 cm\(^{-1}\). This is also true concerning another...
prominent peak at 2140 cm$^{-1}$ that we find grows proportionally to the excitation wavelength.

To quantify the SERS dependence on excitation wavelength, the signal is integrated for each of the 738, 1336, and 2140 cm$^{-1}$ bands and are plotted as a function of excitation wavelength, as shown in Figure 5a, for 10$^{-7}$ M adenine with MNPs with and without the addition of 10$^{-2}$ M NaCl. The SERS signals for the two prominent peaks discussed at 738 and 1336 cm$^{-1}$ exhibit maxima for excitation around 450 to 500 nm. The 2140 cm$^{-1}$ increases drastically with an increasing wavelength up to 600 nm. Furthermore, the addition of NaCl causes almost complete quenching of this peak.

To bring out the trends, the SERS signals at 1336 and 2140 cm$^{-1}$ are normalized to the 738 cm$^{-1}$ integrated peak values and are plotted in Figure 5b as a function of excitation wavelength. The ratio at 2140 cm$^{-1}$ is maximum in the UV for the 1336 cm$^{-1}$ band, which is in agreement with the literature. The 2140 cm$^{-1}$ increases as a function of excitation wavelength up to 600 nm. (c) 738 and 1336 cm$^{-1}$ bands are normalized to their respective bands for suspensions without NaCl. It is easy to observe that the addition of NaCl increases the enhancement at longer excitation wavelengths due to the agglomeration of Ag.

![Graph](image-url)

Figure 5. (a) SERS spectra of 10$^{-7}$ M adenine is plotted as a function of excitation wavelength. The integrated peak at 738, 1336, and 2140 cm$^{-1}$ for samples prepared with and without the addition of 10$^{-2}$ M NaCl. Peak enhancement is observed for excitation around 500 to 600 nm. (b) 1336 and 2140 cm$^{-1}$ are normalized to the 738 cm$^{-1}$ band in order to observe the relative relationship among the bands as a function of excitation wavelength, as can be seen the ratio is higher in the UV for the 1336 cm$^{-1}$ band, which is in agreement with the literature. The 2140 cm$^{-1}$ increases as a function of excitation wavelength up to 600 nm. (c) 738 and 1336 cm$^{-1}$ bands are normalized to their respective bands for suspensions without NaCl.

To quantify the effect of the addition of NaCl, the SERS bands at 738 and 1336 cm$^{-1}$ measured for samples with 10$^{-2}$ M NaCl are normalized to the corresponding bands without NaCl and are plotted in Figure 5c. As seen in Figure 3b, the addition of NaCl to the adenine/Ag suspension drops the extinction at 400 nm by about a factor of two and broadens the secondary plasmon peak to cover the range of 600–800 nm, indicative of NP agglomeration. The addition of NaCl impacts the SERS spectra as one predicts from the extinction spectral response. The addition of NaCl results in lower enhancement for shorter excitation wavelengths of less than 500 nm corresponding to the reduction observed in the extinction spectrum due to the addition of NaCl. The SERS signals exhibit similar intensity for samples with and without NaCl in the 500 to 600 nm region corresponding to the indifference observed in the extinction spectra. At longer excitation wavelengths, the SERS signals for samples with the addition of NaCl display higher signals corresponding to the agglomeration exhibited by the NPs which contribute to enhanced signals.

2.4. Adenine as Aerosol. For the aerosol studies, suspensions similar to the bulk samples are prepared: pure adenine for spontaneous Raman spectra and adenine mixed with 10$^{-10}$ M 40 nm Ag NPs and 3 × 10$^{-2}$ M NaCl solution for SERS studies. Droplets of the suspension are introduced into the linear electrode dynamic quadrupole (LEQ) trap for study. The initial diameter of the generated droplets ranges from 35 μm (22 pL) to 50 μm (65 pL). Under ambient conditions, the droplets dry within several milliseconds, resulting in particles that are 4 to 6 μm in diameter. Our LEQ trap is capable of trapping particles greater than 0.5 μm in diameter under ambient airflow conditions. Therefore, for studying aerosols composed of dilute analytes as in our SERS studies.

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studies, an inert material such as NaCl was added to create micron-sized particles after water evaporation, in order to facilitate ease of trapping and interrogation. The Raman and SERS spectra are recorded under identical experimental conditions using 500 mW of laser power (10 kW/cm² fluence) and exposure time of 300 s (Raman) and 100 s (SERS).

The measured spontaneous Raman spectrum from a 5 µm pure adenine particle generated from a 10⁻¹ M droplet is plotted in Figure 6a along with the spontaneous Raman spectrum from a 10⁻¹ M pure adenine particle generated from a 10⁻¹ M droplet is plotted in Figure 6a along with the spontaneous Raman spectrum of bulk adenine suspension discussed in Figure 2. Due to the long exposure time of 300 s, the weak Raman line of atmospheric oxygen, O₂ (1554 cm⁻¹) is recorded during the aerosol measurement due to the long 300 s exposure time and is highlighted. Similarly, the SERS spectrum from a 5 µm NaCl particle with 10⁻⁶ M adenine and 10⁻¹⁰ M Ag NPs is plotted in Figure 6b along with the corresponding SERS spectrum of the same concentration of adenine in bulk aqueous suspension, also discussed in Figure 2. Notable are subtle shifts in the major bands between aqueous and dry adenine and between the spontaneous Raman and SERS spectra. Dotted lines are drawn at the center of the SERS measurement from aerosol to highlight the subtle differences in the spectra between aqueous and dry adenine for SERS and spontaneous Raman spectra.

![Figure 6](https://pubs.acs.org/doi/10.1021/acsomega.1c00207)

Figure 6. (a) Spontaneous Raman signal of 10⁻¹ M adenine as aerosol and bulk suspensions. The Raman spectra of atmospheric oxygen (1554 cm⁻¹) is also measured during the aerosol measurement due to the long 300 s exposure time and is highlighted. (b) SERS spectra of 10⁻⁶ M adenine as aerosol and bulk suspensions. Dotted lines are drawn at the center of the SERS measurement from aerosol to highlight the subtle differences in the spectra between aqueous and dry adenine for SERS and spontaneous Raman spectra.

| Table 1. Raman and SERS Bands of Adenine in Comparison to the Literature |
|--------------------------|--------------------------|--------------------------|
|                      | Spontaneous Raman 532 nm | SERS Aqueous 400 to 800 nm; Dry at 512 nm | SERS 785 nm | SERS 632 nm |
|                      | aqueous                  | dry-aerosol              | colloids    | electrode   | island     |
|                      | 334                      | 540                      | 543         | 536         | 559        |
|                      | 567                      | 625                      | 626         | 624         | 624        |
|                      | 663                      | 754                      | 731         | 732         | 732        |
|                      | 789                      | 961                      | 958         | 998         | 954        |
|                      | 1254                     | 1000                     | 1245        | 1262        | 1094       |
|                      | 1257                     | 1027                     | 1244        | 1270        | 1049       |
|                      | 1334                     | 1279                     | 1244        | 1270        | 1049       |
|                      | 1541                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1544                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1545                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1554                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1564                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1565                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1574                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1584                     | 1280                     | 1244        | 1270        | 1049       |
|                      | 1594                     | 1280                     | 1244        | 1270        | 1049       |

https://doi.org/10.1021/acsomega.1c00207
ACS Omega 2021, 6, 10150−10159
dry particles compared to the aqueous suspension of adenine for the same two peaks. Nevertheless, the SERS and the reported Raman peaks for the dry and aqueous samples agree well with the peak positions experimentally and theoretically modeled and compiled from the literature by Nergui et al. as well as peaks reported by others.37,38

SERS peak measurements for an excitation wavelength of 632 nm along with their corresponding Raman band assignments are reported for three SERS measurement modalities, Ag colloids, Ag electrode, and Ag island, by Giese and McNaughton and are also included in Table 1. Our aqueous SERS peaks agree well with those reported aqueous SERS peaks, and our aerosol SERS measurements correlate well with the electrode and island measurements. SERS measurements of aqueous adenine with Ag colloid and MgSO4 for an excitation wavelength of 785 nm is reported by Bell and Sirimuthu and are also reproduced in Table 1. Their reported bands agree well with those reported aqueous SERS spectra recorded from a bare and coated 20 μm PSL, and the equivalent diameter of adenine ranges from 5 × 106 to 107 as the concentration varied from 10−5 to 10−8 M. Therefore, conservatively, the overall analytical enhancement factor for adenine as aerosols can be stated as 6 × 106. These enhancement factors are in good agreement to the enhancement factors reported for adenine as a bulk suspension.

2.5. PSL Beads as Aerosol. When droplets are generated and dried down from suspensions that contain the analytes of interest and MNPs, the residual dry aerosols contain MNPs embedded throughout the particle. However, when the analytes or sampled aerosols are solid, the added MNPs can only coat the surface of the particle and therefore the measured SERS signal and enhancement are only representative of the molecules at the surface of the aerosol. To quantify SERS from such solid aerosols, we use PSL beads as the surrogate. A suspension of PSL beads and MNPs is used to generate droplets that dry to form aerosol consisting of PSL beads surface coated with MNPs. The spontaneous Raman and SERS spectra recorded from a bare and coated 20 μm PSL, respectively, are shown in Figure 8a. Both Raman and SERS spectra were obtained using 500 mW of laser power (10 kW/cm² fluence) and 100 s exposure time. The spontaneous Raman and SERS spectra correlate well with the prominent peaks at 620, 1002, 1157, 1187, 1453, 1606, 2937, and 3084 cm⁻¹. These values are plotted in Figure 7 as a function of concentration, particles in the size range of 4–6 μm are generated at each concentration. The mean of the integrated peaks, after baseline subtraction, is computed for the same two peaks. Nevertheless, the SERS and the reported Raman peaks for the dry and aqueous samples agree well with the peak positions experimentally and theoretically modeled and compiled from the literature by Nergui et al. as well as peaks reported by others.37,38

The spontaneous Raman signal in Figure 7 is corrected for variation in particle size and camera exposure differences between the SERS and Raman measurements. The approximate number of molecules present in the aerosol is listed along the secondary x-axis on the top of Figure 7 and ranges from 107 to 108 molecules. The variation in the data is largely due to the wide distribution in particle sizes (mass varies by a factor of 3.4 for particles ranging in size between 4 and 6 μm in diameter) as well as possible variation in the particle morphology in terms of proximities of adenine molecules to MNPs among NaCl molecules. The SERS signal exhibits a linear response with a slope of near unity at lower concentrations and shows saturation and quenching at concentrations higher than 10⁻⁶ M. The experimentally observed saturation range of 10⁻⁶ M for aerosol is in good agreement with the single-layer close contact concentration of 2 × 10⁻⁶ M and experimental observation for the bulk suspension case. As the concentration of the analyte is further increased beyond the saturation region, quenching can occur due to reabsorption of the elastic and Raman scattering light.

In order to quantify the SERS response of adenine as a function of concentration, particles in the size range of 4–6 μm are generated at each concentration. The mean of the integrated peaks, after baseline subtraction, is computed for about 20 particles that exhibit SERS for the two bands at 734 and 1330 cm⁻¹. These values are plotted in Figure 7 as a function of adenine concentration with error bars representing one standard deviation along with the spontaneous Raman signal from pure adenine aerosols generated from 10⁻¹ M solution. The 10⁻¹ M solution resulted in consistently larger particles with a mean diameter of 7.5 μm; in this manner, the reported spontaneous Raman signal in Figure 7 is corrected for variation in particle size and camera exposure differences between the SERS and Raman measurements. The approximate number of molecules present in the aerosol is listed along the secondary x-axis on the top of Figure 7 and ranges from 10⁷ to 10⁸ molecules. The variation in the data is largely due to the wide distribution in particle sizes (mass varies by a factor of 3.4 for particles ranging in size between 4 and 6 μm in diameter) as well as possible variation in the particle morphology in terms of proximities of adenine molecules to MNPs among NaCl molecules. The SERS signal exhibits a linear response with a slope of near unity at lower concentrations and shows saturation and quenching at concentrations higher than 10⁻⁶ M. The experimentally observed saturation range of 10⁻⁶ M for aerosol is in good agreement with the single-layer close contact concentration of 2 × 10⁻⁶ M and experimental observation for the bulk suspension case. As the concentration of the analyte is further increased beyond the saturation region, quenching can occur due to reabsorption of the elastic and Raman scattering light.

When considering the composition of the particles discussed in Figure 7, even for particles generated from the highest concentration of adenine (10⁻³ M), the mass fraction composition of a nominally 5 μm aerosol particle is 98.8% NaCl, 1.1% Ag NPs, and 0.08% adenine. Therefore, the aerosols are mainly composed of the inert constituent NaCl used to facilitate trapping under ambient conditions. The estimated number of MNPs for each aerosol particle is around 5 × 10⁵, and the number of adenine molecules range from 5 × 10⁵ (equivalent to 100 ag in mass or a 50 nm diameter sphere) to 5 × 10⁸ (equivalent to 100 fg in mass or a 500 nm diameter sphere) per aerosol particle, as shown in the top secondary x-axis label of Figure 7. The ratio of adenine molecules to each MNP is 100 at the limit of detection concentration of 10⁻⁸ M. The analytical enhancement factor can be computed by taking the ratio of the measured SERS signal to the spontaneous Raman signal normalized by their appropriate concentrations from Figure 7. The enhancement factor for the 734 cm⁻¹ band ranges from 9.5 × 10⁵ to 1.8 × 10⁷ and for the 1330 cm⁻¹ band ranges from 6.4 × 10⁶ to 2.2 × 10⁷ as the concentration varied from 10⁻⁶ to 10⁻⁸ M. Therefore, conservatively, the overall analytical enhancement factor for adenine as aerosols can be stated as 6 × 10⁶. These enhancement factors are in good agreement to the enhancement factors reported for adenine as a bulk suspension.

ACS Omega 2021, 6, 10150−10159
prior paper. The theoretical enhancement factor can be measured for adenine in bulk and aerosol and R6G in a single-layer molecule contribution calculations are corroborated by the percentage of particles that are present in a single outer layer that contributes to the enhancement factor. We correlate well with the measured enhancement factor for 5 μm PSLs and is plotted in Figure 8b. The linearity was demonstrated for concentrations ranging from 10^-8 to 10^-6 M and exhibiting saturation at higher concentrations. A SERS analytical enhancement of 6 × 10^6 was measured for suspended individual particles with a detection limit of 10^-8 M (5 × 10^5 molecules or 100 ag in mass or 50 nm equivalent diameter) with a ratio of about 100 adenine molecules per Ag NP. Similarly, an analytical enhancement factor of 10^6 was measured from adenine as a bulk suspension with signal linearity in the same concentration range of 10^-8 to 10^-6 M. Distinct shifts between the Raman and SERS spectra are observed for dry (aerosol) and aqueous suspensions that agree with values reported by other researchers. The consistent shifts in the presence of water and the enhanced sensitivity of SERS lend itself as a potential technique to study the water content of individual atmospheric aerosols, an important area of research.

The SERS spectra of adenine as a bulk suspension was investigated as a function of excitation wavelength ranging from 400 to 800 nm. The two main peaks at 738 and 1336 cm^-1 exhibit maxima for excitation in the 450–500 nm range for 40 nm Ag NPs used in this study with the ratio at 1336 to 738 cm^-1 band being the highest in the UV compared to their visible and near infrared counterparts. Two peaks not referenced in literature were also observed, one at 1685 cm^-1 only for the shortest excitation wavelength of 410 nm and second at 2140 cm^-1, that grew proportionally to the excitation wavelength up to 600 nm. The effect of the addition of NaCl to the adenine/Ag suspension on the SERS spectra as referenced in literature were also observed, one at 1685 cm^-1 only for the shortest excitation wavelength of 410 nm and second at 2140 cm^-1, that grew proportionally to the excitation wavelength up to 600 nm. The effect of the addition of NaCl to the adenine/Ag suspension on the SERS spectra as a function of excitation energy was investigated. The SERS amplitude increased at the longer emission bands due to the enhancement.

3. CONCLUSIONS

Spontaneous Raman and SERS measurements have been conducted from bulk samples of suspensions and from single aerosol particles held in an LEQ trap. SERS measurements from commercially available Ag NPs were evaluated to identify MNPs with good SERS yield. SERS was measured from two types of aerosol particles, aerosol composed of adenine where the MNPs were distributed thorough the particle and aerosol composed of PSL beads with MNPs distributed only on the surface. SERS signals were recorded from 5 μm aerosols composed of NaCl with varying trace concentrations of adenine and Ag NPs while being held in a LEQ trap. Signal linearity was demonstrated for concentrations ranging from 10^-8 to 10^-6 M and exhibiting saturation at higher concentrations. The SERS spectra of adenine as a bulk suspension was investigated as a function of excitation wavelength ranging from 400 to 800 nm. The two main peaks at 738 and 1336 cm^-1 exhibit maxima for excitation in the 450–500 nm range for 40 nm Ag NPs used in this study with the ratio at 1336 to 738 cm^-1 band being the highest in the UV compared to their visible and near infrared counterparts. Two peaks not referenced in literature were also observed, one at 1685 cm^-1 only for the shortest excitation wavelength of 410 nm and second at 2140 cm^-1, that grew proportionally to the excitation wavelength up to 600 nm. The effect of the addition of NaCl to the adenine/Ag suspension on the SERS spectra as a function of excitation energy was investigated. The SERS amplitude increased at the longer emission bands due to the enhancement.
agglomeration of MNPs that shifted the plasmon resonance band to longer emissions in the extinction spectra.

SERS was recorded from aerosols containing single PSL beads coated with MNPs only on the surface and used as a surrogate for solid aerosols. We demonstrated an enhancement factor of about 30 for 5 μm PSL beads, and theoretical extrapolation shows the possibility to reach an enhancement of at least 140 for 1 μm PSL beads but were not able to demonstrate this due to limitations of the current experimental setup. This also demonstrates the need for us to explore non-spherical geometries of MNPs such as faceted MNPs or hot-spot generation that would improve the SERS enhancement factor and enable SERS measurement from individual solid micron-sized particles in real time.

4. EXPERIMENTAL SETUP

The experimental setup is described in detail elsewhere. In brief, the setup is designed to easily measure Raman spectra from either suspended single aerosol particles held in a LEQ trap or from bulk samples in a cuvette. A 532 nm wavelength CW laser is used as the Raman light source for all the Raman studies presented here. A 657 nm wavelength diode laser is colinear with the 532 nm laser and is used to monitor the position of the trapped particles by collecting the scattered light onto position-representative pixels of a CCD camera. Positional control of particles within the trap is accomplished by balancing the forces of gravity and a downward air flow against an electrostatic balancing field at the bottom of the chamber. By monitoring the position of the aerosol using the CCD camera, we provide a real-time feedback to adjust the DC balancing potential, maintaining the particle at a fixed position in the center of the focal volume of the collection lens nominally to within a few percent of their diameters. Droplets in the size range of 30–100 μm are generated, charged, and introduced into the LEQ by means of a nominally 100 μm ID glass capillary (see Hart et al. for details on the design, operation of the LEQ trap, and the introduction of charged droplets). If the droplets are mainly composed of water or other volatile liquids, as is the case in our current study, they evaporate relatively quickly (<1 s) to form solid (nearly dry) micron-sized particles depending on the suspended or soluble residue. Besides the constant filtered room airflow, at a nominal rate of 0.2 L/min, no other environmental controls are implemented to control the temperature or humidity in the aerosol chamber.

Most of the spectra reported in this paper are obtained by using laser powers between 10 mW and 500 mW, with a beam waist of about 80 μm, resulting in laser fluences of 0.2 to 10 kW/cm². Acquisition times range from 10 to 300 s. All the SERS measurements are conducted by preparing samples using commercially available colloids of Ag, 40 nm PELCO NanoXact (Ted Pella), unless specified otherwise. The samples are prepared, and spectra were measured as soon as possible, which is within a period of 10 min for bulk measurements and within 30 min for the aerosol measurements.

All the spectra are presented after background subtraction. For quantification of the Raman peaks, the intensity under the curves is integrated after baseline subtraction. The reported analytical enhancement factors are computed from the ratio of the measured and integrated SERS signal normalized to the concentration of the sample to the spontaneous Raman signal normalized to the concentration of the same analyte in the same sample modality (liquid or aerosol).

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Notes

The authors declare no competing financial interest.

Acknowledgments

This work was funded by the Office of Naval Research (ONR 61153N).

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