Can vibrational sum frequency scattering spectra be measured from the surface of 40 – 100 nm aerosols in a cloud containing $10^6$ particles / mL?

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Abstract
Understanding the interfacial properties of aerosol particles is important for science and medicine, crucial for air quality, human health, and environmental chemistry. Qian et al. presented vibrational sum frequency scattering (SFS) measurements of organic molecules on aerosol particles.¹ Relating a $10^6$ particle / mL 40-100 nm size distribution to vibrational sum frequency scattering spectra, it was concluded that the vibrational spectra reported on the surface structure of 40 - 100 nm aerosol particles. Here, we show that the SF scattering power of such small particles at the given density is ~$10^7$ smaller than the detection limit of the presented SFS experiment. We determine the detectable number density of particles, both theoretically and experimentally, to demonstrate the limits of the SFS method. We also propose possible origins of the measured data.

Introduction
Aerosol science would benefit greatly from understanding the interfacial structure of airborne particles. However, measuring the surface structure in situ is challenging because of the weak second-order nonlinearity needed to generate a surface response, the dispersive / scattering nature of the sample, the dilution of particles (~ $10^6$ / mL), and the size range of the majority of them (10 - 100 nm). Indeed, vibrational surface SFS spectra as well as non-resonant surface second harmonic scattering (SHS, Fig. 1A, which is comparable) measured from particles dispersed in solution of this size range have been reported with samples containing ~$10^{11}$ particles / mL.²³ Since there is no principle difference in the mechanism and rules that govern nonlinear scattering for particles that are airborne or dispersed in solution,⁴ the results by Qian et al. raise questions as to the nature of the source of the SF scattering object(s), as there is a difference on the order of ~ $10^5$-$10^7$ between the expected scattering power and the detected spectra.

Therefore, we first explicitly determine the number of particles that can be reasonably measured for a certain size. To do so, we combine theoretical predictions per particle with experiment. We will first consider the throughput of the SFS/SHS experiment and consider its size and number density dependence, then provide a signal-to-noise ratio analysis of various comparable experiments. Using this analysis in combination with SFS and SHS experiments
performed on the same samples, we determine the detection limit in terms of particle density for a certain size. Finally, we discuss several explanations to explain the difference in terms of detected intensity and expected aerosol intensity.

**Size dependence.** Vibrational SFS and non-resonant SHS are second-order nonlinear optical techniques. The intensity of the generated photons obey the following expression:

\[ I(\omega_0) \propto N_p |\Gamma^{(2)}(R, \theta, \chi^{(2)})|^2 \frac{E_1 E_2}{\tau A} f \]  

with \( N_p \) the particle density, \( \Gamma^{(2)}(R, \theta, \chi^{(2)}) \) the effective (single) particle susceptibility, which depends on the radius \( R \), the scattering angle \( \theta \), and the surface susceptibility of the particle \( \chi^{(2)} \), \( E_i \) the pulse energies of the participating beams, \( \tau \) the pulse duration, \( A \) the overlap area and \( f \) the repetition rate. The effective particle susceptibility that determines the response of a single particle \( \Gamma^{(2)}(R, \theta, \chi^{(2)}) \) is highly size dependent and for \( R \sim < 200 \) nm, \( \Gamma^{(2)} \propto R^3 \) \( (I(\omega_0) \propto R^6) \). For larger particles, this size dependence levels off, reaching \( I(\omega_0) \propto R^3 \) at \( R \sim 1000 \) nm. For \( R < 200 \) nm, the Rayleigh-Gans-Debye theory works well to describe the data, while for larger sizes nonlinear Mie theory needs to be used. For water droplets in air, however, the refractive index contrast ensures that for micron-sized or larger particles scattering light is emitted in every direction.

**Table 1: Experimental parameters.** PPP (SSS) refers to all beams polarized in (perpendicular to) the scattering plane.

|                      | SFS as in Ref. 1 | SFS as in Refs. 2,5 | SHS as in Refs. 6,7 |
|----------------------|------------------|---------------------|---------------------|
| **Fundamental wavelength** | 1025 nm          | 800 nm              | 1030 nm            |
| **Repetition rate**   | 100 kHz          | 1 kHz               | 200 kHz            |
| **OPA range**         | 2500 – 4500 nm   | 2600 – 20000 nm     | NA                 |
| **IR pulse energy at the sample (\( \mu J \))** | 2                | 5-10 \( \mu J \)   | 300 nJ             |
| **Visible pulse linewidth (cm\(^{-1}\))** | 8 cm\(^{-1}\)    | 12 cm\(^{-1}\)     | NA                 |
| **Visible pulse energy (\( \mu J \))** | 6 \( \mu J \)    | 5-10 \( \mu J \)   | NA                 |
| **Collection angle range (\( \theta \))** | 90\(^{\circ} \) \pm 30\(^{\circ} \) | \( \theta_{\text{max}} \) \pm 10\(^{\circ} \) | -90\(^{\circ} \) \(< \theta < +90\(^{\circ} \) (3.4\(^{\circ} / \theta) |
| **Max. SNR ratio (PPP or SSP)** | 11               | 5 - 15              | 16 - 26            |
| **SNR ratio SSS bulk H\(_2\)O** |                 |                     | 18 - 21            |
Signal to Noise Ratio. To relate the experimental throughput of the experiments conducted by Rao and co-workers we compare the signal to noise ratio (SNR) of Ref.1 to previously published vibrational SFS and non-resonant SHS data. Table 1 shows the experimental parameters that relate the 3 experiments. The SFS experiment reported in Ref.1 has a comparable SNR compared to previously published SFS data and a 1.4 - 2.4 smaller SNR to non-resonant SHS. Because SHS and SFS have comparable SNRs, we retrieve the particle vs size dependence from SHS. The primary reason to do so is that the SHS intensity of any particle surface can be compared both experimentally and theoretically to the known incoherent bulk response of neat water, which therefore represents a calibration benchmark. With a known hyperpolarizability tensor of water, it is therefore possible to explicitly compute the theoretical response that matches 10 % of the magnitude of the intensity recorded with SNR = 1. We take this as the detection limit of the SFS and non-resonant SHS experiments of particles. Thus, we compute using the theory in Refs.8,9, as a function of particle radius, which number density of particles is needed to generate an intensity that matches 10 % of the incoherent neat bulk water (SSS) intensity. We insert typical values for the surface susceptibility ($\chi^{(2)}$ =10^{-22} m^2/V) and the surface potential ($\Phi_0$ =-100 mV), which represent the surface properties of the particles.

Estimation of particle density vs size dependence. The line in Fig. 1B shows the detection limit in terms of # particles / mL as a function of the radius of the particles. For a 20 nm radius, this means 2.5 x 10^{13} particles / mL are needed to generate the desired SF intensity. Moving to larger particles, we arrive at 5.6 x 10^{10} particles / mL (50 nm radius), 4.2 x 10^{7} (500 nm radius), and finally, extrapolating to non-resonant SH imaging, 1 for objects in the size range of 5 – 10 microns.10 For diameters close to 100, 200 and 300 nm, data points from angle-resolved non-resonant second harmonic scattering measurements6,7 are shown. Based on this result, we estimate that 10^{6} particles / mL can only generate a detectable response if R > 1000 nm. Alternatively, 40 nm particles would have to be present at a density of 2.5 x 10^{13} particles / mL, as indicated by the arrow. Neither of these criteria are met in Ref.1. Fig. 1C shows SFS spectra of deuterated hexadecane droplets with a 109 ± 1 nm average hydrodynamic radius stabilized with 8 mM sodium dodecyl sulfate (SDS), following the protocol of Ref.5. SFS spectra were recorded with particle densities between 10^{11} / mL and 10^{13} / mL, achieved by diluting a stock emulsion (size distribution is shown in the inset). In agreement with Fig. 1B, the recorded SF intensity vanishes below a particle density of 10^{12} / mL. Fig. 1D shows data measured by non-resonant SHS for the same sample diluted with 0.8 mM SDS solution. In both experiments, no detectable
signal can be obtained below $4.9 \times 10^9$ particles/mL, in agreement with predictions of Fig. 1B for identically-sized objects.

**Figure 1: Number density vs size dependence.** A: Illustration of energy schemes of vibrational sum frequency scattering and non-resonant second harmonic scattering. B: Number density necessary to generate a signal-to-noise ratio $= 1$ as a function of particle size, assuming the minimal detectable intensity comprises 10% of the non-resonant SHS response of neat bulk water. The colored area is inaccessible to current non-resonant SHS and vibrational SFS instruments. C, D: Vibrational SFS (C) and non-resonant SHS measurements (D) of SDS stabilized $d_{34}$-hexadecane nanodroplets in D$_2$O measured at different droplet densities, ranging from $1.2 \times 10^{13}$#/cm$^3$ (blue trace) to $1.2 \times 10^{11}$#/cm$^3$ (orange trace, which we consider the detection limit). The number of droplets is computed from the used volume in combination with the hydrodynamic diameter measured by DLS (shown in the inset of C). The spectra in the SFS plot are offset for clarity. The SHS measured intensity (D, black dots) and standard error (grey error bars) are plotted with trend lines for both the intensity above and below the noise level (dashed lines). The detection limit was determined to be at the intersection of both lines at $4.9 \times 10^9$#/cm$^3$.

**Discussion and Conclusion.** Although the values of $\chi^{(2)}$, the scattering angle range, or the surface potential may change, given the difference examined here (a factor of $10^7$ for a particle of 40 nm diameter) these details are relatively unimportant as they would create a maximum difference in the range 0.1 – 10. Since the instrument used in Ref.¹ is not outperforming the instruments used here (Table 1), this brings about the question what actually generates the
unexpectedly strong SFS response. Based on Eq. (1), there are only two candidates for increasing the scattered intensity by x $10^7$: The size of the particles, with the scattering objects being much larger than reported, or $\chi^{(2)}$, which should then increase by $\sim 10^3$. A single particle of a few microns in size could easily overpower the emission of all other particles and generate the measured SF intensity, for example $I(1 \mu m)/I(10 \text{ nm}) \sim (10^2)^3$. To get insight here, one would have to measure the SF scattering patterns, as was done in Ref.2. A time-dependent intensity trace would provide information about the stability of the intensity.11 The second option might revolve around the crystallization of surfactant in a semi-crystalline layer on the surface of the particles. Extremely dilute crystallites have also shown to produce large SFS intensities.12

Summarizing, vibrational SFS from aerosols where 40-100 nm single particle surfaces are probed at densities of $10^6 / \text{mL}$ is not possible with currently available experiments.

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Author contributions
S.R. conceived and designed the work. A.M carried out the theoretical calculations. T.W.G and A.S.C performed the SFS/SHS experiments. A.M, T.W.G and S.R wrote the manuscript. T.W and S.R. directed the work. All authors discussed the results and contributed to the manuscript.

Data availability
The data sets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

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