Response to reviewer 2:

My main issue with this review article is that ignores a lot of recent work in the field and focuses on older papers, e.g.:

Author's Response: Thank you for the constructive comments. The reviewer has commented that we missed a lot of recent publications on various topics. While the suggestions are well taken, we like to emphasize that this paper focuses on the use of **single-particle Raman spectroscopy** to examine the physical and chemical **processes** of atmospheric particles. We describe techniques of particle maneuvering that allow single-particle Raman spectroscopy such as EDB, deposited particles, and optical trapping. However, it is **not** our intention to conduct a detailed examination of the application of these techniques beyond single-particle Raman spectroscopy. Hence, in our review, we put less emphasis on publications focusing on other applications of these trapping techniques. We focus on investigating these physical and chemical processes of particles by Raman instead of the particle properties or detailed descriptions of these processes investigated by other techniques. The overall aim of the paper is to introduce single-particle Raman spectroscopy as a useful tool to examine a host of processes of atmospheric relevance.

The following paragraph has been added to the revised manuscript:

This paper focuses on the use of single-particle Raman spectroscopy to examine the physical and chemical processes of atmospheric particles. We describe techniques of particle maneuvering that allow single-particle Raman spectroscopy such as EDB, deposited particles, and optical trapping. However, it is not our intention to conduct a detailed examination of the application of these techniques beyond single-particle Raman spectroscopy. Hence, in this review, we put less emphasis on literature related to other applications of these trapping techniques. We focus on investigating these physical and chemical processes of particles by Raman instead of the particle properties or detailed descriptions of these processes investigated by other techniques. The overall aim of the paper is to introduce single-particle Raman spectroscopy as a useful tool to examine a host of processes of atmospheric relevance.

Section 2.1.1.: Has there been no EDB work since that 1980 Ray and Davis paper?

Author's Response: There has been lots of EDB work since Ray and Davis (1980). We take that the authors refer to publications related to the development and advancement of electrodynamic trapping of papers for spectroscopic characterizations. We have added recent representative works on new development of new EDB approaches to the manuscript:

In addition to the traditional single-particle EDB (Davis and Ray, 1980; Chan et al., 1992), other EDB set-ups, for example, quadrupole (Q)-EDB and comparative kinetic (CK)-EDB, have been developed. Q-EDB allows the trapping of multiple droplets simultaneously. During chemical reactions, individual particles are released one at a time for mass spectroscopy analysis while the rest of the particles are kept levitated for in-situ spectroscopic characterization (Singh et al., 2017; Jacobs et al., 2017; Singh et al., 2018; Kohli and Davies, 2021). CK-EDB employs a reference droplet with known composition and hygroscopic property, which serves as an accurate probe for the environmental conditions in which the tested droplet is examined. It affords hygroscopicity measurements and mass-transfer kinetic measurements on the droplets at high RH (>99%) (Davies et al., 2013; Rovelli et al., 2016; Marsh et al., 2019).

Section 2.1.2.: Mostly references from 10 years ago. Tons of Raman work involving optical traps since then. No mention of cavity-enhanced Raman scattering.

Author's Response: We have updated representative optical trap works in the manuscript. Since this paper focuses on Raman spectroscopy but not the isolation of single particles, we have only highlighted literature that focuses on the former. We consider cavity-enhanced Raman scattering as the coupling of WGMs (or MDRs) in the Raman spectra. WGMs are separately discussed later in the manuscript.

The following paragraph has been added to the manuscripts.

In addition to radiation pressure traps, photophoretic traps and universal optical traps are two emerging alternatives (Redding et al., 2015a; Redding and Pan, 2015). The former is specifically for light-absorbing particles. The latter employs a hollow beam to trap either transparent and light-absorbing particles using radiation pressure force and photophoretic force, respectively (Gong et al., 2018b). Using these techniques, Raman characterizations have been made on light-absorbing particles in recent years, including bioaerosols (Wang et al., 2015a; Redding et al., 2015a; Redding et al., 2015b; Gong et al., 2018a, 2019), aromatic compounds (Kalume et al., 2017b; Kalume et al., 2017a; Gong et al., 2018a), carbon nano-tubes (Pan et al., 2012; Gong et al., 2018a) and soot (Uraoka et al., 2017).

Section 2.2: Perhaps Refs 39, 40 are somewhat recent WGM references? Can't tell as they don't appear in the references section as they are not in the ACP style. As it stands, this section is very poor.

Author's Response: We have corrected the formatting of the references:
They can accurately determine size with a resolution down to ~5 nm, refractive index, and even shell-core morphology of the mixed organic-inorganic particles based on the Mie theory (Gorkowski et al., 2017; Rafferty and Preston, 2018; Sullivan et al., 2020; Gorkowski et al., 2020). The optical effects complicate the Raman measurements for chemical analysis, although they provide additional information for the sizing and refractive index of the particles based on Mie theory. We refer readers to the references for the interactions between Mie scattering and Raman spectroscopy (Chan et al., 1991; Krieger et al., 2012; Nadler et al., 2019).

Section 3.1: Mostly references from 10+ years ago

Author's Response: We have updated representative references in the manuscript:
There are numerous hygroscopicity applications on various specific systems, including model inorganics, organics, and their mixtures (Chu et al., 2015; Laskina et al., 2015; Wang et al., 2021b; Tobon et al., 2021; Zhang et al., 2021a; Ashraf et al., 2021) mineral dust (Liu et al., 2008), secondary organic aerosols (Wu et al., 2020), atmospheric-relevant biological macromolecules (Mael et al., 2021) using single-particle Raman spectroscopy. It should be noted that evaporation of some components and precipitation of some salts could occur during the RH cycling in hygroscopicity measurements (Li et al., 2017; Cai and Zhao, 2018; Ma et al., 2019a; Ma et al., 2019b; Wu et al., 2020; Li et al., 2021). Single-particle Raman spectroscopy can probe such processes in-situ by the disappearance of some characteristic peaks (evaporation) or changes of their FWHH (precipitation) (Braban et al., 2003; Wang et al., 2017).

Section 3.2: Mostly references from 10+ years ago

Author's Response: We have updated relevant references in the manuscript, but in fact, there are only two relevant publications using Raman spectroscopy to our knowledge.

The AN-AS double salts were recently reported in ambient particles in Beijing (Sun et al., 2019b; Wang et al., 2021a).

Section 3.4: There has been so much work on LLPS in the last 5 years that is not referenced here (and a lot of the papers referenced here have nothing to do with single particle Raman spectroscopy).

Author's Response: We have included the representative LLPS works in recent years and replaces some of the references with more appropriate ones. Again, we only focus on those works that use Raman.

As mentioned above, partial crystallization can lead to a separation of solid and liquid mixed phases. Separation of two or even more liquid phases, namely liquid-liquid phase separation (LLPS), is also possible (Song et al., 2012b; Song et al., 2018; Huang et al., 2021; Ma et al., 2021). LLPS can be triggered by the interactions between inorganic, organic solutes and particulate water in mixed particles (You et al., 2012; Renbaum-Wolff et al., 2016). This phenomenon is mainly attributed to the low solubility of some non-polar or weakly polar organics, especially in the presence of inorganic salts, which may further decrease the solubilities of organics as the salting-out effects (Setschenow, 1889).

Optical microscopy (as a part of a single particle Raman microscope) can directly indicate LLPS by the contrasting colors on appearance, based on the different refractive indices of materials in different phases (You et al., 2012). Single-particle (micro-) Raman spectroscopy can examine LLPS via spatial scanning (micro-Raman), optical imaging (micro-Raman), Raman imaging, and whisper gallery modes (WGMs) with additional chemical information of the different phases (Bertram et al., 2011; Song et al., 2012a). Spatial scanning records distinct micro-Raman spectra at different locations of the particle and reveals LLPS (Bertram et al., 2011; Wu et al., 2018a) such as core-shell structures (e.g., an aqueous core surrounded by a BC-containing organic shell) (Brunamonti et al., 2015). However, Raman spatial scanning requires accurate focusing of the laser onto different targeted phases, which can be difficult when phases are separated into multiple small inclusions (Buajarern et al., 2007b).

Using spatial scanning and optical imaging, Ma et al. (2021) reported an organic shell-aqueous core LLPS in deposited 1, 2, 6-hexanetriol/ammonium sulfate mixed particles. However, different substrates for deposited particles could affect their LLPS behavior (Ma et al., 2021). Though LLPS of an organic/AS mixed particle has been observed on both hydrophobic (i.e., PTFE) and hydrophilic (i.e., glass) substrates, the former shows an organic shell with an AS inner core while the latter shows an opposite configuration (Zhou et al., 2014b). To eliminate interaction with substrates, Ishizaka et al. (2021) used levitated droplets and found both core-shell and partially engulfed LLPS. The observed configurations of the two phases are well consistent with thermodynamic predictions based on interfacial tensions and relative volume ratios of two immiscible phases (Ishizaka et al., 2021).

Another approach for identifying LLPS is Raman imaging of the whole particle in one single measurement. Typical Raman measurements bin the vertical pixels of a CCD to enhance the signal-to-noise ratio while the horizontal pixels represent the wave number after chromatic dispersion by a grating. Zhang et al. (2004) used collection optics to obtain an image of a particle in an EDB on the slit of a monochromator. Instead of using vertical binning, the vertical pixels registered the vertical profile of the Raman scattering (e.g., edge to center to edge) of the particle (Zhang et al., 2004). Chu and Chan (2017) reported that the core-shell phase separation in a mixed sucrose-ammonium sulfate particle with a sucrose molar fraction of 50% at <5% RH, but not at 70%RH. As shown in Fig. 3a, b (<5% RH), the accumulated C-H signal on the two sides indicates the presence of an organic-rich coating and an organic-deficient core. In contrast, the even distribution of the C-H signal in Fig. 3c (70% RH) suggests that the particle is likely homogeneous (Chu and Chan, 2017a). Kalume et al. (2018) observed temporally resolved LLPS in a diethyl phthalate and glycerol mixed droplet. Upon evaporation, diethyl phthalate migrated to the surface and formed an outer layer, and glycerol was more concentrated in the interior of the droplet (Kalume et al., 2018).

Additionally, WGMs have also been utilized to infer the occurrence of LLPS and the specific particle morphologies. For example, different resonance structures appear in the Raman spectra when core-shell or engulfed phase separation occurs (Buajarern et al., 2007a, b; Kwamena et al., 2010; Song et al., 2013; Marcolli and Krieger, 2020). Sharps peaks generated by WGMs in spectra can be found if the spatial distribution of particulate species is symmetric, such as those in core-shell separated and homogeneously mixed particles though the number, location, and intensity of WGMs peaks are different. In contrast, the engulfed phase-separated particles do not show any WGMs peaks (Sullivan et al., 2020). Utilizing WGMs, Steward et al. (2015) reported the transition between partially-engulfed and core-shell structures at different RH values (Stewart et al., 2015). However, these analyses focus on WGMs but not Raman as a chemical probing technique.

Besides, we have also added recent updates to other sections:

3.5 Determination of pH

Very recently, Cui et al. (2021) reported that water could be used to probe pH in individual model aerosol particles (e.g., $(NH_4)_2SO_4$, NaCl) since the water bands are affected by other components (e.g., ions), as discussed in Sec.3.3. Specifically, the broad water peak at 2600-3800 cm^{-1} could comprise many overlapping peaks, representing the O-H vibration of water molecules in different local environments. The addition of solutes affects the local environment of water molecules and changes the relative intensities of the overlapped peaks. Hence, the activity of specific solutes can be obtained by analyzing the overlapped water peaks after rigorous calibration, and the pH of the aerosol particle can be calculated (Cui et al., 2021).

4.1 Multiphase formation of secondary inorganic aerosols (SIA)

Angle et al. (2021) reported an enhanced sulfate formation in TMI-containing droplets compared to that in TMI bulk solutions. This enhancement is greater than that can be explained by the higher TMI/bisulfite concentrations in aerosol than in bulk. It suggests that surface effects and potentially aerosol pH gradients play important roles in the S(IV) oxidation process in aqueous aerosols (Angle et al., 2021).

4.3 Multiphase oxidation of aerosol particles

Milsom et al. (2021) reported the ozonolysis of fatty acid-soap mixed particles, using oleic acid and sodium oleate as models. In these particles, the strong interactions between the soap carboxylate and the carboxylic acid form crystalline structures (Milsom et al., 2021). Upon ozonolysis, the decay of C=C (~1600cm^{-1}) was faster in liquid oleic acid droplets than crystalline oleic acid-soap particles, although the crystalline structure was eventually broken by ozonolysis. Uraoka et al. (2017) studied the multiphase reactions of optically-trapped soot particles with ozone and OH radicals. C=O vibrations were observed under both ozone and OH exposure. The graphitic domain was suggested to undergo OH oxidation based on the increase in the ratio of the disorder (D) to the graphite (G) domain from Raman spectra (Uraoka et al., 2017).