

The Morphology of Internally Mixed SOA/DOP Particles and the Uptake of Gas-Phase DOP During SOA Formation

Alla Zelenyuk¹, Timothy D. Vaden¹, Chen Song¹, Rahul A. Zaveri¹, and Dan Imre²

¹Pacific Northwest National Laboratory, Richland, WA; ²Imre Consulting, Richland, WA



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Abstract

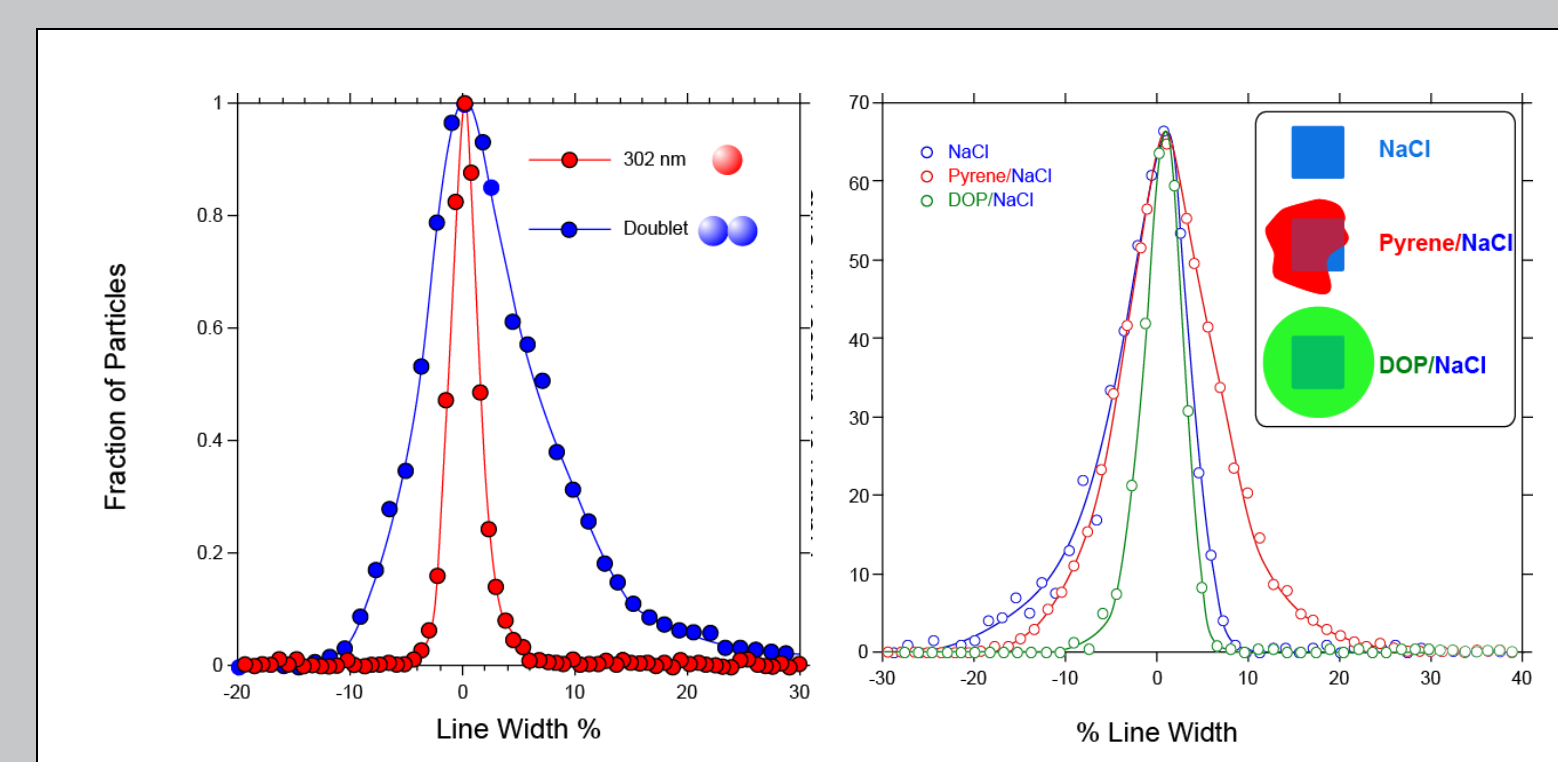
Primary organic aerosol (POA) and associated vapors can play an important role in determining the formation and properties of secondary organic aerosol (SOA). If SOA and POA are miscible, POA will significantly enhance SOA formation and some POA vapor will incorporate into SOA particles. When the two are not miscible, condensation of SOA on POA particles forms particles with complex morphology. In addition, POA vapor can adsorb to the surface of SOA particles increasing their mass and affecting their evaporation rates. To gain insight into SOA/POA interactions we present a detailed experimental investigation of the morphologies of SOA particles formed during ozonolysis of α -pinene in the presence of dioctyl phthalate (DOP) particles, serving as a simplified model of hydrophobic POA, using a single particle mass spectrometer (SPLAT) and a differential mobility analyzer (DMA). Ultraviolet (UV) laser depth-profiling experiments were used to characterize two different types of mixed SOA/DOP particles: those formed by condensation of the oxidized α -pinene products on size-selected DOP particles and by condensation of DOP on size-selected α -pinene SOA particles. The results show that the hydrophilic SOA and hydrophobic DOP do not mix, but instead form layered phases. In addition, an examination of homogeneously nucleated SOA particles formed in the presence of DOP vapor shows them to have an adsorbed DOP coating layer that is ~4 nm thick and carries 12% of the particles mass. These results may have implications for SOA formation and behavior in the atmosphere, where numerous organic compounds with various volatilities and different polarities are present.

Methods: Shape & Morphology

We have demonstrated that using our single particle mass spectrometer (SPLAT) and a differential mobility analyzer (DMA) it is possible to characterize with great detail the properties of internally mixed particles. Here we show examples of NaCl particles coated with liquid DOP and with solid pyrene to form spherical and aspherical particles, respectively. The measured mobility (d_{mob}) and vacuum aerodynamic diameters (d_{va}) yield quantitative measure of particle density and dynamic shape factors, and the mass spectral intensity patterns as a function of laser fluence is used to identify which of the substances are on the surface and which are inside.

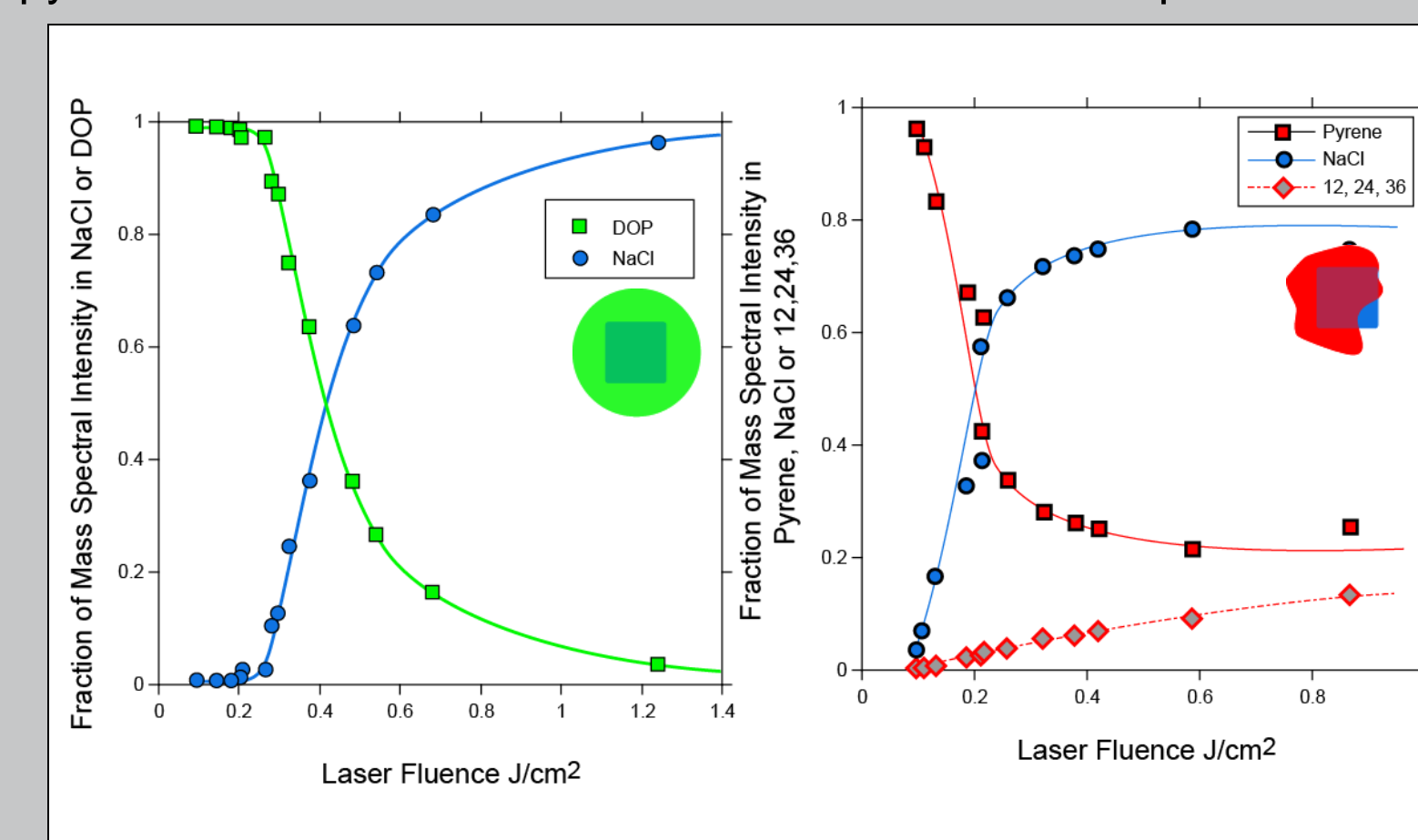
Distinguishing between Spherical and Aspherical Particles

The extremely high sizing resolution of the SPLAT/DMA system has made it possible to establish an unambiguous relationship between particle asphericity and the line-shape of the vacuum aerodynamic diameter distribution. In particular we demonstrated that asphericity causes broadening of the d_{va} distributions. The left figure below illustrates the effect of asphericity on the line shape of the size distribution of the doublet of the PSL spheres. The right figure shows the size distributions of aspherical NaCl particles and NaCl coated with DOP and pyrene, the former being narrow and the latter is broader than NaCl.



Particle Morphology: "Depth-Profiling"

The figures below show the changes in relative mass spectral intensity pattern as a function of laser power. At low laser power, in both cases, the mass spectral intensity is dominated by organics and NaCl is barely visible. As the laser power is increased the NaCl mass spectral intensity increases. In the case of DOP, at highest laser power DOP becomes nearly invisible. Pyrene coated NaCl shows a different pattern, but nevertheless is also displays a pattern in which NaCl is barely observed at low power and at higher powers the NaCl peaks dominate. The pyrene data indicate that some of the core NaCl is exposed.



Methods (cont.)

Quantitative Multidimensional Characterization

The table below demonstrates that the SPLAT measurements yield quantitative information on particle size, composition, including volume and weight fractions of its different constituents, density, morphology, asphericity, and dynamic shape factor.

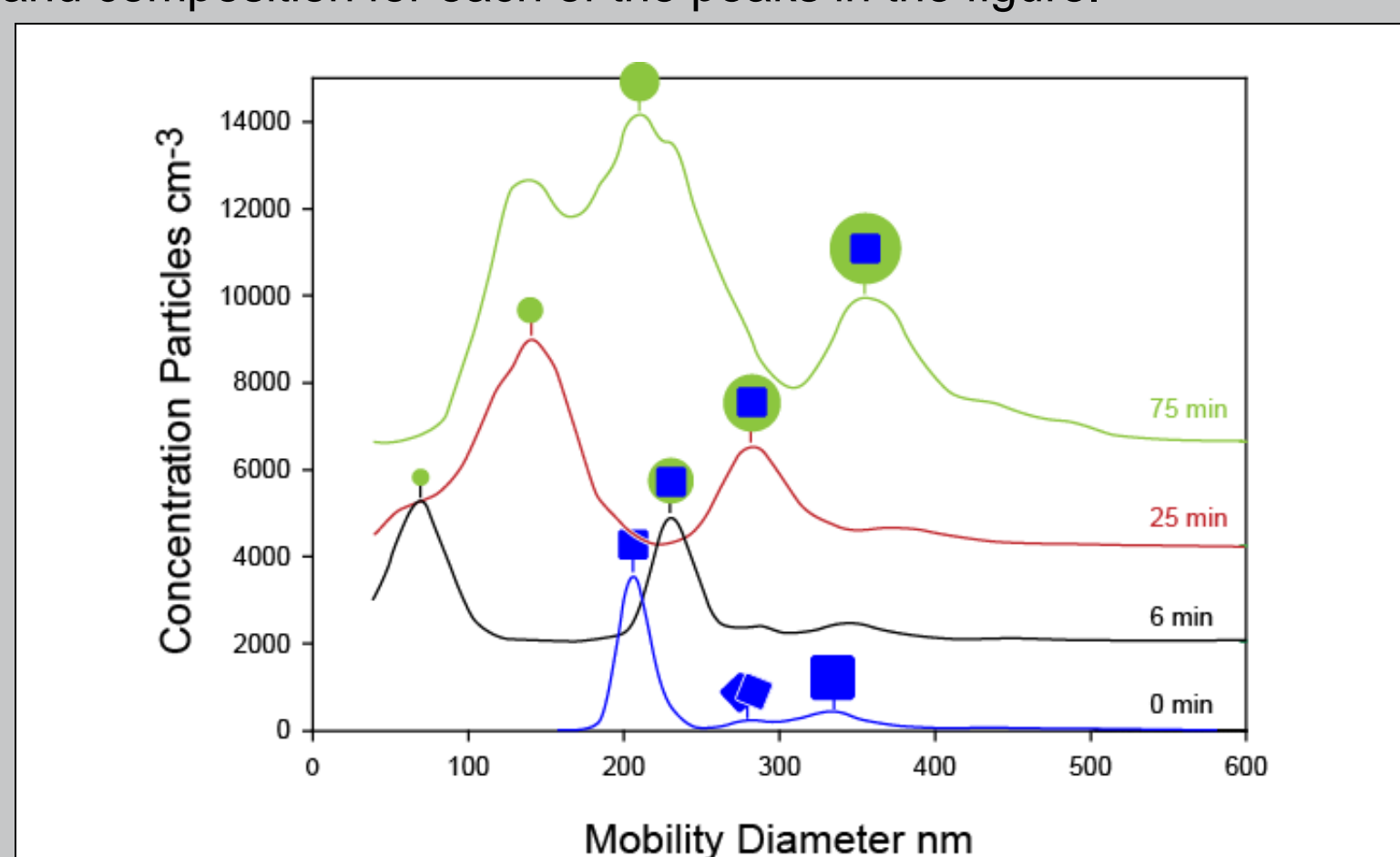
d_{va} NaCl seed (nm)	d_{va} (nm)	d_{va} (nm)	DOP V_f	DOP W_f	Mass ρ (g/cm ³)	Calc ρ (g/cm ³)
139	212	272	0.72	0.535	1.284	1.32
139	257	298	0.84	0.71	1.164	1.17
139	408	427	0.96	0.92	1.046	1.03
215	272	420	0.50	0.32	1.542	1.57
215	312	420	0.67	0.48	1.346	1.37

d_{va} NaCl seed (nm)	d_{va} (nm)	d_{va} (nm)	Pyr. V_f	Pyr. W_f	ρ_{int}	DSF
139	241	272	0.743	0.63	1.13	1.155

SOA coated NaCl particles

To test the efficacy of the depth-profiling technique to the organics that comprise SOA we first probe the morphology of NaCl particles coated with oxidation products from the ozonolysis of α -pinene.

The figure below shows the mobility size distributions of NaCl and SOA particles as a function of reaction time. $t=0$ corresponds to injection of 200 ppb of α -pinene into the 100 L Teflon bag that contains ~600 ppb of ozone and ~250 ppm of cyclohexane used as an OH scavenger. The 200 nm NaCl particles grow to 360 nm as they are coated with SOA. Homogeneously nucleated SOA particles formed in two nucleation events grow to 175 nm and 150 nm respectively. Two additional small peaks at 280 nm and 321 nm (in the $t=0$ trace), corresponding to NaCl dimers and doubly-charged NaCl particles respectively, are marked. Cartoons of the particles are shown to denote particle size, morphology, shape, and composition for each of the peaks in the figure.



SOA coated NaCl: Shape & Phase

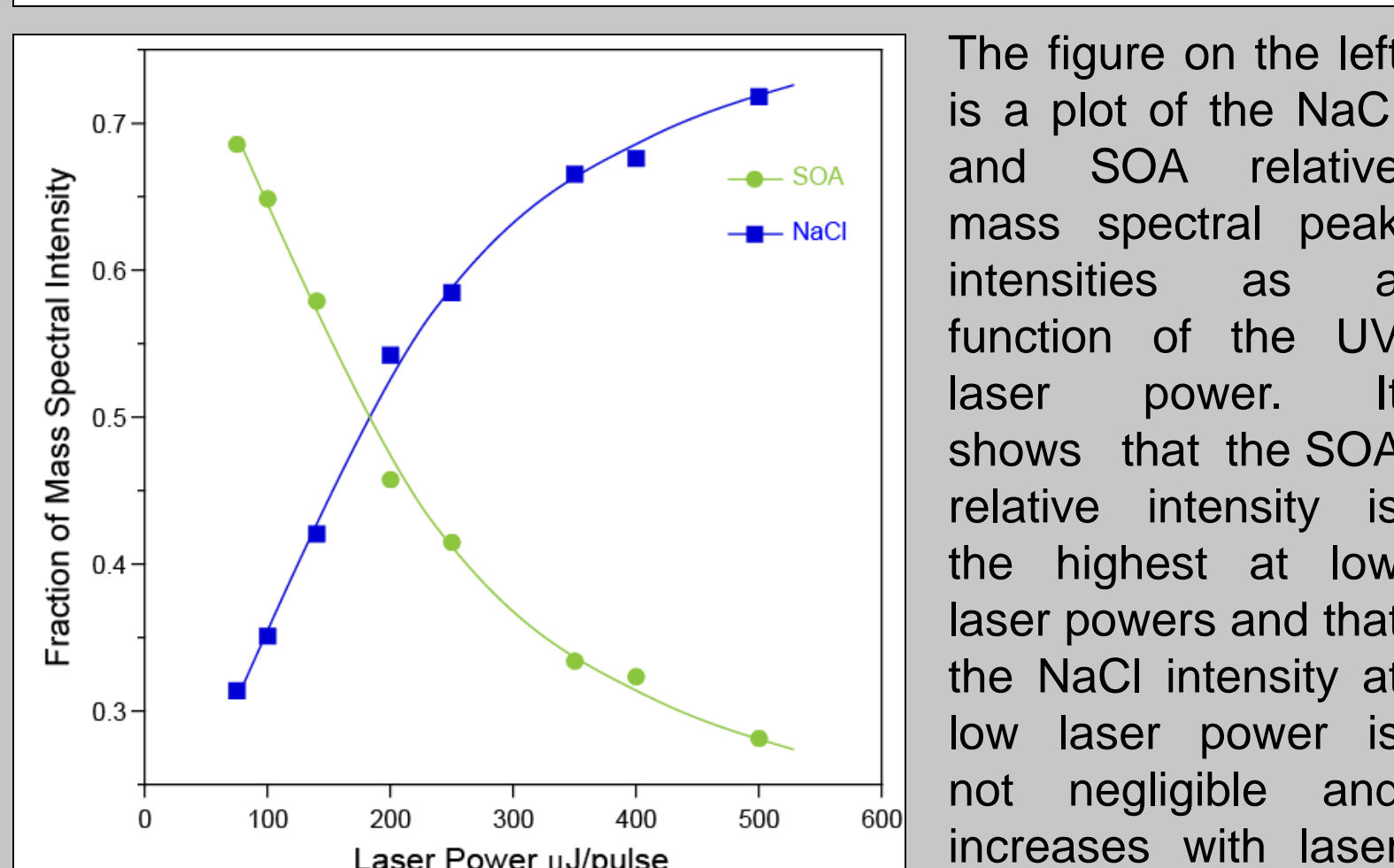
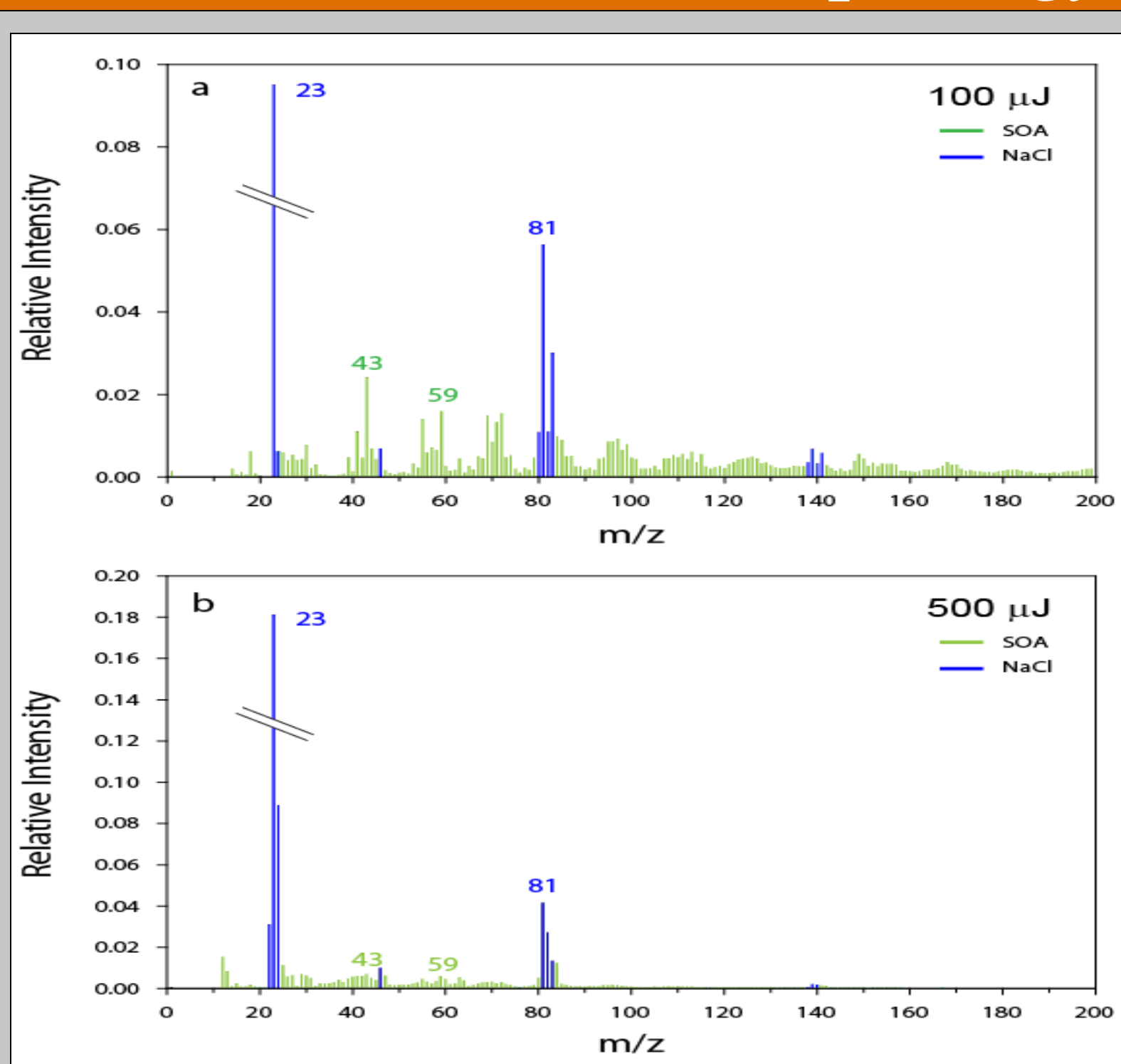
The figure on the left shows the line shape of the d_{va} distributions of the uncoated NaCl particles and NaCl particles coated with SOA. For the uncoated NaCl particles the d_{va} distribution is broad and asymmetric because these particles are aspherical. Once coated, the distribution narrows to FWHM 5%, indicating that the coated particles are spherical. The mobility and vacuum aerodynamic diameters of 360 and 477 nm for coated NaCl particles yield a density of 1.33 g cm⁻³, consistent with SOA density of 1.21 g cm⁻³ and a dynamic shape factor of 1.08 for NaCl. We have previously shown that SOA particles formed by α -pinene oxidation with ozone are spherical, but have prior to this experiment not eliminated the possibility that they are solid spheres. However, the observation that SOA coated aspherical NaCl particles are spherical strongly suggests that the mixture of organics that make up this SOA is liquid at room temperature.

The next figure shows the mass spectra of SOA coated NaCl particles at two different UV laser powers. At low laser power the intensities of SOA mass spectral peaks are relatively high, although NaCl peaks are easily observed even at the lowest laser power. At higher UV laser power the NaCl peak intensity is much higher than that of SOA. It indicates that SOA is on the surface and that we can "drill" into the NaCl core. These results are very similar to what we have seen for DOP coated NaCl particles presented earlier, except that the mass spectra of SOA coated NaCl particles has higher NaCl intensity at low laser power.

SOA coated NaCl: Morphology

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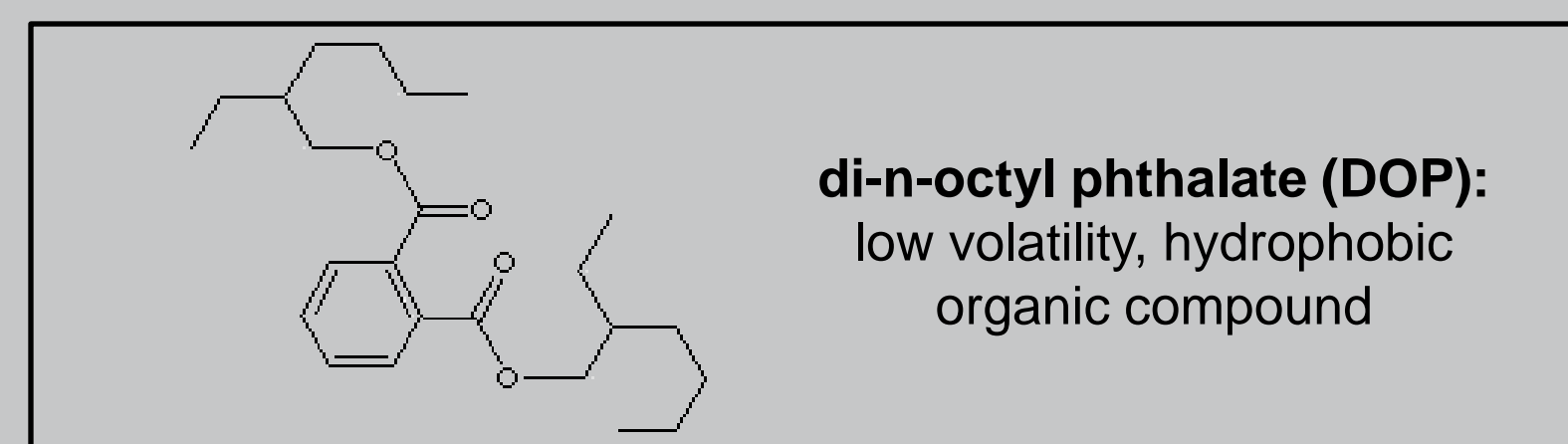
SOA coated NaCl: Morphology



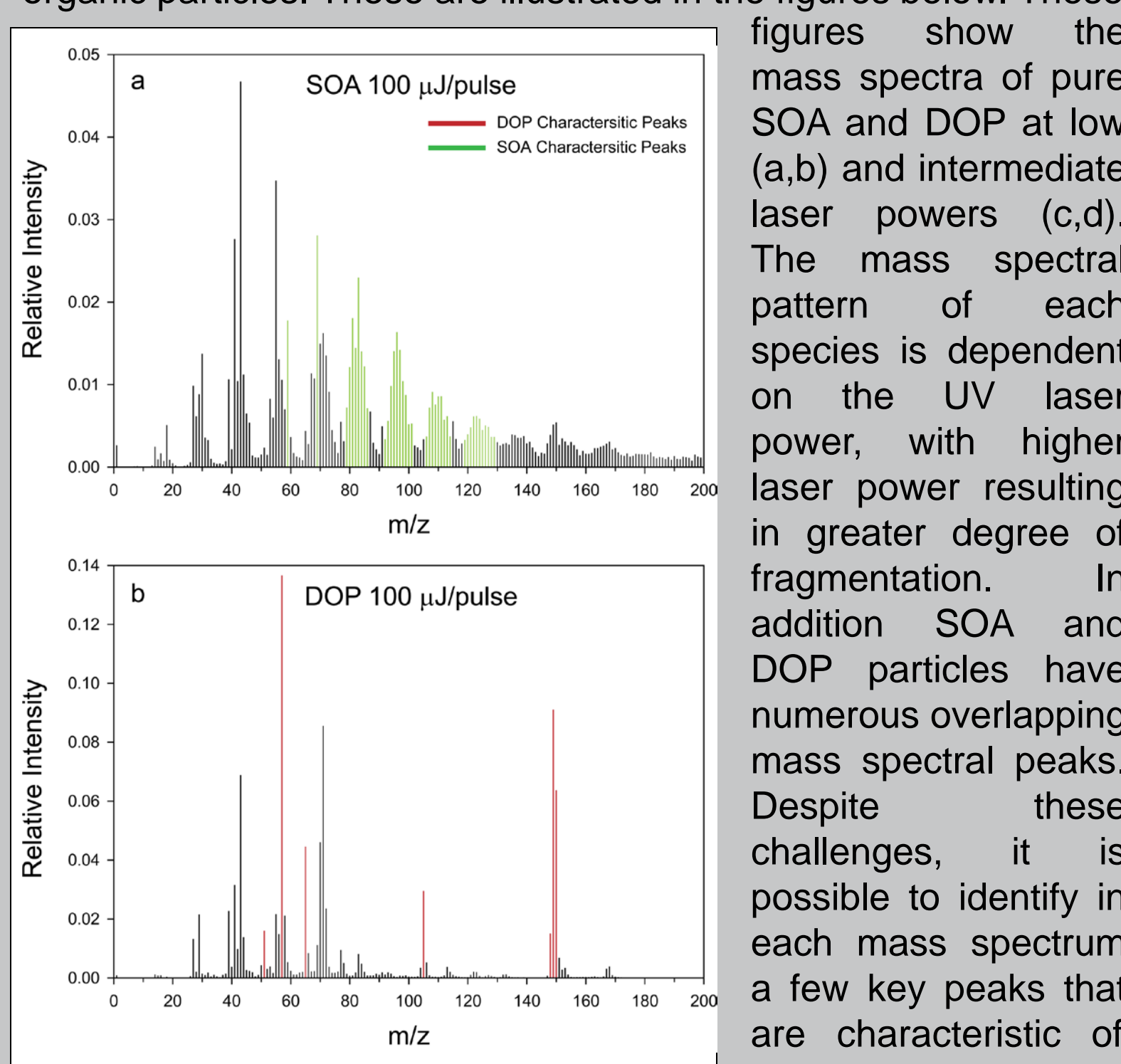
Before we look at the mass spectral intensity patterns we note that it is possible to circumvent the complications associated with analysis of the power dependent SOA/DOP particle mass spectra by generating particles of two opposite morphologies: one with SOA coated DOP and another with DOP-coated SOA, as shown below.

Mixed SOA/DOP Particles

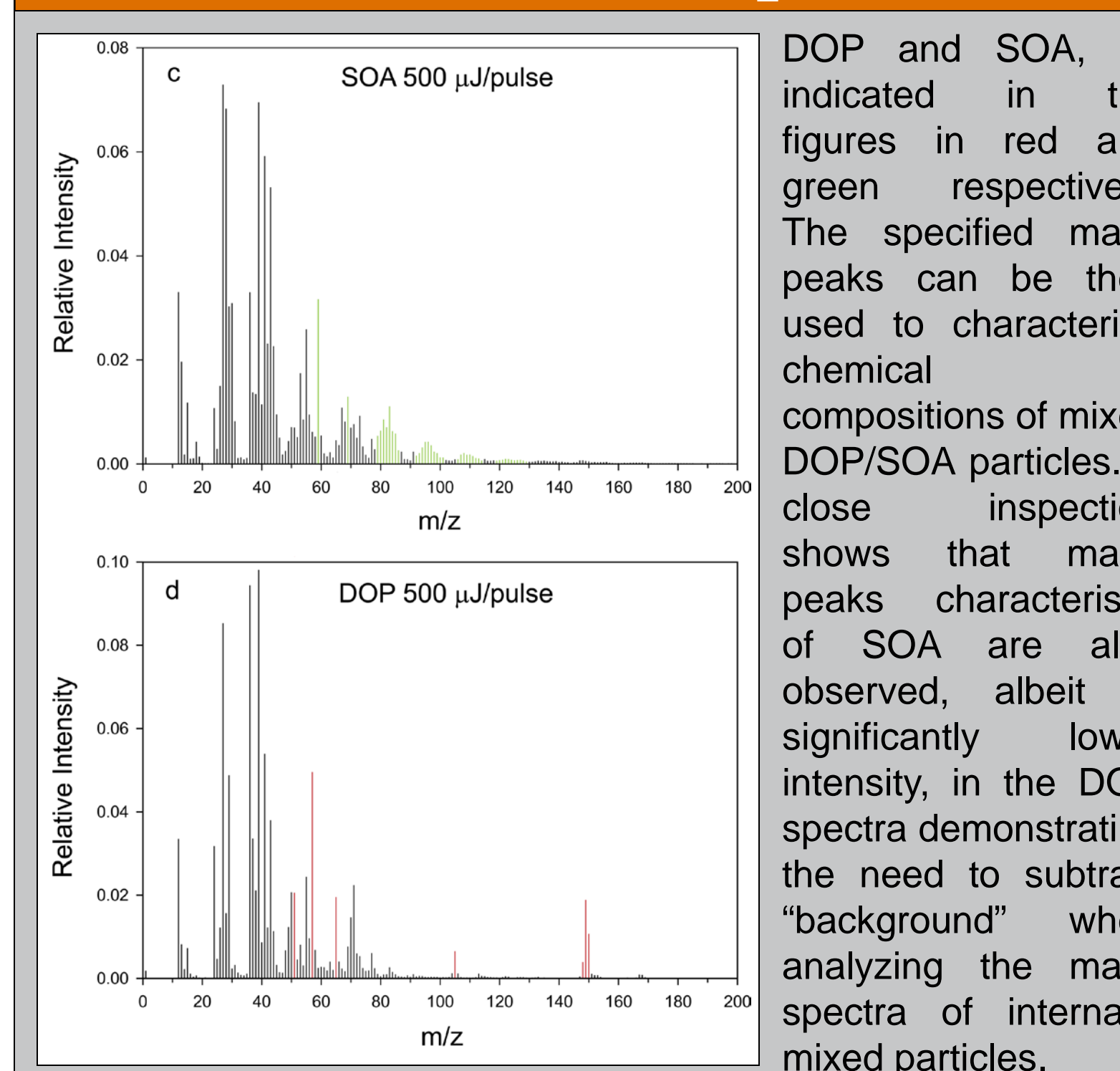
The morphology of internally mixed DOP/SOA particles is of interest because of their relevance to organic aerosol in the atmosphere. Traditional semi-empirical SOA models can ignore the fact that most POA are hydrophobic and the chemicals in SOA tend to be hydrophilic and treat pre-existing POA as a mass into which additional oxidized products can dissolve. It might, however, be more reasonable to assume that the two organic compounds form particles composed of separate phases, in which case the impact on SOA formation is not clear. In the present study hydrophobic DOP particles serve as a proxy for POA and the oxidation products of α -pinene represent SOA.



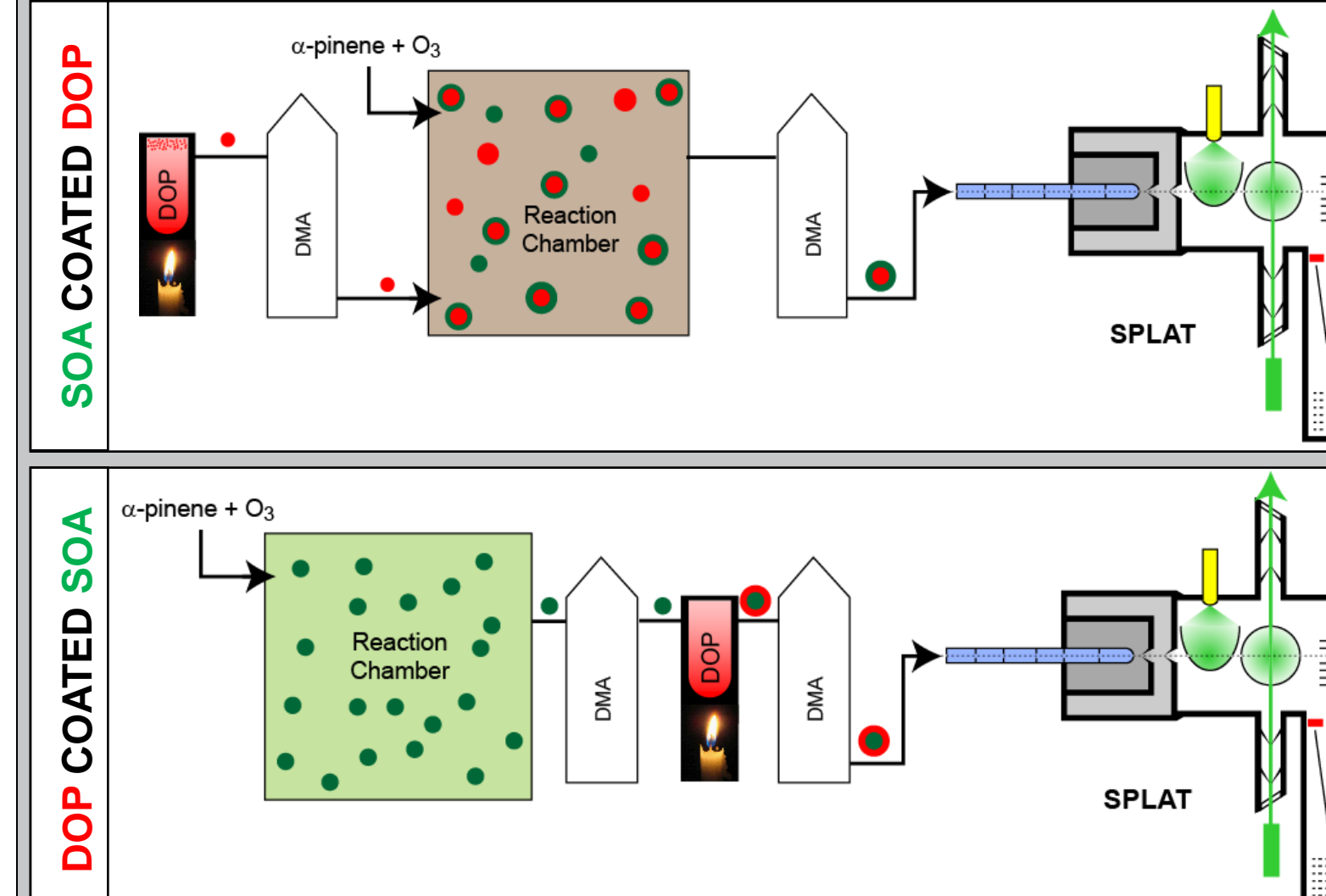
An important requirement of the depth-profiling technique is the ability to use mass spectra to distinguish the relevant chemical compounds in the mixed particles. While this is straightforward for the NaCl/SOA system, several complicating factors arise in mixed organic particles. These are illustrated in the figures below. These figures show the mass spectra of pure SOA and DOP at low (a,b) and intermediate laser powers (c,d). The mass spectral pattern of each species is dependent on the UV laser power, with higher laser power resulting in greater degree of fragmentation. In addition SOA and DOP particles have numerous overlapping mass spectral peaks. Despite these challenges, it is possible to identify in each mass spectrum a few key peaks that are characteristic of



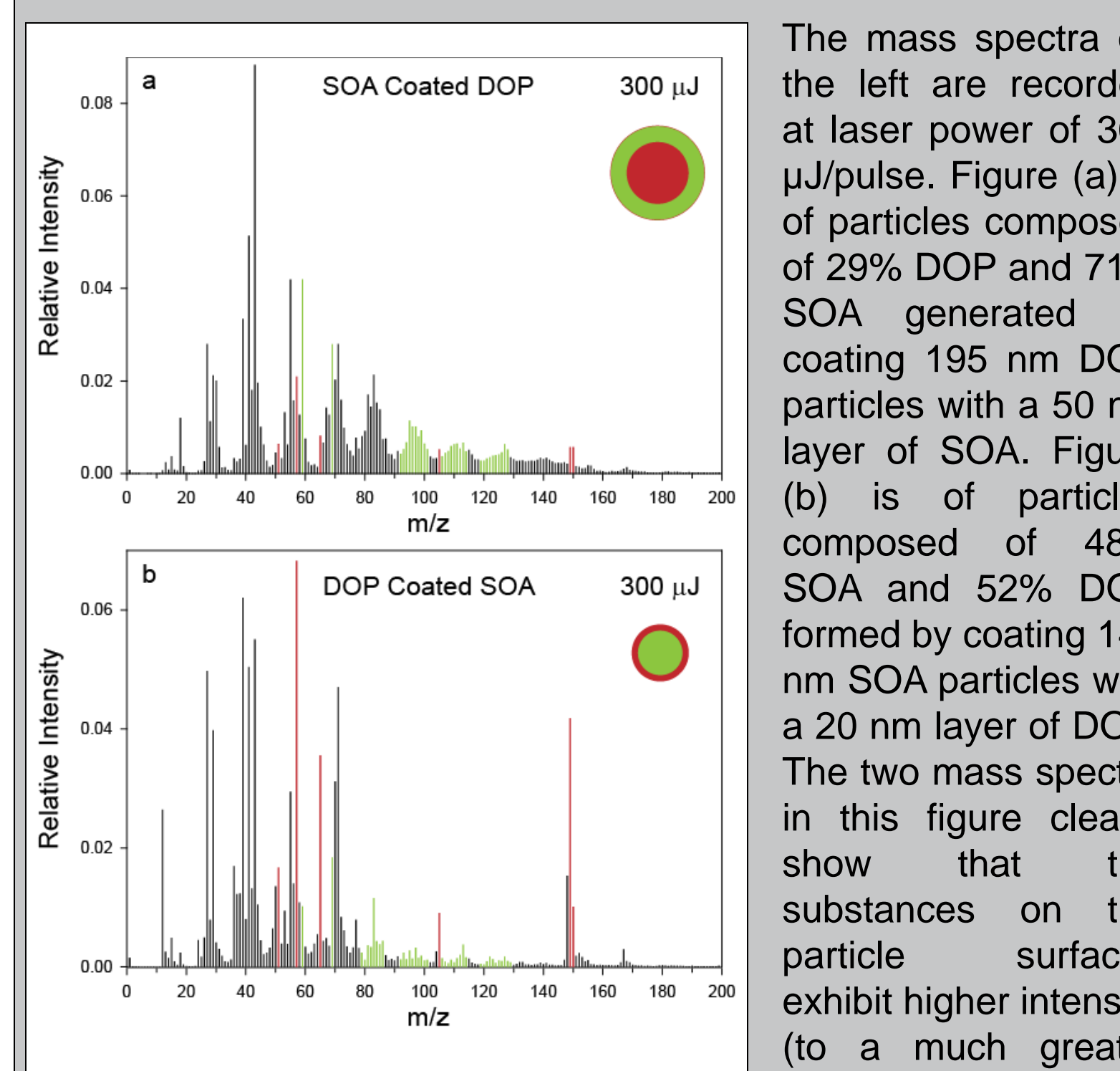
Mixed SOA/DOP particles



The figure on the left is a plot of the NaCl and SOA relative mass spectral peak intensities as a function of the UV laser power. It shows that the SOA relative intensity is the highest at low laser powers and that the NaCl intensity at low laser power is not negligible and increases with laser power. We conclude that SOA forms a liquid coat on the surface of the NaCl core, and that a small fraction of the NaCl is dissolved in it. The fact that NaCl is slightly soluble in SOA explains the relatively high NaCl intensity observed even at lowest laser power.



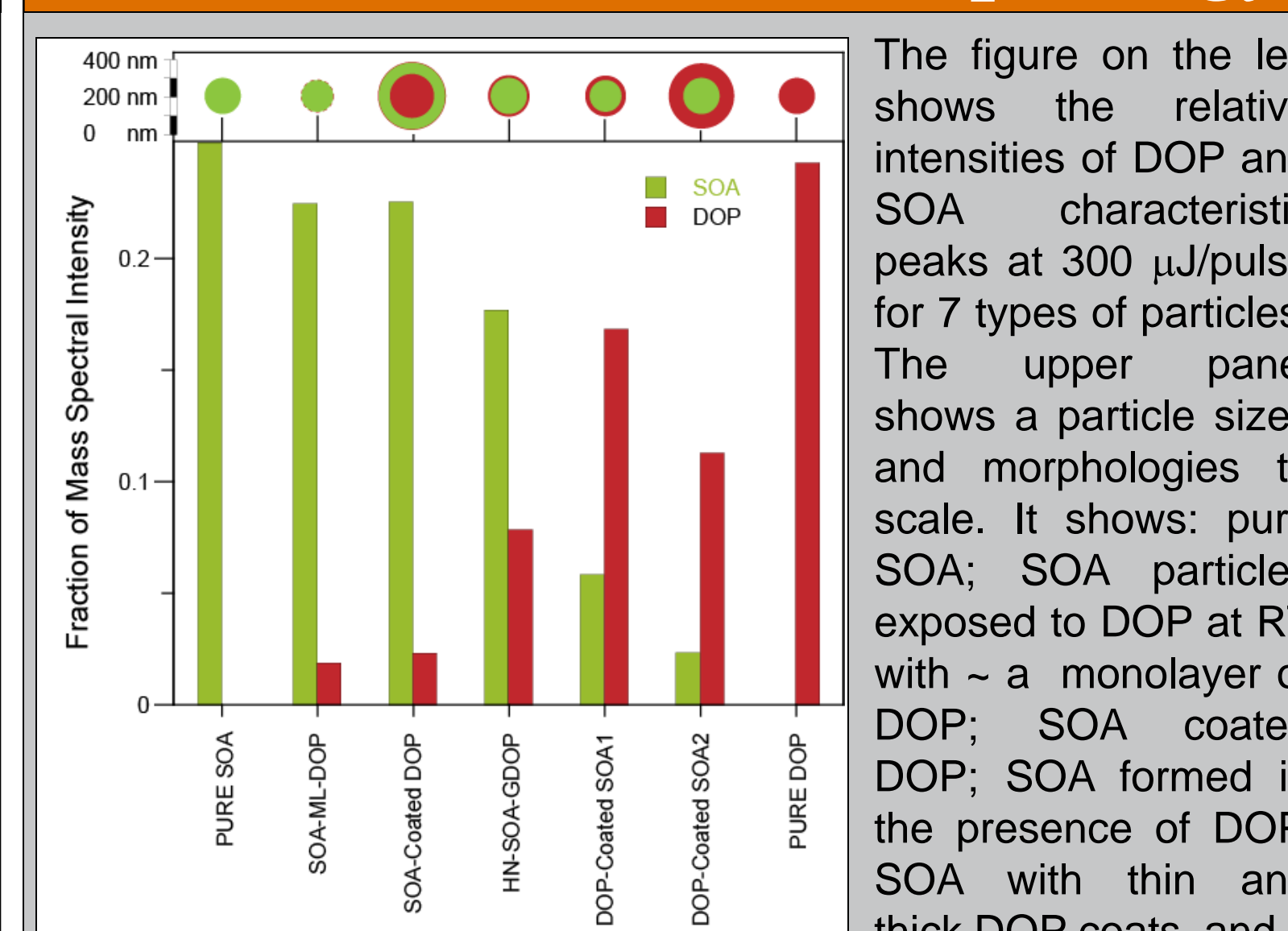
If SOA and DOP form a homogeneous single phase the relative mass spectral intensities at any given laser power should be independent of particle type and instead reflect only concentrations. If on the other hand the two substances are immiscible and form distinct phases, the mass spectra at low laser power should be dominated by the substance on the surface.



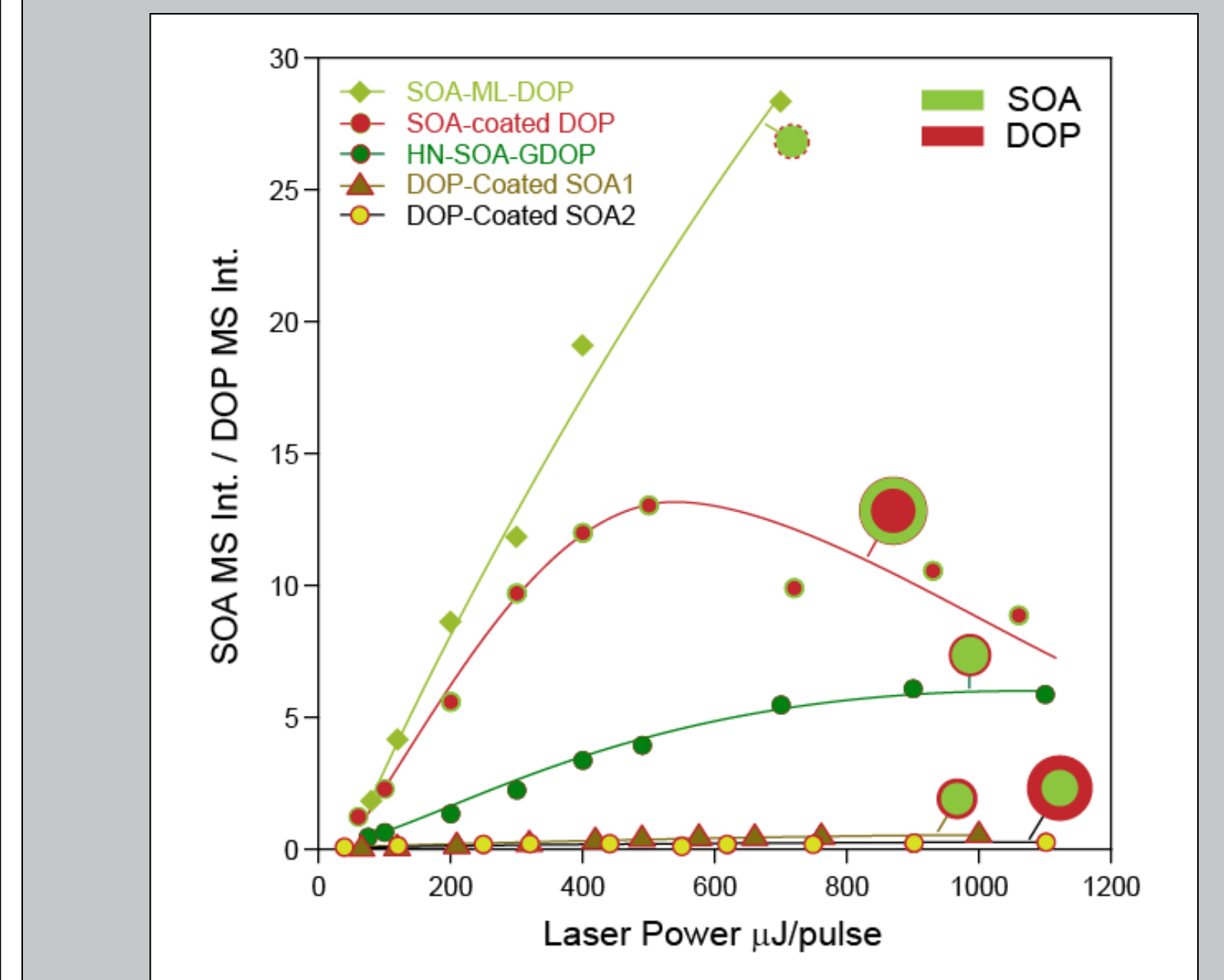
The mass spectra on the left are recorded at laser power of 300 μJ/pulse. Figure (a) is of particles composed of 29% DOP and 71% SOA generated by coating 195 nm DOP particles with a 50 nm layer of SOA. Figure (b) is of particles composed of 48% SOA and 52% DOP formed by coating 140 nm SOA particles with a 20 nm layer of DOP. The two mass spectra in this figure clearly show that the substances on the particle surfaces exhibit higher intensity (to a much greater degree than could be

explained simply by the relative compositions), providing unequivocal proof that SOA is not miscible in DOP and that the particles are structured in separate layered phases. It is worth noting that only one of these two forms of layered SOA/DOP particles is in the equilibrium state and that the mass spectra clearly show that once generated, both forms survive for many hours. In other words, both SOA on DOP and DOP on SOA are kinetically stable on atmospherically relevant time scale. We will show below that close examination of the mass spectra at even lower laser power shows that the SOA coated DOP particles have an additional thin DOP coat. The mass spectra of the two opposing morphology particle types resolved the solubility question, but there is more to be learned from this experiment. There are 7 types of particles and the mass spectral intensity as function of laser power, all of which carry important information.

Mixed SOA/DOP: Morphology



The figure on the left shows the relative intensities of DOP and SOA characteristic peaks at 300 μJ/pulse for 7 types of particles. The upper panel shows a particle sizes and morphologies to scale. It shows: pure SOA; SOA particles exposed to DOP at RT with ~ a monolayer of DOP; SOA coated DOP; SOA formed in the presence of DOP, SOA with thin and thick DOP coats, and pure DOP. These data show that in all cases the coating materials exhibit greater mass spectral intensity at lower laser powers. The most surprising and therefore, interesting observation is that SOA particles formed by homogeneous nucleation in the presence of DOP vapor (HN-SOA-GDOP) have a significant amount of DOP signal. In fact, at 300 μJ/pulse these particles have higher DOP intensity than SOA-coated DOP particles! In other words, the data demonstrate that when SOA particles form and grow in the presence of gas-phase DOP, which must be present in the Teflon bag at a vapor pressure of 1.25×10^{-7} Torr or less, they adsorb a significant amount of DOP. Based on the DOP intensity we conclude that HN-SOA-GDOP particles are coated with a DOP layer that is ~4 nm thick, and carries ~12% of the particle mass. This estimate is consistent with these particles' measured density of 1.19 ± 0.02 gm cm⁻³. The figure below shows the observed SOA/DOP MS intensity ratios for the five internally mixed SOA/DOP particle types as a function of UV laser power.



As expected, SOA-ML-DOP particles have the highest SOA signals followed by SOA-coated DOP particles. The data for these SOA-coated DOP particles also show that when the laser power is increased above 500 μJ/pulse, the relative DOP intensity increases with laser power, suggesting that at these laser powers the DOP core becomes observable. This behavior strongly suggests that the DOP signal observed in these particles at the very low laser power is due to a small amount of surface DOP, which means that the SOA-coated DOP particles have a thin (~2 nm), but detectable DOP coat.

Conclusions

- Depth-profiling experiments of SOA-coated NaCl particles showed that SOA produced by ozonolysis of α -pinene forms a liquid coating around the solid NaCl cores.
- Depth-profiling experiments of mixed SOA/DOP particles were used to unambiguously demonstrate that the hydrophilic SOA and hydrophobic DOP exist in separate phases and form layered spherical particles.
- We demonstrated that SOA particles adsorb hydrophobic gas phase semivolatile organic compounds present at or below their vapor pressure.
- SOA particles formed in the presence of these organics acquire a layer that impacts their mass and gas to particle partitioning.
- Organic coatings could change the rate of SOA evaporation and rates of heterogeneous reactions with OH or O₃. Furthermore, the observation that particles can exist in layered phases due to the adsorption of ambient SVOCs has far-reaching implications for models of SOA formation that are based on an assumption of ideal or near-ideal solution behavior for different organic species.

Reference: Vaden, Song, Zaveri, Imre, and Zelenyuk, PNAS, Atmospheric Chemistry Special Feature, doi:10.1073/pnas.0911206107 (2010).