

Interactive comment on “Glass formation and unusual hygroscopic growth of iodine acid solution droplets with relevance for iodine oxide particles in the coastal marine boundary layer” by B. J. Murray et al.

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The referees' comments are italicised and our response is in plain text.

However, contrary to the title, and many of the statements throughout the manuscript, I see much less relevance to the atmosphere than the authors. The problem lies in the fact that, although iodine oxides may provide the initial stable clusters, even in the very strong source regions with high emission fluxes of molecular iodine, particles of any significant size (beyond a few nm diameter) will contain negligible amounts of iodine

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oxides. The properties of particles of a few tens of nanometres or greater will be largely unaffected by those of the components making up the initially stable cluster. This is because of the abundance of material in even the clean marine atmosphere which, although not as involatile as the iodine oxide vapours that act as nucleants, can readily grow particles once the Kelvin term reduces exponentially above a few nanometres. The condensable iodine oxide vapours may be as high as a few ppb within a few centimetres or a metre or so of the emission source, but are too reactive or condensable to persist more widely. This gives the nucleated clusters a few seconds to grow in the very high concentrations in the coastal hotspots. Even in the most rapidly growing coastal particle events, growth rates are order of magnitude too slow for them to have occurred predominantly by condensation of iodine oxide vapours. Air would need to move slowly within a few metres of seaweed for tens of km along the coast to give the growth rates of tens of nm/hour would be needed for the particles to contain a significant fraction of iodine oxides. Air becomes mixed vertically and horizontally in the boundary layer far too rapidly for this behaviour. This behaviour is recognised in the paper (page 7881, "Under suitable conditions these particles may grow, through the condensation of OTHER condensable vapours (Makela et al., 2002; Saunders et al., 2010), to sufficiently large sizes that they can serve as cloud condensation nuclei (McFiggans et al., 2010)" so one could be forgiven for thinking that the atmospheric relevance has been mischievously rather than mistakenly exaggerated. Example statements relating to the concern above: p7881, line 10: "There has been some debate in the literature over the most likely composition of iodine oxide particles with insoluble I2O4 and the soluble I2O5 being identified as the most likely candidates". The debate has been over the stoichiometric composition of the initially formed clusters, not molecular identification of iodine-containing particles. Is it likely that the stable tetroxide or pentoxide are the actual molecules comprising bulk particles in the atmosphere, when they are likely to be the products of the condensation of many various oxides and there will likely be water and many other components present?

We clearly did not make it sufficiently clear that we think our results are relevant for the

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very small cluster which initially form in the atmosphere and also to laboratory experiments where iodine oxide particles were grown in the absence of other condensable vapours. We think these results are highly relevant for iodine mediated particle formation in the marine boundary layer since we present results relevant for properties of the initially formed clusters and also shed light on previous laboratory experiments which were designed to help our understanding of particle formation in the marine boundary layer. Specifically, we consider that it is crucial to have unambiguous measurements of hygroscopic growth of individual pure components if the interpretation of the growth of more complex mixed component aerosol is to rest on a secure foundation. The measurements presented here are ideal in this regard, performed on particle sizes that are large enough to justify us neglecting the influence of the surface curvature term in determining particle size, i.e. the measurements provide a clear picture of the thermodynamics of iodic acid solution and the potential departure of iodic acid aerosol from a thermodynamically equilibrated state.

The beginning of the last paragraph of the introduction now reads: 'In this paper, we use a Raman microscope coupled to a temperature and humidity controlled stage to explore the physical state of micrometer sized iodic acid solution droplets and two types of electrodynamic balances to quantify the hygroscopic growth and probe the rate at which they lose water. An advantage of using micrometer sized droplets is that they are large enough to justify us neglecting the influence of the surface curvature term in determining particle size, hence the measurements provide a clear picture of the thermodynamics of iodic acid solution and the potential departure of iodic acid aerosol from a thermodynamically equilibrated state. These measurements allow us to address two issues.'

We compared our results to the measurements of hygroscopic growth described in the Vakeva et al. paper in which particles of 8-10 nm had very small growth factors. The referee is correct in pointing out that these particles most likely contained other materials in addition to iodine oxides and water. We have adjusted or removed the

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discussion of relevance of our growth curve measurements to the Vakeva et al paper.

Changes have been made to the introduction: 'Ultrafine particles (8 and 10 nm) sampled during low tide particle 'bursts' at Mace Head in Ireland are also reported to have a characteristic hygroscopic growth factor of less than 1.1 at an RH of 90% Väkevå, 2002 1009, ruling out sulfate or sea salt aerosol which are known to have much greater growth factors. These natural particles are likely to contain a mixture of condensable material; for example, Mäkelä et al. (2002) showed that the ultrafine particles sampled at low-tide periods at the same coastal location contained iodine in addition to sulphur. In addition, Vaattovaara et al.2006 1059 report significant amounts of organic compounds contribute to particles of 5-6 nm, whereas particles smaller than 3-4 nm are dominantly made of iodine oxides.' Also, changes have been made to section 3.3 which now reads: 'This value is consistent with the small diameter growth factors observed for particles generated under humid conditions in the laboratory Jimenez, 2003 202;McFiggans, 2004 189. We suggest that the hygroscopic growth measurements in previous laboratory studies of iodine oxide particles are consistent with the aerosol being composed of aqueous iodic acid solutions. The growth factor information alone does not rule out the possibility that those iodine oxide particles were I₂O₄. However, given that the elemental composition measurements of laboratory generated material indicate an I₂O₅ composition (the anhydrous crystalline form of iodic acid) Saunders, 2005 180, it is likely that the material generated in those previous experiments was iodic acid if there was sufficient water present or I₂O₅ if generated under very dry conditions. These experimental studies also suggest that the nucleation mode particles initially produced in the marine boundary layer are composed of iodic acid. Given the humid conditions there it will always be in an aqueous liquid state, which would facilitate uptake of other condensable materials.'

We have also altered the conclusions section which now reads: 'Our laboratory experiments show that iodic acid solution droplets have a very low propensity to crystallise on drying to low RH. Instead they form an amorphous solid or semi-solid state which

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retains significant amounts of water. The hygroscopic growth of iodic acid solution droplets is very small, which is surprising considering HIO₃ and I₂O₅ are highly soluble. Such droplets grow by only 20% between 20 and 90 % RH and we determine the hygroscopicity parameter (κ), as defined by Petters et al. 2007 1007, for iodic acid droplets is 0.024. This value is within the range commonly associated with weakly soluble organic materials and secondary organic aerosol particles Petters, 2007 1007. Hygroscopicity parameter values for highly soluble inorganic species normally fall in the range of 0.5 to 1.4. Iodine oxide particles generated in laboratory experiments also have very small growth factors. This has led previous authors to conclude that iodine oxide particles must be insoluble and they went on to suggest the composition of iodine oxide particles was the insoluble I₂O₄ rather than the highly soluble I₂O₅ or HIO₃ Jimenez, 2003 202. Here we have shown that the very small hygroscopic growth factors of laboratory generated particles are consistent with these aerosol particles being composed of aqueous iodic acid. We also suggest that the initially formed nucleation mode particles, which are thought to be composed of iodine oxides, in the marine boundary layer are also composed of aqueous iodic acid. Under the humid conditions of the marine boundary layer, these droplets will exist in a liquid state. However, the retention of water at low RH, due to the formation of amorphous solid or semi-solid states, must be taken into consideration when interpreting hygroscopic growth measurements.'

The title has been adjusted to reflect the fact that marine boundary layer particles are only initially composed of iodine oxide. We think it is important to mention the marine boundary layer in the title, because this is the community that will be interested in this work. The title now reads: 'Glass formation and unusual hygroscopic growth of iodic acid solution droplets with relevance for iodine mediated particle formation in the marine boundary layer'.

Finally, we have inserted an addition paragraph at the end of section 3 which is a brief discussion of how our results offer an explanation for the dependence of H₂SO₄

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uptake coefficient on RH: 'The physical state of iodine oxide particles most likely influences their growth. Saunders et al. (2010) show that the uptake coefficient of H₂SO₄ on iodic acid particles decreases dramatically at low RH (their Figure 13). This is consistent with the formation of an amorphous solid or semi-solid at below 15% RH in which the diffusion of H₂SO₄ into the particles is kinetically limited. This will not be a limitation to growth in the marine boundary layer where the humidity is such that the accommodation coefficient is around 0.7, but does help us to understand these laboratory measurements (Saunders et al., 2010).'

p7881, line 13: "Ultrafine particles sampled during low tide particle "bursts" at Mace Head in Ireland were reported to have a characteristic hygroscopic (diameter) growth factor (based on electrical mobility diameters, $D_{final}/D_{initial}$) of less than 1.1 at an RH of 90% (Vakeva et al., 2002), ruling out sulfate or sea salt aerosol which are known to have much greater growth factors." Given that it is unlikely that the particles will have grown in situ from condensation of iodine oxides, the authors are invited to comment on the relevance of these measured growth factors of ambient particles.

We have adjusted this paragraph and placed a greater emphasis on the laboratory experiments. We have made it clear that the particles measured by Vakeva et al may contain significant amounts of other material.

p7881, line 13: The authors correctly state that "Makela et al. (2002) showed that the ultrafine particles sampled at low- tide periods at the same coastal location contained iodine of biogenic origin". However Makela et al clearly stated that "it was not possible to quantitatively determine the iodine content in the particles", and the iodine oxide fraction and hygroscopicity of particles in the field is not necessarily related given the likely low fraction of iodine oxides.

The reference to the Makala et al paper has been modified to state that both sulfur and iodine were detected in the particles. In addition we mention Vaattovaara (ACP, 2006) who suggests there is significant organic present in these aerosol particles.

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Rather than trying to relate the current study to the atmospheric observations, it is more valid to build the study on lab studies as in the statement on p7881, line 21: "In general, a small growth factor indicates a weakly soluble material or an insoluble material internally mixed with a small amount of soluble material (Swietlicki et al., 2008; Vakeva et al., 2002). Since I2O5 is highly soluble (263.2 g per 100 g of water at 298 K, Kumar et al., 2010), Jimenez et al. (2003) concluded that I2O4 was the most likely composition of iodine oxide particles. However, elemental analysis of particles generated photochemically from I2 in the presence of O3 revealed a composition consistent with I2O5 (Saunders and Plane, 2005)". The lab studies of Jimenez are likely to relate to particles much richer in iodine oxides than atmospheric ufps. If the particles were made from I2O5, the hygroscopicity measured in such a study would indeed imply that there is an inconsistency with the assumption of particles made of a substance exhibiting high bulk solubility having high growth factor.

We have made the relevance of our work much clearer. The focus is now more on the initial particles formed in the atmosphere as well as the particles formed in laboratory experiments.

Another example of an imbalanced contextual basis for the paper starts on line 5, p 7882: The arguments relating iodine oxide ultrafine particles to the fashionable discussion of the amorphous phase state of ambient particulates is rather contrived. I understand that it is necessary to bridge the discussion between the earlier atmospheric discussion of coastal ufps to the later lab studies of HIO3 behaviour. However, as stated earlier, the behaviour of a trace component is unlikely to determine the particle properties. This is particularly true of a property such as viscosity where even trace contaminants in a bulk liquid can act as a plasticiser. Perhaps the authors would like to give an example of the opposite (a trace component forcing increased viscosity) as a precedent for their contentions.

We do not appreciate why the reviewer considers this section contrived. The fact that later in the paper we show that on drying these particles form a glass rather than

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crystallise and retain water has important implications for hygroscopic growth measurements. This is critically important and an introduction to the states which could form is therefore necessary.

We have inserted the following sentence which should help the reader appreciate the significance of this discussion. The first sentence of the discussion now reads: 'The physical state of the initially formed atmospheric iodine oxide particles and those formed in the laboratory is an unresolved issue and the physical state of aerosol particles on drying is critical for understanding hygroscopic growth measurements Mikhailov, 2009 1011.'. And later on we inserted the following sentence: 'For iodine oxide particles in the humid marine boundary layer kinetic limitations to growth are not likely to be significant, but knowledge of the phase state at low humidity is critical for understanding hygroscopic growth measurements.' In addition, we have added the following to the last paragraph in the introduction: 'These measurements allow us to address two issues. Firstly, the thermodynamic measurements provide crucial equilibrium data for interpreting hygroscopic growth of freshly nucleated particles in the marine boundary layer. Secondly, iodic acid is a further example of the formation of amorphous kinetically arrested states which has implications for how growth factor measurements are interpreted and the reference condition used to determine growth factors. This has consequences for interpreting atmospheric and laboratory measurements.'

Notwithstanding the whole of my main criticism above, an entire industry has surrounded studies of the other major atmospheric nucleant, sulphuric acid. Granted, there is much more sulphate in ambient particulate material than iodine (because sulphur compounds are not only emitted in great abundance in thin strips along some coastline), but this fact should not preclude studies into the properties of iodine oxides as a minor aerosol component. I therefore suggest that the manuscript is suitable for publication when the authors have satisfactorily addressed my major criticism of context above (including those aspects of the study where particle properties could not

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possibly reflect those of iodine oxides), probably by simply focussing on the interesting laboratory experiments without exaggerated statements of relevance, and the following less serious concern.

See our response above. The key criticism of the reviewer seems to be our reference to the Vakeva et al measurements. This has been corrected throughout.

Less serious concerns: The interpretation of the experimental results is sometimes erratic and possibly subjective: bottom 7888 - top p7889: it has been shown that iodine oxide particles are aspherical and hence the mobility will not be the same as that of a sphere. Restructuring under humidification would undoubtedly affect the recorded mobility. Similarly, restructuring by reducing viscosity enhancing flow would lead to a change in mobility indistinguishable by cause. Morphology and phase are only applicable to non-liquid particles so would require some probe other than phase state to distinguish the cause.

It is not clear to us what the referees' criticism is here or why the referee thinks we are erratic and subjective in our interpretation of the results. We have attempted to provide a broader range of possible explanations that are consistent with our measurements and those which already appear in the literature. Rather than being subjective, we actually feel this provides a more honest appraisal of the full range of possible explanations, rather than asserting that the behaviour is consistent, for example, with water uptake into capillaries etc. The sentence at the end of section 3.1 has been modified: 'An alternative explanation that is different in microphysical origin might be that the particles generated under dry conditions were amorphous solids.' The words 'morphology' and 'phase' do apply to liquid particles, a liquid is a phase and will tend to take a spherical morphology.

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