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## Molecular scale evidence of new particle formation *via* sequential addition of HIO<sub>3</sub>

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### Abstract

Homogeneous nucleation and subsequent cluster growth leads to the formation of new aerosol particles in the atmosphere<sup>1</sup>. Nucleation of sulphuric acid and organic vapours is thought to be responsible for new particle formation over continents<sup>1,2</sup> while iodine oxide vapours have been implicated in particle formation over coastal regions<sup>3–7</sup>. Molecular clustering pathways involved in atmospheric particle formation have been elucidated in controlled laboratory studies of chemically simple systems<sup>2,8–10</sup>. But no direct molecular-level observations of nucleation in atmospheric field conditions involving either sulphuric acid, organic or iodine oxide vapours have been reported to date<sup>11</sup>. Here we report field data from Mace Head, Ireland and supporting data from northern Greenland and Queen Maud Land, Antarctica that allow for the identification of the molecular steps involved in new particle formation in an iodine-rich, coastal atmospheric environment. We find that the formation and initial growth process is almost exclusively driven by iodine oxoacids and iodine oxide vapours with average resulting cluster O:I ratios of 2.4. Based on

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#### Author Contributions

MS, NS, TJ, SR, JKa, AF, OP performed the field measurements, MS, NS, TJ, JKo and HJ, analysed the data, HH suggested the chemical mechanism and performed quantum chemical calculations, SR, TB and MS performed the laboratory experiments, MS, VMK and COD wrote the manuscript. MS, MK, HJ and COD designed the measurements, DC and COD organised the Field Study at Mace Head and contributed to the data analysis. All authors contributed to data interpretation and contributed to the final manuscript development.

#### Author information

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**Computer code** TofTools for Matlab, used for mass spectrometer data processing, is available upon request.

the high O:I ratio, together with observed high concentrations of iodic acid,  $\text{HIO}_3$ , we suggest that cluster formation primarily proceeds by sequential addition of iodic acid  $\text{HIO}_3$ , followed by intra-cluster restructuring to  $\text{I}_2\text{O}_5$  and recycling of water in the atmosphere or upon drying. Overall, our study provides ambient atmospheric molecular-level observations of nucleation, supporting the previously suggested role of iodine containing species in new particle formation<sup>3–7, 12–18</sup>, and identifies the key nucleating compound.

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Elucidation of the key question “how do new clusters and particles form in the atmosphere?” has failed to date due to the lack of a measurement technique sufficiently sensitive to detect or identify the chemical composition of nucleating clusters, given that most new atmospheric particle formation events occur at modest intensities. An exception, in terms of nucleation burst intensity, is coastal new particle formation where exceptionally high formation and growth rates, relative to any other environment, have been observed<sup>3,7</sup>. The observed rapid new particle formation and growth in coastal air requires extraordinarily high production rates of particle precursors. Biogenic emissions of iodine vapors, mainly  $\text{I}_2$ [<sup>14–15,19</sup>], from marine algae have been implicated in the production of I atoms by photolysis reactions. I atoms would then rapidly react in a chain of reactions initiated by ozone to form IO radicals<sup>3,12,20–21</sup>,  $\text{OIO}_3$ ,<sup>21,22</sup>,  $\text{HIO}_3$ ,<sup>12</sup>,  $\text{HIO}_3$  (Iodic acid)<sup>23</sup>,  $\text{I}_2\text{O}_{2-4}$ [<sup>3</sup>] and  $\text{I}_2\text{O}_5$ [<sup>16</sup>] – all potential precursors of new particles. Particle production from yet unidentified iodine containing vapours has also been experimentally demonstrated<sup>3,12,13</sup>. Laboratory experiments starting from  $\text{I}_2$  and ozone suggested that particles formed in dry conditions are composed of  $\text{I}_2\text{O}_5$ [<sup>16, 17</sup>].

To pursue identification of the molecular steps involved in new particle formation in an iodine-rich environment, a field campaign was performed at Mace Head coastal station on Irish west coast in August – October 2013. A suite of novel instrumentation, and in particular, a nitrate ion based CI-API-TOF mass spectrometer capable of resolving the chemical composition of freshly formed electrically neutral clusters<sup>9</sup>, was applied (Supplementary Information).

Throughout the campaign, new particle formation associated with low tide and subsequent exposure of seabed macro-algae to ambient air was observed almost every day (Supplementary Information Figure S1). An example of a new particle formation event is shown in Figure 1. Soon after noon when the low tide occurred, a strong burst (**a**) of new particles was detected with total concentration of  $>1.5$  nm particles exceeding  $10^6 \text{ cm}^{-3}$  and 1.5 – 3 nm clusters reaching concentrations of the order of  $10^5 \text{ cm}^{-3}$  (Supplementary Information Figure S2). Because of the short time between the emission source and the measurement site particles rarely grew up above 10-20 nm. However, previous studies have demonstrated that these particles reach cloud condensation nuclei (CCN) sizes in a matter of few hours<sup>24</sup>.

Preceding the new particle production event, a strong increase in iodic acid,  $\text{HIO}_3$ , signal was seen (**b**) with concentrations reaching  $10^8 \text{ molecules cm}^{-3}$  during the course of the event. The observation of iodic acid was unexpected as there have, hitherto, been no reported observations of its presence in ambient air. At the same time, neutral iodine oxide clusters up

to over 2000 atomic mass units were detected, confirming that iodine oxides (including HIO<sub>3</sub>) were almost solely responsible for new particle formation.

The chemically ionized cluster distribution, representing originally neutral clusters that have charged upon chemical ionization (Supplementary Information), is shown in Figure 2. The depicted mass defects (i.e. total deviation of the molecule/cluster mass from the integer mass defined as the sum of neutrons and protons in the atom nuclei of the molecules) emphasize the high iodine and oxygen content of the measured clusters because oxygen has a moderate and iodine a strong negative mass defect. Even though sulphuric acid, methyl sulphonic acid and highly oxidized multifunctional organic vapours<sup>25</sup> were detected, neutral clusters were composed almost exclusively of iodine and oxygen and, to a very small extent, of hydrogen. Chemically ionized clusters contained either none (an odd number of I) or one hydrogen atom (an even number of I), suggesting one (odd I) or two (even I) hydrogen atoms in their original neutral form. Minute quantities of sulphuric acid, as well as nitrogen, in form of ammonia or nitric acid, were detected in clusters, but pure iodine oxide clusters clearly dominated over the other compounds.

The average oxygen to iodine ratio (O:I) was generally 2.4, but varied between 2.2 and 2.6 for a fixed number of iodine atoms. This shows that simple condensation of OIO[12], I<sub>2</sub>O<sub>3</sub>[17] or I<sub>2</sub>O<sub>4</sub>[17] alone, or any combination of compounds with O:I of two or below, is not sufficient to explain the observed cluster formation. However, compounds such as I<sub>2</sub>O<sub>5</sub>[16,17,26] or HIO<sub>3</sub>[23] should have a major contribution to the cluster production. Signals attributable to I<sub>2</sub>O<sub>5</sub> were low, suggesting that I<sub>2</sub>O<sub>5</sub> condensation alone unlikely explains the observed cluster growth. However, the relatively high concentrations of iodic acid, HIO<sub>3</sub>, point toward its major role in the cluster buildup.

The concentration of HIO<sub>3</sub> during the events reached 10<sup>8</sup> cm<sup>-3</sup> and should have been considerably higher in the immediate vicinity of algae beds. Such detected concentration would be sufficient to explain the observed cluster growth rates (Supplementary Information, Table S1). Further evidence on the role of HIO<sub>3</sub> comes from the observed cluster concentrations (Figure 3) which depend close to linearly on the HIO<sub>3</sub> concentration. Near linear dependencies of cluster and vapour concentrations can in general be caused by arbitrary combinations of clustering mechanisms and sinks. In this particular case, the formation rates are so high that the sinks are likely to play a negligible role. Thus, the linear dependency indicates that the clusters grow by sequential HIO<sub>3</sub> additions, which are much faster than the competing evaporation or fragmentation processes. The critical role of HIO<sub>3</sub> was found also in a series of supplementary laboratory experiments (Supplementary Information, Figures S4-S11). A chemical mechanism producing iodic acid from primary molecular iodine emissions remains unclear. However, the formation of clusters can, to a large extent, be explained by the uptake of iodic acid and subsequent reaction of two HIO<sub>3</sub> molecules in the cluster, resulting in formation of I<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O with water evaporating from the cluster (Figure 2). Such a mechanism perfectly explains also the feature that the hydrogen content in the detected (chemically ionized) clusters was either one (even I) or zero (odd I). It should be noted that sampled clusters are exposed to decreased water vapour concentration after entering the vacuum of the mass spectrometer, so further restructuring of HIO<sub>3</sub> to I<sub>2</sub>O<sub>5</sub> can take place upon dehydration. Thus, it may be that corresponding clusters

in the atmosphere are more hydrated and contain more iodic acid than could be directly inferred from the mass spectra. The general mechanism of the sequential  $\text{HIO}_3$  addition outlined above, however, remains unaffected even when further dehydration takes place during the sampling.

The average O:I ratio of 2.4 suggests that besides the major role of  $\text{HIO}_3$ , other iodine oxoacids – iodic acid ( $\text{HIO}_2$ ) or hypoiodous acid ( $\text{HIO}$ ) – could act in the same way as  $\text{HIO}_3$ . That would readily explain the variation of oxygenation in the observed clusters. Both acids were detected during the event, but with much lower intensities than that of iodic acid with lower limit concentration estimates of  $2 \cdot 10^6$  molecules  $\text{cm}^{-3}$  and  $1 \cdot 10^6$  molecules  $\text{cm}^{-3}$  for iodic and hypoiodous acid, respectively, during the peak concentration period. Rather than these small iodine oxoacids, it is likely that non-hydrogen containing compounds with two iodine atoms ( $\text{I}_2\text{O}_{2.5}$ ) have been condensed on clusters to some extent. Condensation of IO or OIO should have been less pronounced because hydrogen atom was detected only in every second group of the clusters separated by  $\text{I}_2\text{O}_5$ . Addition of IO or OIO to a cluster, formed according to above proposed scheme, would result in hydrogen containing peaks in the cluster spectrum also for odd number of I. The overall mechanism should therefore be a mixture of straightforward addition of  $\text{HIO}_3$  accompanied by restructuring and water recycling and less pronounced addition of  $\text{HIO}$ ,  $\text{HIO}_2$  and/or  $\text{I}_2\text{O}_{2.5}$  compounds. Figure 2 depicts the process starting from  $\text{HIO}_3$  molecule and proceeding purely *via* addition of  $\text{HIO}_3$  accompanied with the loss of water. However, a parallel process, involving only non-acidic iodine oxides,  $\text{I}_2\text{O}_{2.5}$ , cannot be fully excluded. In the mass range of 1000–2000 Da, 65% to 73% of the total cluster mass can be readily explained by  $\text{HIO}_3$  and  $\text{I}_2\text{O}_5$ , while the minimum of 27% (in case only  $\text{I}_2\text{O}_3$  is co-condensing) or the maximum of 35% (only  $\text{I}_2\text{O}_4$  is co-condensing) of this mass is explained by less-oxygenated compounds.

In addition to Mace Head, we employed a CI-API-TOF mass spectrometer at two field campaigns carried out at high-latitude sites exposed periodically to marine air masses: Station Nord in northern Greenland during February – August 2015 and Aboa research station in Queen Maud Land, Antarctica, during November 2014 – February 2015 (Supplementary information). In Greenland, we started to observe elevated concentrations of iodic acid after the sunrise in late February, often associated with new particle formation events. During such events, the  $\text{HIO}_3$  concentrations tended to be much higher than that of sulphuric acid (Fig. S12), and it seems that the cluster formation could be explained virtually purely with the  $\text{HIO}_3$  clustering mechanism (Fig. S13). In Antarctica, we measured gas-phase iodic acid well above the instrumental limit-of-detection despite the distance of more than 100 km to the Antarctic coast (Fig. S15). This observation suggests that the oceanic areas surrounding the Antarctic continent may be strong sources of molecular iodine that is converted to iodic acid in gas phase reactions either at the emission area or during the transportation to our measurement site.

Our measurements point toward prominent gas-phase iodic acid production associated with iodine emissions from different coastal areas, and show that this compound forms very actively growing molecular clusters. However, iodine is not only emitted in coastal areas but also in the open ocean environment<sup>27,28</sup> as well as from Arctic and Antarctic sea ice<sup>29–33</sup>. At the present stage, it remains uncertain if the described particle formation mechanism

plays a role in the open ocean environment and if it can make an important contribution to climate-relevant processes.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

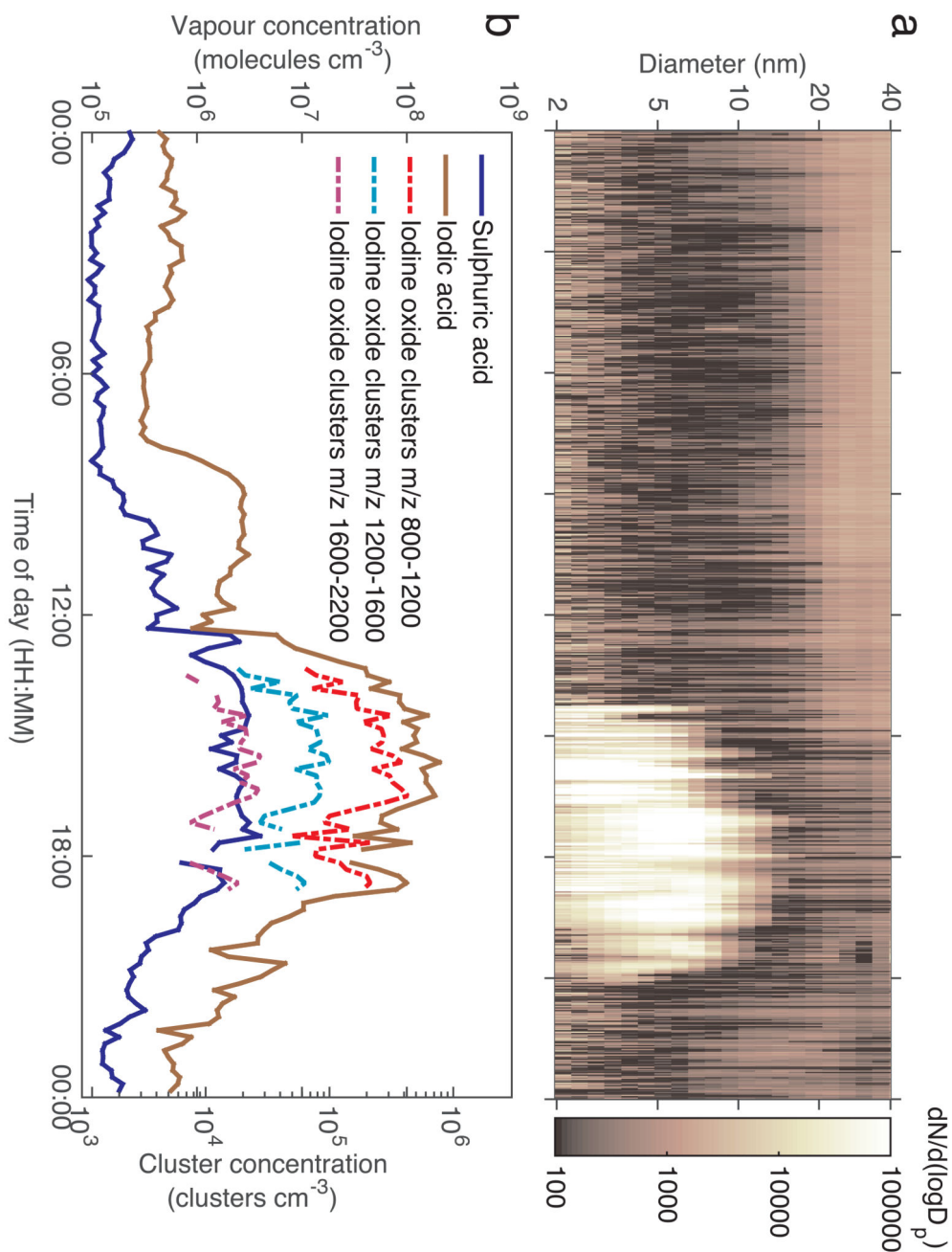
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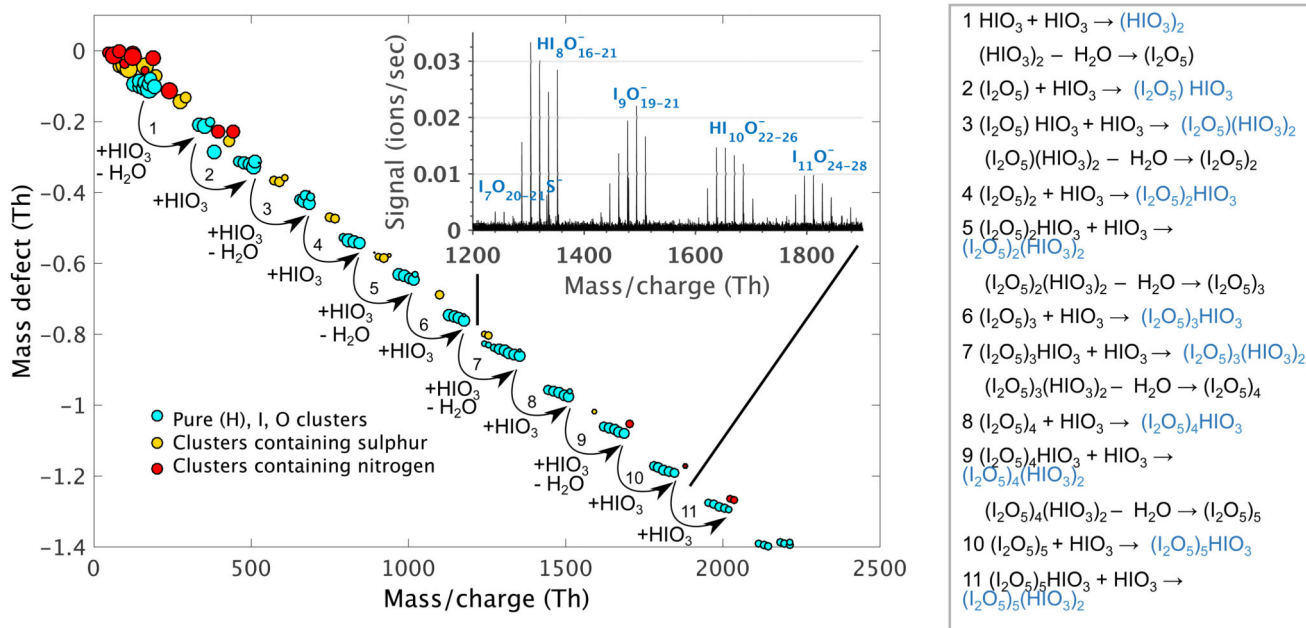
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**Figure 1. Typical particle formation event recorded at Mace Head.**

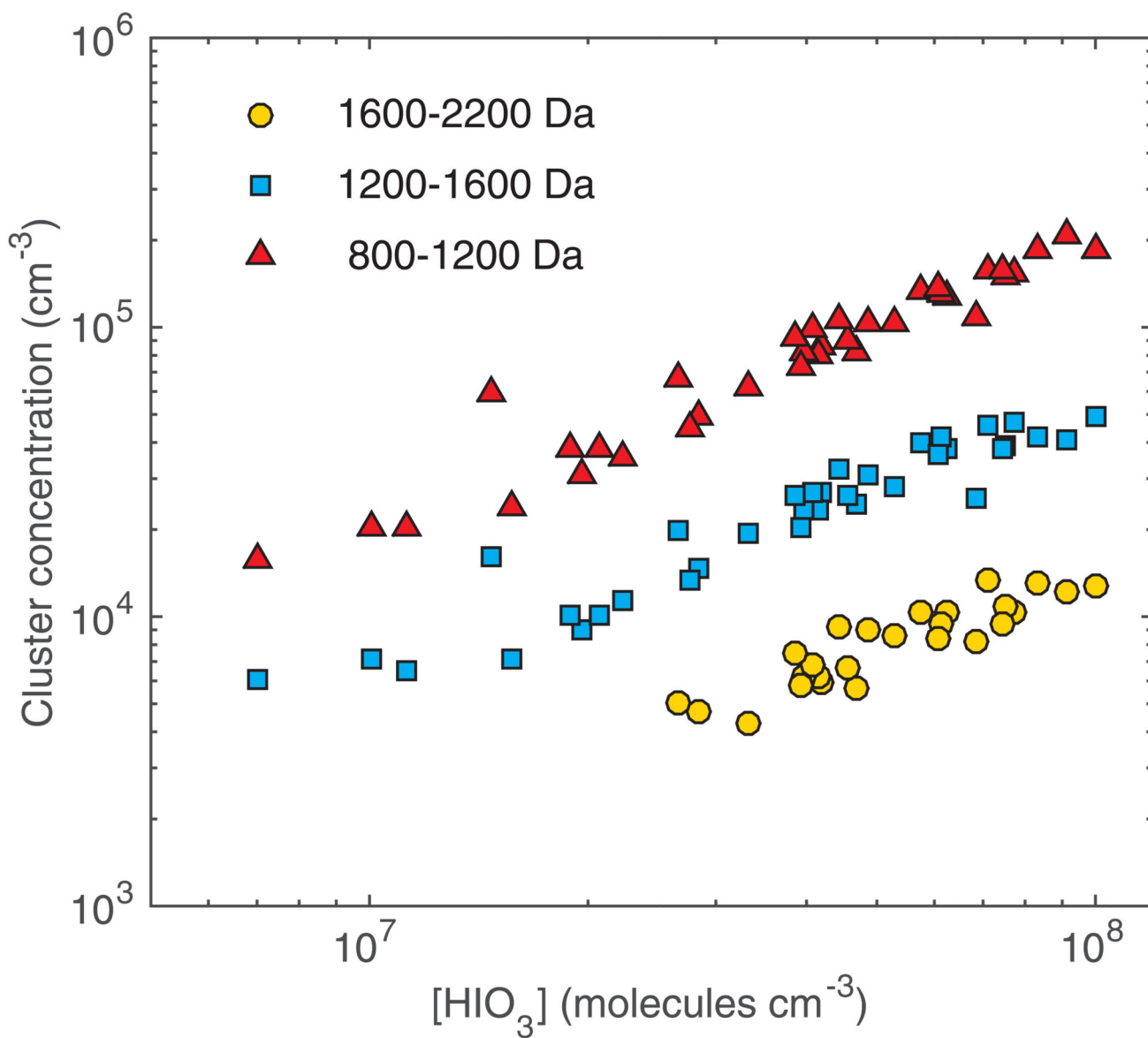
**a**, The event is initiated slightly after noon at low tide resulting in iodine emissions from marine algae. Particles grow rapidly to 2-10 nm sizes. When the tide gets high again after ~6 hours the particle production stops. **b**, The event is associated with a slight increase of sulphuric acid, thought typically to be the key player in atmospheric nucleation, but much more predominant increase in iodic acid with peak concentration above  $10^8 \text{ cm}^{-3}$  is observed. Together with iodic acid, iodine oxide clusters with masses exceeding 2000 Da are observed.



**Figure 2. Mass defect vs. cluster mass plot depicting the abundance and atomic composition of nucleating neutral clusters during the event.**

Cluster distribution is dominated by iodine oxides. Mechanism explaining the cluster formation starting from iodic acid,  $\text{HIO}_3$ , and proceeding through further addition of iodic acid is highlighted in the figure. It should be noted that neutral cluster loses one hydrogen upon chemical ionization and that part of restructuring reactions can take place only upon detection; thus in the atmosphere, depicted clusters may be more hydrated, i.e., part of  $\text{I}_2\text{O}_5$  can be in form of two iodic acid molecules.





**Figure 3.** Cluster concentrations, grouped into three mass classes, depend almost linearly on the HIO<sub>3</sub>-concentration suggesting that the main clustering mechanism is addition of HIO<sub>3</sub>.