Molecular-level study on the role of methanesulfonic acid in iodine oxoacids nucleation

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Abstract. Iodic acid (HIO₃) and iodous acid (HIO₂) have been identified to nucleate effectively by the Cosmosics Leaving OUtdoor Droplets (CLOUD) experiment at CERN (He et al., 2021, Science), yet it may be hard to explain all HIO₃-induced nucleation. Given the complexity of marine atmosphere, other precursors may be involved. Methanesulfonic acid (MSA), as a widespread precursor over oceans, has been proven to play a vital role in facilitating nucleation. However, its kinetic impacts on synergistic nucleation of iodine oxoacids remain unclear. Hence, we investigated the MSA-involved HIO₃-HIO₂ nucleation process at the molecular level using density functional theory (DFT) and Atmospheric Clusters Dynamic Code (ACDC). The results show that MSA can form stable molecular clusters with HIO₃ and HIO₂ jointly via hydrogen and halogen bonds, as well as electrostatic attraction after proton transfer to HIO₂. Thermodynamically, the MSA-involved clustering can occur nearly without free-energy barrier, following HIO₂-MSA binary and HIO₃-HIO₂-MSA ternary pathway. Furthermore, adding MSA significantly enhance the rate of HIO₃-HIO₂-based cluster formation, even up to 10¹-fold at cold marine regions with rich MSA and scarce iodine, such as polar Ny-Ålesund and Marambio. Thus, the proposed more efficient HIO₃-HIO₂-MSA nucleation mechanism may provide theoretical evidence for explaining the frequent and intensive burst of marine iodine particles.

1 Introduction

Marine aerosol, the primary natural aerosol (O'Dowd and Leeuw, 2007), significantly impacts global climate, radiation balance, and even human health (Wang et al., 2010; Pöschl, 2005). New particle formation (NPF) is a main source of marine aerosols, which proceeds via nucleating and subsequent growth (Lee et al., 2019; Zhang, 2010; Kulmala et al., 2013; Zhang et al., 2012). And the nucleation, forming critical clusters at 1-2 nm from gaseous precursors, is the pivotal step affecting NPF (Zhang, 2010; Kulmala et al., 2013). However, the chemicals involved in nucleation and the underlying mechanisms remain poorly understood, due to technological limitations in the molecular-level analysis. Additionally, the lack of comprehensive, long-term ocean observations, further hinders our knowledge of marine NPF.

Recent field studies suggest that marine NPF events are closely related to atmospheric iodine-bearing molecules emitted by algae (Yu et al., 2019; Baccarini et al., 2020; Beck et al., 2021). During the NPF events in coastal (e.g., Mace Head and...
Zhejiang) (Sipilä et al., 2016; Yu et al., 2019) and polar oceans (e.g., Arctic Ocean) (Baccarini et al., 2020), the nucleating processes are mainly driven by iodic acids (HIO₃). Yet in fact, the self-nucleation of HIO₃ alone cannot explain the observed NPF rates (Rong et al., 2020). More recently, the Cosmosics Leaving OUtdoor Droplets (CLOUD) experiment at CERN has found that iodosic acid (HIO₂) plays a key role in stabilizing HIO₃, enabling effective nucleation by the sequential addition of HIO₃ followed by HIO₂ (He et al., 2021). Further theoretical studies uncover that the stabilizing effect of HIO₂ on HIO₃ stems from its role as a base in clustering (Zhang et al., 2022b; Liu et al., 2023). Despite the efficient nucleation of HIO₃ and HIO₂, acceptably consistent with the CLOUD measurement (Zhang et al., 2022a), it is hard to account for all HIO₃-induced nucleation in the real atmosphere with complex chemicals (Ma et al., 2023). Thus, other essential precursors in marine atmosphere might potentially affect HIO₃-HIO₂ nucleation, but which and how remain largely unexamined.

Methanesulfonic acid (MSA), as a typical marine sulfur precursor, is widespread over oceans (Saltzman et al., 1983; Read et al., 2008; Chen et al., 2012; Yan et al., 2019) with considerable atmospheric concentrations (10⁵ – 10⁶ molec. cm⁻³) (Eisele and Tanner, 1993; Dal Maso et al., 2002; Chen et al., 2018; Yan et al., 2019). Moreover, MSA has been shown to initiate nucleation with vital atmospheric precursors, such as ammonia and amines, enhancing cluster formation (O'Dowd et al., 2002; Bork et al., 2014; Shen et al., 2019; Shen et al., 2020; Brean et al., 2021; Liu et al., 2022). Important, current evidence suggests that MSA can also form stable clusters with HIO₃ or HIO₂ individually, but none of the resulting binary nucleation can explain field measurements well (Ning et al., 2022; Wu et al., 2023). Despite the stabilizing effect of MSA on iodine oxoacids, it remains unknown whether MSA can synergistically nucleate with HIO₃ and HIO₂, as well as the induced kinetic impacts on clustering. Furthermore, given the coexistence of MSA and HIO₃ in different marine regions (Quéléver et al., 2022; Beck et al., 2021), the HIO₃-HIO₂-MSA nucleating mechanism may differ under distinct ambient conditions, but it remains unrevealed.

Herein, we have systematically investigated the HIO₃-HIO₂-MSA nucleation involving in MSA, including (HIO₃)ₓ(HIO₂)y(1 ≤ x + y + z ≤ 5, 0 ≤ z ≤ 3) clusters, by combining quantum chemical (QC) approach and Atmospheric Clusters Dynamic Code (ACDC) (McGrath et al., 2012). To probe the nature of cluster formation, the wavefunction analysis was performed to investigate the intermolecular interactions. And the Gibbs free energies of cluster formation were calculated to evaluate cluster stability. Moreover, a series of ACDC simulations were executed to delve into the influence of MSA on nucleation rates and mechanisms under varying atmospheric conditions, such as precursor concentration and temperature.

2 Methods

2.1 Quantum Chemical Calculations

To locate the low-lying isomers of (HIO₃)ₓ(HIO₂)y(1 ≤ x + y + z ≤ 5, 0 ≤ z ≤ 3) clusters, the multi-step conformer search was adopted here (details in Supporting Information (SI)). The resulting stable clusters with the lowest energies were identified at ωB97X-D/6-311++G(3df,3pd) (for C, H, O, and S atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom)
level of theory (Francl et al., 1982; Peterson et al., 2003), and the corresponding Cartesian coordinates were collected in Table S6. In addition, the structures of pure-HIO₃, pure-HIO₂, pure-MSA, HIO₃-HIO₂, HIO₃-MSA and HIO₂-MSA clusters in the present study were adopted from the previous studies (Rong et al., 2020; Zhang et al., 2022b; Liu et al., 2023; Ning et al., 2022; Wu et al., 2023). All density functional theory (DFT) calculations were carried out using the Gaussian 09 package (Frisch et al., 2009). The single-point energy was calculated at the RI-CC2/aug-cc-pVTZ (for C, H, and O atoms) + aug-cc-pV(T+d)Z (for S atom) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory (Hättig and Weigend, 2000) by TURBOMOLE program (Ahlihisch et al., 1989), because of its success in fitting with the experiments (Lu et al., 2020; Kürt et al., 2018; Rong et al., 2020; Almeida et al., 2013). In the present study, the Gibbs formation free energy (ΔGᵣₑᶠ, kcal mol⁻¹) of the HIO₃-HIO₂-MSA clusters at the reference pressure (1 atm) was calculated as:

\[ ΔGᵣₑᶠ = ΔEᵣᵢ-C₂ + ΔGₜₜ₉ₓ-D, \]

where ΔEᵣᵢ-C₂ is the electronic contribution and ΔGₜₜ₉ₓ-D is the thermal contribution to free energy. And the ΔGᵣₑᶠ at different temperatures (T = 268 – 298 K) were calculated using the Shermo 2.0 code (Lu and Chen, 2021) and collected in Table S1. Further given the effect of vapor pressures of the precursor, the ΔGᵣₑᶠ was converted to ΔG(P₁, P₂, …, Pₙ) (Vehkamäki, 2006) by the Eq. (2):

\[ ΔG(P₁, P₂, …, Pₙ) = ΔGᵣₑᶠ - k_B T \sum_{i=1}^{n} N_i \ln \left( \frac{P_i}{Pᵣₑᶠ} \right), \]

where n is the number of components within the cluster, k_B denotes the Boltzmann constant, T signifies the temperature, Nᵢ refers to the number of molecules of type i in the number of components in the cluster and Pᵢ is the partial pressure of component i in the vapor phase.

### 2.2 Wavefunction Analysis

To probe the binding nature within molecular clusters, wavefunction analysis was conducted using Multiwfn 3.7 (Lu and Chen, 2012). The electrostatic potential (ESP) on the van der Waals (vdW) surface was calculated to identify active interaction sites. Specifically, the negative ESP region is electron-rich, while the positive ESP region is electron-deficient, potentially leading to mutual non-covalent interactions, such as hydrogen bonds (HBs) and halogen bonds (XBs). To further quantify the bond strength, the electron density ρ(r), Laplacian electron density ∇²ρ(r) and energy density H(r) at bond critical points (BCPs) were calculated based on the atoms in molecules (AIM) theory (Lane et al., 2013).

### 2.3 Atmospheric Clusters Dynamic Simulations

To explore nucleation kinetic, the Atmospheric cluster dynamics code (ACDC) (McGrath et al., 2012) was adopted here to compute the cluster formation rates, steady-state concentrations, and formation pathways by explicit solution of the birth-death equations (Eq. (3)).
\[
\frac{dC_i}{dt} = \frac{1}{2} \sum_{j<i} \beta_{ij} C_j C_{(i-j)} + \sum_{j} \gamma_{(i+j)\rightarrow i} C_{i+j} - \frac{1}{2} \sum_{j<i} \gamma_{i\rightarrow j} C_i + Q_i - S_i,
\]

where the subscripts \((i, j, i-j \text{ and } i+j)\) denote different clusters or monomers, \(C_i\) is the concentration of cluster \(i\), \(\beta_{ij}\) and \(\gamma_{(i+j)\rightarrow i}\) represent the cluster collision and evaporation rate coefficient, respectively. And \(Q_i\) and \(S_i\) denote the external source and sink terms, respectively. The \(\beta_{ij}\) is calculated as follows:

\[
\beta_{ij} = \left(\frac{3}{4\pi}\right)^{1/6} \left(\frac{6k_B T}{m_i} + \frac{6k_B T}{m_j}\right)^{1/2} \left(V_i^{1/3} + V_j^{1/3}\right)^2,
\]

where \(m_i\) and \(V_i\) represent the mass and volume of cluster \(i\), respectively. And \(V_i\) is calculated by Multiwfn 3.7 (Lu and Chen, 2012). The \(\gamma_{(i+j)\rightarrow i}\) is calculated by the Eq. (5):

\[
\gamma_{(i+j)\rightarrow i} = \beta_{ij} P_{ref} \exp\left(\frac{\Delta G_{i+j} - \Delta G_i - \Delta G_j}{k_B T}\right),
\]

where \(P_{ref}\) is the reference pressure at 1 atm, and \(\Delta G\) is the formation free energy of the cluster.

### 3 Results and Discussion

Here, conformational analysis was first carried out to study how MSA affects intermolecular interactions in the HIO\(_3\)-HIO\(_2\)-MSA clusters. And the thermodynamic analysis was employed to assess stability of the formed clusters. To gain insights into nucleation mechanisms, a series of ACDC simulations were executed under varying atmospheric conditions.

#### 3.1 Cluster Conformational Analysis

Strong interactions among nucleating precursors are pivotal for forming stable clusters. To evaluate the binding potential of MSA with HIO\(_3\) and HIO\(_2\), we calculated the ESP-mapped molecular vdw surface to identify interaction sites. As illustrated in Fig. 1, MSA has a positive ESP maximum (+63.95 kcal mol\(^{-1}\)) at the H atom of its \(-\text{OH}\) group, serving as a HB donor. The iodine atoms of HIO\(_3\) and HIO\(_2\) with positive ESP maximum (+51.90 and +45.26 kcal mol\(^{-1}\)), can act as effective XB donors. Additionally, the oxygen atoms in the S=O group (from MSA) and I=O group (from HIO\(_3\) and HIO\(_2\)) with strong electronegativity can act as HB or XB acceptor sites, due to the lone pair electrons. Therefore, as shown in Fig. 1(d), MSA, HIO\(_3\), and HIO\(_2\) have the potential to form clusters via intermolecular HBs andXBs.
As present in Fig. 2, all the identified HIO\textsubscript{3}-HIO\textsubscript{2}-MSA clusters are structurally stabilized by the network of HBs (blue dashed lines) and XBs (red dashed lines). Within these clusters, the inward-facing oxygen atom and hydroxyl (-OH) group in MSA facilitates its being involved in forming more HBs and XBs, compared to the HIO\textsubscript{3}-HIO\textsubscript{2} clusters (Fig. S1). Statistically, within HIO\textsubscript{3}-HIO\textsubscript{2}-MSA clusters, the percentage of XBs (61%) is higher than that of HBs (39%). Notably, during the HIO\textsubscript{3}-HIO\textsubscript{2}-MSA cluster formation, HIO\textsubscript{2} behaves like a base and is protonated by MSA instead of HIO\textsubscript{3}, likely due to greater acidity of MSA than HIO\textsubscript{3}. After the MSA-driven proton transfer to HIO\textsubscript{2}, the resulting electrostatic interactions between the formed ion pairs (CH\textsubscript{3}SO\textsuperscript{3} – H\textsubscript{2}IO\textsuperscript{4+}) further stabilize the clusters. Taken together, MSA can form clusters with HIO\textsubscript{3} and HIO\textsubscript{2} via HBs, XBs, and electrostatic attraction between ion pairs after proton transfer.

To further quantify bond strength within HIO\textsubscript{3}-HIO\textsubscript{2}-MSA clusters, the topological analysis was performed based on the atoms in molecules (AIM) theory. The electron density \( \rho(r) \), Laplacian electron density \( \nabla^2 \rho(r) \), energy density \( H(r) \) at the corresponding bond critical points (BCPs) in the studied HIO\textsubscript{3}-HIO\textsubscript{2}-MSA clusters were calculated and collected in Table S2. The \( \rho(r) \) is generally positively associated with the bond strength. For the HIO\textsubscript{3}-HIO\textsubscript{2}-MSA clusters, \( \rho(r) \) values at the BCPs of the HBs range from 0.0090 to 0.0869 a.u., exceeding the reported threshold of HB (0.002 – 0.040 a.u.) (Koch and Popelier, 1995; Grabowski, 2004). And the associated values of \( \nabla^2 \rho(r) \) at these BCPs range from 0.0310 to 0.1180 a.u., falling within the suggested range for HB (0.014 – 0.139 a.u.) (Koch and Popelier, 1995; Grabowski, 2004). Meanwhile, for O=I=O XB, the \( \rho(r) \) and \( \nabla^2 \rho(r) \) values within HIO\textsubscript{3}-HIO\textsubscript{2}-MSA clusters range from 0.0068 to 0.1999 a.u. and 0.0288 to 0.1744 a.u.,
respectively. Collectively, MSA can stabilize HIO$_3$-HIO$_2$ clusters via more relatively strong HBs and XBs, while also protonating HIO$_2$ to form ion pairs.

Figure 2. The most stable configurations of the HIO$_3$-HIO$_2$-MSA ternary clusters identified at the oB97XD/6-311++G(3df, 3pd) (for C, H, O, and S atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory. The lengths of bonds are given in Å.

3.2 Cluster Formation Pathways and Free Energy Surface

To explore how MSA affect HIO$_3$-HIO$_2$-based nucleation kinetic, the ACDC simulations were employed to reveal the nucleating mechanism under varying atmospheric conditions. Based on the field measurement (Berresheim et al., 2002; Chen et al., 2018; Sipilä et al., 2016; Beck et al., 2021), the ranges of [MSA], [HIO$_3$], and [HIO$_2$] are set to be $10^6 - 10^8$, $10^6 - 10^8$ and $2.0 \times 10^4 - 2.0 \times 10^6$ molec. cm$^{-3}$, respectively. Here, the condensation sink (CS) coefficient is set to be $2.0 \times 10^{-3}$ (Dal Maso et al., 2002) and temperature ($T$) is 278 K. Under such conditions, the molecular-level nucleation pathways and the corresponding branching ratios are depicted in Fig. 3(a). The detailed branch ratio is also observed at 278 K (Fig. S2) and 268 K (Fig. S3). Furthermore, to comprehend how the growth occurs thermodynamically, we herein calculated the Gibbs free energies ($\Delta G$, Eq. (2)) along the main clustering pathway at the conditions of $T = 268 - 278$ K, [HIO$_3$] = $1.0 \times 10^6$, [HIO$_2$] = $2.0 \times 10^4$, and [MSA] = $5.0 \times 10^6$ molec. cm$^{-3}$ (Fig. 3(b) and Fig. S4).
Figure 3. (a) Top: main cluster growth pathway of the HIO$_3$-HIO$_2$-MSA nucleating system at $T = 278$ K, $CS = 2.0 \times 10^{-3}$ s$^{-1}$, [HIO$_3$] = 1.0 $\times$ 10$^6$, [HIO$_2$] = 2.0 $\times$ 10$^4$, [MSA] = 5.0 $\times$ 10$^6$ molec. cm$^{-3}$.

Bottom: branch ratio of flux out under varying [MSA] (10$^6$ – 10$^8$ molec. cm$^{-3}$).

(b) Free energy surface of cluster formation

$T = 278$ K, [HIO$_3$] = 1.0 $\times$ 10$^6$, [HIO$_2$] = 2.0 $\times$ 10$^4$, [MSA] = 5.0 $\times$ 10$^6$ molec. cm$^{-3}$.
3) and $[\text{HIO}_3]$ ($10^6$ – $10^8$ molec. cm$^{-3}$). The yellow and purple arrows (or bar) denote MSA-involved and non-MSA flux out (or branch ratio), respectively. (b) The Gibbs free energies of cluster formation ($\Delta G$, kcal mol$^{-1}$) based on the main clustering pathway in HIO$_3$-HIO$_2$-MSA nucleation system.

As shown in Fig. 3(a), the clustering pathways, at $T = 278$ K, $CS = 2.0 \times 10^3$ s$^{-1}$, $[\text{HIO}_3] = 1.0 \times 10^6$, $[\text{HIO}_3] = 2.0 \times 10^4$, and $[\text{MSA}] = 5.0 \times 10^5$ molec. cm$^{-3}$, can be categorized into two main types: i) MSA-involved pathways, including HIO$_2$-MSA and HIO$_3$-HIO$_2$-MSA nucleation; and ii) non-MSA pathways, primarily involving HIO$_2$-HIO$_2$ nucleation. For the HIO$_2$-MSA pathway, the initial formation of (HIO$_2$)$_2$(MSA)$_1$ heterodimer occurs without any energy barrier (Fig. 3(b)). And the subsequent cluster growth mainly proceeds via sequential addition of HIO$_2$ or MSA monomer, partly coupled with cluster collisions. Specifically, 63% of (HIO$_2$)$_2$(MSA)$_2$ results from (HIO$_2$)$_2$(MSA)$_1$ colliding with MSA monomer with energy barrier of 1.00 kcal mol$^{-1}$, while 36% from barrierless combination of two (HIO$_2$)$_1$(MSA)$_1$ cluster. At this point, kinetic drives growth across the collision of (HIO$_2$)$_2$(MSA)$_1$ with MSA monomer, instead of following the lowest energy pathway. This is because the collision frequency of (HIO$_2$)$_1$(MSA)$_1$ and a HIO$_2$ monomer is relatively higher, stemming from the higher [HIO$_2$]. Then, the formed (HIO$_2$)$_2$(MSA)$_2$ further collides with a HIO$_2$ monomer, yielding the stable (HIO$_2$)$_2$(MSA)$_2$ cluster against evaporation. As to HIO$_2$-HIO$_2$-MSA nucleation, the formation of (HIO$_2$)$_2$(HIO$_2$)$_2$(MSA)$_1$ cluster arises from i) the collision of (HIO$_2$)$_2$(MSA)$_1$ with (HIO$_2$)$_2$(HIO$_2$)$_1$ (18%, energy barrier: 1.00 kcal mol$^{-1}$), and ii) (HIO$_3$)$_1$(HIO$_2$)$_1$ with (HIO$_2$)$_1$(MSA)$_1$ (62%, energy barrier: 0.17 kcal mol$^{-1}$), as well as iii) (HIO$_3$)$_1$(HIO$_2$)$_2$ binding with a MSA monomer (20%, energy barrier: 3.80 kcal mol$^{-1}$). In addition, for the non-MSA pathway marked by purple arrows, 76% of (HIO$_2$)$_2$(HIO$_2$)$_2$ cluster formation arises from the collision between two (HIO$_3$)$_1$(HIO$_2$)$_1$ cluster, which accords closely with the barrierless pathway shown in Fig. 3(b).

Overall, the MSA-involved pathways contribute more to cluster formation of 74%, while non-MSA path accounts for only 26%. Although the HIO$_3$-HIO$_2$-MSA growth pathway is less favorable than the HIO$_2$-HIO$_2$ and HIO$_2$-MSA pathways at $T = 278$ K, it can become barrierless at the lower temperature of 268 K (Fig. S4). This result may be explained by the fact that the lower temperature results in a decrease in the evaporation rates of the HIO$_3$-HIO$_2$-MSA clusters (Table S4 and Table S5). Taken together, these findings highlight the direct and significant involvement of MSA in HIO$_3$-HIO$_2$ nucleation, facilitating cluster formation.

As presented in the bottom of Figure 3(a), the contribution of different clustering pathways to the flux out varies with precursor concentrations. With increasing [MSA] from $10^6$ to $10^8$ molec. cm$^{-3}$, the contribution of MSA-involved pathways rises from 1% to 99% during nucleation. And at the median [MSA] of $10^7$ molec. cm$^{-3}$, the MSA-involved pathway contributes 86%, whereas the non-MSA pathway accounts for just 14%. In contrast, the ratio of MSA-involved pathways decreases (from 86% to 0%) with increasing concentrations of iodine oxoacids. At higher [HIO$_3$] of $10^8$ molec. cm$^{-3}$, the HIO$_3$-HIO$_2$ pathway dominates nucleation. Overall, the results suggest that MSA’s contribution to cluster formation is positively related to [MSA] but negatively linked to [HIO$_3$]. Predictably, the kinetic impact of MSA on HIO$_3$-HIO$_2$ nucleation is more pronounced in marine regions with richer MSA away from iodine sources.
3.3 Enhancement on Cluster Formation Rates

Guided by the clustering pathway analysis, MSA has shown its potential to participate in the HIO$_3$-HIO$_2$-based nucleation, but its detailed impacts on cluster formation rates (\(J, \text{ cm}^{-3} \text{ s}^{-1}\)) remain uncertain. Herein, the influence of MSA on \(J\) under different atmospheric conditions are systematically analyzed below.

Figure 4 presents the simulated \(J\) of HIO$_3$-HIO$_2$-MSA (red bar) and HIO$_3$-HIO$_2$ system (grey bar) against the varying temperatures \((T = 258 – 298\text{ K})\) at \(CS = 2.0 \times 10^{-3}\text{ s}^{-1}\), [HIO$_3$] = \(1.0 \times 10^7\), [HIO$_2$] = \(2.0 \times 10^5\), and [MSA] = \(1.0 \times 10^7\) molec. cm$^{-3}$. Clearly, \(J\)(HIO$_3$-HIO$_2$-MSA) is consistently higher than \(J\)(HIO$_3$-HIO$_2$), highlighting the enhancement of MSA on HIO$_3$-HIO$_2$-based clustering under common atmospheric temperatures. Specifically, both \(J\)(HIO$_3$-HIO$_2$-MSA) and \(J\)(HIO$_3$-HIO$_2$) are negatively dependent on \(T\), due to reduced cluster evaporation caused by low \(T\). As a result, MSA could promote nucleation with higher \(J\), especially at the colder regions, such as polar oceans.

![Cluster formation rate vs temperature](image)

**Figure 4.** Simulated cluster formation rates \(J\) (cm$^{-3}$ s$^{-1}$) against varying atmospheric temperatures: \(T = 258 – 298\text{ K}, CS = 2.0 \times 10^{-3}\text{ s}^{-1}\), [HIO$_3$] = \(1.0 \times 10^7\), [HIO$_2$] = \(2.0 \times 10^5\), and [MSA] = \(1.0 \times 10^7\) molec. cm$^{-3}$.

In fact, apart from atmospheric temperature, precursor concentrations may vary regionally or seasonally, further affecting nucleation. So, to comprehensively reveal the effect of MSA, here we defined and calculated MSA-driven enhancement factor \(R\) (Eq. (6)) under varying concentrations of MSA, HIO$_3$, and HIO$_2$ (i.e., [MSA], [HIO$_3$], and [HIO$_2$], unit: molec. cm$^{-3}$).

\[
R = \frac{J(\text{HIO}_3\text{-HIO}_2\text{-MSA})}{J(\text{HIO}_3\text{-HIO}_2)} = \frac{J(\text{[HIO}_3] = x, \text{[HIO}_2] = y, \text{[MSA]} = z)}{J(\text{[HIO}_3] = x, \text{[HIO}_2] = y)}
\]  

(6)

where \(J(\text{HIO}_3\text{-HIO}_2\text{-MSA})\) and \(J(\text{HIO}_3\text{-HIO}_2)\) represent the cluster formation rate of HIO$_3$-HIO$_2$-MSA and HIO$_3$-HIO$_2$ system, respectively. \(x, y\) and \(z\) are the adopted [HIO$_3$], [HIO$_2$], and [MSA], respectively.

As seen from Fig. 5, with [MSA] ranging from \(10^6\) to \(10^8\) molec. cm$^{-3}$ (Fig. 5(a) – (c)), the maximum \(R\) increases from 5 to \(10^4\)-fold, which is primarily due to MSA-mediated synergistic nucleation with HIO$_3$ and HIO$_2$ (recalling Sect. 3.2). Even
at a median [MSA] of $1.0 \times 10^7$ molec. cm$^{-3}$, the resulting $R$ can reach approximately 10$^2$-fold. In contrast, $R$ is decayed at conditions of higher [HIO$_3$] and [HIO$_2$]. That is, the enhancing effect of MSA on $J$ is limited in near-iodine source regions. Naturally, in regions with sparser iodine, the promoting effect of MSA is significant. To sum up, MSA can promote nucleation, particularly in marine regions characterized by lower $T$, lower [HIO$_3$] and [HIO$_2$].

Figure 5. Enhancement strength $R$ of MSA on cluster formation rates at varying precursor concentrations: [HIO$_3$] = $10^6 - 10^7$, [HIO$_2$] = $2.0 \times 10^4 - 2.0 \times 10^6$ molec. cm$^{-3}$, (a) [MSA] = $1.0 \times 10^6$ molec. cm$^{-3}$, (b) [MSA] = $1.0 \times 10^7$ molec. cm$^{-3}$, and (c) [MSA] = $1.0 \times 10^8$ molec. cm$^{-3}$, $T$ = 278 K, CS = $2.0 \times 10^{-3}$ s$^{-1}$.

3.4 Comparison with Field Observations

To further access the atmospheric implication of the proposed HIO$_3$-HIO$_2$-MSA nucleation, we herein simulated $J$ in Fig. 6 based on the ambient conditions of the typical polar regions (e.g., Ny-Ålesund and Marambio) and the mid-latitude marine regions (e.g., Mace Head and Réunion). As shown in Fig. 6(a), the $J$(HIO$_3$-HIO$_2$-MSA) simulated at $T$ = 268 K, CS = $4.0 \times 10^{-4}$ s$^{-1}$, [HIO$_3$] = $10^5 - 10^6$, [HIO$_2$] = $2.0 \times 10^3 - 2.0 \times 10^4$, and [MSA] = $10^6 - 10^8$ molec. cm$^{-3}$ was compared with field observations in coastal Ny-Ålesund (Beck et al., 2021; He et al., 2021). Both $J$(HIO$_3$-HIO$_2$-MSA) and $J$(HIO$_3$-HIO$_2$) increase with the rising [HIO$_3$] and [HIO$_2$]. Importantly, the addition of MSA effectively promotes $J$ to a higher level (orange area), aligning with most field measurement ($2.1 \times 10^4 - 2.7 \times 10^4$ cm$^{-3}$ s$^{-1}$, gray area) (Beck et al., 2021). Even when [MSA] is as low as $1.0 \times 10^6$ molec. cm$^{-3}$ (the orange line below), the $J$(HIO$_3$-HIO$_2$-MSA) can be two orders of magnitude higher than the observed $J$ of $2.1 \times 10^4$ cm$^{-3}$ s$^{-1}$ (the gray line below). Moreover, the simulated $J$ in Fig. 6(b) was obtained at the conditions of coastal Marambio, Antarctic: $T$ = 273 K, CS = $1.0 \times 10^{-4}$ s$^{-1}$, [HIO$_3$] = $10^5 - 10^6$, [HIO$_2$] = $2.0 \times 10^3 - 2.0 \times 10^4$, and [MSA] = $10^6 - 10^7$ molec. cm$^{-3}$ (Quéléver et al., 2022; He et al., 2021). Compared to $J$(HIO$_3$-HIO$_2$), the MSA-enhanced $J$(HIO$_3$-HIO$_2$-MSA) is overall higher, better fitting with the field observations ($10^4 - 2.0 \times 10^4$ cm$^{-3}$ s$^{-1}$, gray area) (Quéléver et al., 2022). These findings imply that MSA potentially plays a vital role in cold polar oceanic regions, particularly with higher [MSA] during NPF events.
In addition, the influence of HIO₃-HIO₂-MSA nucleation over the relatively warmer mid-latitude marine areas, such as Mace Head and Réunion, was investigated here (Fig. S5). We found that $J$(HIO₃-HIO₂-MSA) is slightly higher than $J$(HIO₃-HIO₂), especially at regions with high concentrations of iodine oxoacids (e.g., Mace Head), showing a relatively limited enhancement of MSA on nucleation. Based on the simulated $J$(HIO₃-HIO₂) ($\sim 10^4$ cm⁻³ s⁻¹), iodine nucleation can pretty much explain the NPF events of Mace Head (Fig. S5(a)), which provides potential theoretical evidence for explaining the previous findings (Sipilä et al., 2016).

Overall, at the mid-latitude oceans, especially near iodine source like Mace Head, MSA may have limited enhancement on nucleation. In this case, abundant iodine oxoacids dominate clustering process. While in the colder polar regions, particularly with higher [MSA] like Marambio, MSA indeed significantly facilitate HIO₃-HIO₂ nucleation, suggesting a vital role in polar NPF.

![Figure 6](image_url). Comparison with the simulated cluster formation rates ($J$, cm⁻³ s⁻¹) and field observations at the ambient conditions of (a) Ny-Ålesund ($T = 268$ K, CS = $4.0 \times 10^{-4}$ s⁻¹, [HIO₃] = $10^5 - 10^6$, [HIO₂] = $2.0 \times 10^3 - 2.0 \times 10^4$, and [MSA] = $10^6 - 10^8$ molec. cm⁻³), (b) Marambio ($T = 273$ K, CS = $1.0 \times 10^{-4}$ s⁻¹, [HIO₃] = $10^3 - 10^5$, [HIO₂] = $2.0 \times 10^3 - 2.0 \times 10^4$, and [MSA] = $10^6 - 10^7$ molec. cm⁻³). The orange area, purple line and gray area represent $J$(HIO₃-HIO₂-MSA), $J$(HIO₃-HIO₂), and $J$(Field observation), respectively.

### 4 Conclusion

The present study systematically investigates HIO₃-HIO₂-based nucleating process enhanced by MSA at the molecular level by QC calculations and ACDC simulations. The results indicate that MSA can structurally stabilize HIO₃-HIO₂-based clusters by building the intricate networks with more HBs and XBs. Also, during clustering, MSA replaces HIO₃ in protonating HIO₂ to form ion pairs, resulting in relatively strong electrostatic attractions. Moreover, thermodynamic analyses suggest that MSA-involved clustering is nearly barrierless. Compared to previously reported HIO₃-HIO₂ system, the MSA-involved synergistic nucleation with HIO₃ and HIO₂ proceeds more efficiently, through two additional clustering pathways: i) HIO₂-MSA binary and ii) HIO₃-HIO₂-MSA ternary pathway. And the resulting enhancement of MSA on nucleation is
stronger at colder regions, especially with richer MSA, but weaker in the environments near iodine source. Further comparison with field observations indicates that the HIO$_3$-HIO$_2$-MSA synergistic nucleation play a limited role in the mid-latitude oceans, particularly with abundant iodine (e.g., Mace Head), but an important role in the colder polar regions (e.g., Ny-Ålesund and Marambio).

This study highlights the essential enhancing role of MSA in iodine oxoacids nucleation, and the proposed HIO$_3$-HIO$_2$-MSA synergistic nucleation may help to explain the observed abundant iodine particles during marine NPF events. In addition to MSA, given the complex oceanic atmosphere, other potential nucleation precursors, such as sulfuric acid and amines, may also affect the HIO$_3$-HIO$_2$ nucleation process, further contributing to the formation of marine iodine particles, which deserves future studies.

255 **Data availability.** The data in this article are available from the corresponding author upon request (anning@bit.edu.cn and zhangxiuhui@bit.edu.cn).

**Supplement.** The supplement related to this article is available online at:

**Author contribution.** XZ designed and supervised the research. JL and NW performed the quantum chemical calculations and the ACDC simulations. JL, NW and AN analyzed data. JL, AN and XZ wrote the paper with contributions from all of the other co-authors.

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References


