The Rate of Vapor Condensation on Clusters in Ion-Induced Water Cluster Formation

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Abstract — The rate of water vapor condensation on a water cluster is determined from the sticking probability of water molecule on the cluster and the collision cross section between the molecule and cluster. We investigate the mechanisms of enhancement of vapor condensation rate on a water cluster ion by comparing it with that on a neutral water cluster by using the data of sticking probabilities and collision cross sections as a function of the water cluster size.

Key Words: Vapor Condensation Rate, Water Cluster, Water Cluster Ion, Cluster Size.

1. Introduction

The presence of ions enhances the nucleation rate of aerosol particles in a supersaturated vapor1). Detailed knowledge of ion-induced nucleation is needed to understand processes such as the ion chemistry of the stratosphere and the troposphere2), the formation of acid rain, and the ion-induced formation of environmental pollutants3).

Seto et al.4) experimentally investigated the dependence of the cluster growth rate on the cluster-ion size in the condensation of dibutyl phthalate (DBP) vapor. They found that the effect of the cluster charge on the enhancement of the vapor condensation rate increased with decreasing cluster-ion size. To date, however, no general nucleation theory exists that can predict the cluster-size dependence of vapor condensation rates enhanced by the charge of arbitrary types of cluster ions. Such a theory is needed to clarify the role of charge-enhancement of particle nucleation rates.

The rate of vapor condensation on clusters is given by the product of the sticking probability and the collision rate between the cluster and the condensing molecule. The collision rate is calculated as the product of the collision cross section, the relative velocity between the cluster and the condensing molecule, and the concentration of the condensing molecules. The relative velocity is obtained from the translational temperature of the cluster and molecule. The collision cross section can be calculated by the model5) based on the Langevin theory and molecule-cluster interaction potentials. The sticking probability of the molecule to the cluster can be estimated using the model6) built by the RRK theory and the general equation describing the V→T relaxation rates of diatomic molecules. In the present paper, the calculation of the rate of water vapor condensation on a water cluster ion by using the above-mentioned models quantifies the effect of the cluster charge on the enhancement of the vapor condensation rate as a function of cluster size. This calculation reveals the quantitative reason for the enhancement of the nucleation rate from the viewpoint of the dynamics of cluster growth.

2. Vapor Condensation Rate on Clusters

In the early stages of cluster formation, the
attachment of a monomer, A1, produces, at an incorporation rate constant \( k_l \) as expressed by Eq. (1), unstable clusters, \( A_n^* \), which possess sufficient energy for dissociation. The dissociation of a monomer A1 from the vibrationally excited cluster \( A_n^* \) generates a stable cluster, \( A_{n-1} \), at a dissociation rate constant \( k_d \) in Eq. (2). In parallel with this dissociation path, deactivating collisions of the vibrationally excited cluster with inert gas molecules, M, results in the formation of a stable cluster, \( A_n \), at a stabilization rate constant \( k_s \), as given by Eq. (3).

\[
\begin{align*}
A_{n-1} + A_1 & \rightarrow A_n^* \quad (1) \\
A_n^* & \rightarrow A_{n-1} + A_1 \quad (2) \\
A_n^* + M & \rightarrow A_n \quad (n = 2, 3, 4, \ldots) \quad (3)
\end{align*}
\]

The vapor condensation rate, \( r_c \), in the cluster formation stage corresponds to the production rate of \( A_n \). When the sticking probability, \( P_s \), is defined as the ratio of the production rate of \( A_n \) in Eq. (3) to the collision rate between \( A_{n-1} \) and A1 on the left-hand side of Eq. (1), \( r_c \) is given by the product of \( P_s \) and the collision rate between \( A_{n-1} \) and A1 as follows,

\[
r_c = P_s \sigma_{coll} v_t c_m \quad (4)
\]

where \( \sigma_{coll} \) is the collision cross section between \( A_{n-1} \) and A1, \( v_t \) is the relative velocity between \( A_{n-1} \) and A1, \( c_m \) is the molecular concentration of A1, and \( \sigma_{coll} \) gives the collision rate between \( A_{n-1} \) and A1.

3. Collision Cross Section between a Water Molecule and a Water Cluster

The collision cross sections between a water cluster ion \( \text{H}^+(\text{H}_2\text{O})_n \) at the cluster size \( n \) and a water molecule, \( \sigma_{coll,i} \), and between a neutral water cluster \( (\text{H}_2\text{O})_n \) and a water molecule, \( \sigma_{coll,h} \), can be calculated by the method, proposed in reference 5), based on the Langevin theory. For this calculation, we used, as the parameters for the water-water cluster interaction potential, the polarizability of 1.47 \times 10^{-30} \text{ m}^3, the dipole moment of 1.94 Debye, the molecular density in the cluster of 3.34 \times 10^{28} \text{ molecules / m}^3, the molecular radius of 9.58 \times 10^{-11} \text{ m} for \( \text{H}_2\text{O} \), and the van der Waals interaction constant \( C = 4\epsilon\sigma^6 \), where \( \epsilon \) is the depth of the Lennard-Jones potential well between two water molecules (\( \epsilon = 5.25 \times 10^{-21} \text{ J} \)) and \( \sigma \) is the intermolecule distance at which the potential energy is equal to zero (\( \sigma = 2.65 \times 10^{-10} \text{ m} \)).

Fig. 1 shows \( \sigma_{coll,i} \) and \( \sigma_{coll,h} \) as a function of cluster size \( n \) at 273 K. \( \sigma_{coll,i} \) was larger than \( \sigma_{coll,h} \). The ratio of \( \sigma_{coll,i} \) to \( \sigma_{coll,h} \) was as large as 2.0 at \( n = 1 \), decreased with increasing \( n \), and was about 1.1 at \( n = 100 \), as shown in Fig. 2. The reason for the enhancement of the collision cross section in the case of \( \text{H}^+(\text{H}_2\text{O})_n \) was found to be that the attractive force between \( \text{H}_2\text{O} \) and the water cluster was stronger because of the electrostatic attractive force due to charge-dipole and charge-induced dipole interactions. This charge effect weakens with increasing the cluster radii and induces the decrease in the ratio of \( \sigma_{coll,i} \) to \( \sigma_{coll,h} \) with the cluster size as shown in this figure.

4. Sticking Probability of a Water Molecule to a Water Cluster

According to the pseudo-steady state assumption regarding the concentration of \( A_n^* \), \( P_s \) is given by the following equation with the dissociation rate constant \( k_d \) and stabilization rate constant \( k_s \),

\[
\frac{\text{Fig. 1}}{\text{Collision cross sections between a water cluster ion H}^+(\text{H}_2\text{O})_n \text{ and a water molecule, } \sigma_{coll,i} \text{, and between a neutral water cluster (H}_2\text{O})_n \text{ and a water molecule, } \sigma_{coll,h} \text{, as functions of cluster size } n \text{ at 273 K.}}}
\]

\[
\text{Fig. 2} \quad \text{Ratio of } \sigma_{coll,i} \text{ to } \sigma_{coll,h} \text{ as a function of cluster size } n.
\]
$P_s = |k_d/(k_d + k_s)| P_i$ \hspace{1cm} (5)

where $P_i$ is the incorporation probability defined as the ratio of the production rate of $A_n^+$ to the collision rate between $A_{n-1}$ and $A_1$. From Eq. (5), it was found that $P_s$ is nearly equal to $P_i$ for $k_s \gg k_d$ and to zero for $k_d \gg k_s$. In reference 10), the incorporation probability of a water molecule into a water cluster was found to be equal to unity below about 1,000 K for cluster sizes ranging from 2 to 104. Therefore, $P_s$ can be obtained by the estimation of $k_d$ and $k_s$.

The values of $k_d$ and $k_s$ for formation of water cluster ion $H^+(H_2O)_n$ or neutral water cluster $(H_2O)_n$ can be calculated by the methods, proposed in reference 6), based on the RRK theory and the $V \rightarrow T$ relaxation rate equation, respectively. For the calculation of $k_d$ for $H^+(H_2O)_n$, as the vibrational frequency of the bond which is lost in the cluster we used $v = 2.68 \times 10^{12} \text{ s}^{-1}$ obtained from the Stockmayer potential of $H_2O-H_2O$. As the dissociation energy, $V_n$, of vibrationally excited water cluster ions $H^+(H_2O)_n$, $V_2 = 1.96 \times 10^{-19} \text{ J}$, $V_3 = 1.63 \times 10^{-19} \text{ J}$, $V_4 = 1.40 \times 10^{-20} \text{ J}$, $V_5 = 9.76 \times 10^{-20} \text{ J}$, $V_6 = 9.37 \times 10^{-20} \text{ J}$, $V_7 = 9.90 \times 10^{-20} \text{ J}$, $V_8 = 9.96 \times 10^{-20} \text{ J}$, $V_9 = 9.36 \times 10^{-20} \text{ J}$, $V_{10} = 8.81 \times 10^{-20} \text{ J}$, and $V_{11} = 9.17 \times 10^{-20} \text{ J}$ were used from the data\(^{11}\) obtained as the values for the global minima of protonated water clusters using the anisotropic site potential model in good agreement with experimental results\(^{12}\) measured for some cluster sizes at relatively low temperature. Since the values of $V_n(n \geq 12)$ have not been previously reported, we used those obtained by fitting an approximate function of cluster size with the above-mentioned values of $V_i$ through $V_{11}$ and the value of $6.41 \times 10^{-20} \text{ J}$ obtained as the saturated value for neutral water cluster $(H_2O)_n$ at $n > 7$ from the viewpoint that $V_n$ for the water cluster ion should asymptotically approach the same value as that for the neutral water cluster at large $n$. For the calculation of $k_s$ for $(H_2O)_n$, we used $v = 2.68 \times 10^{12} \text{ s}^{-1}$ and, as the dissociation energy of vibrationally excited water cluster $(H_2O)_n^+$, $V_2 = 4.23 \times 10^{-20} \text{ J}$, $V_3 = 9.24 \times 10^{-20} \text{ J}$, $V_4 = 9.74 \times 10^{-20} \text{ J}$, $V_5 = 7.03 \times 10^{-20} \text{ J}$, $V_6 = 6.90 \times 10^{-20} \text{ J}$, and $V_n = 6.41 \times 10^{-20} \text{ J}(n \geq 7)$ obtained\(^{13}\) by using the $ab$ initio molecular orbital (MO) method, where the geometry optimization of the cluster was performed using the B3LYP calculations with Dunning’s correlation consistent sets of the polarization plus valence triple-$\xi$ class (cc-pVTZ).

Fig. 3 shows the dissociation rate constants for water cluster ions, $k_{d,i}$, and for neutral water clusters, $k_{d,h}$, as a function of cluster size $n$ at 273 K. In the small cluster-size region, $k_{d,i}$ was smaller than $k_{d,h}$. Especially at $n$ around 10, there appeared a large difference and the ratio of $k_{d,i}$ to $k_{d,h}$ was about 1/1000. From reference 6), we understand that $k_d$ is given as a function of the dissociation energy $V_n$ and the vibrational freedom of water clusters. In the small cluster-size region, the difference of $V_n$ between $(H_2O)_n$ and $H^+(H_2O)_n$ is large, but this large difference does not generate a large difference of $k_d$, as shown at $n$ smaller than approximately 4 in Fig. 3, because of the small values of the vibrational freedom for such small sized water clusters. As for $n$ around 10, the difference of $V_n$ between $(H_2O)_n$ and $H^+(H_2O)_n$ generates a large difference of $k_d$ as shown in Fig. 3. At the larger $n$, the small difference of $V_n$ between $(H_2O)_n$ and $H^+(H_2O)_n$ causes a small difference of $k_d$ as shown in Fig. 3. The reason for the large difference of $k_d$ at $n$ around 10 was found to be that the water cluster ions $H^+(H_2O)_n$ have larger dissociation energies than the neutral water clusters $(H_2O)_n$ and consequently they are not as easily dissociated as $(H_2O)_n$.

![Fig. 3 Dissociation rate constants for water cluster ions, $k_{d,i}$, and for neutral water clusters, $k_{d,h}$, as a function of cluster size $n$ at 273 K.](image-url)
Fig. 5 shows the sticking probabilities for water cluster ions, $P_{s,i}$, and for neutral water clusters, $P_{s,h}$, surrounded by N$_2$ at 1.01 × 10$^5$ Pa as a function of cluster size $n$ at 273 K. Both $P_{s,i}$ and $P_{s,h}$ dramatically increased from zero to levels close to unity in cluster-size regions of 3 through approximately 20. $P_{s,i}$ was larger than $P_{s,h}$. The ratio of $P_{s,i}$ to $P_{s,h}$ was as large as approximately 1 at $n$ = 3, increased with increasing $n$, and was approximately unity at $n$ > 20, as shown in Fig. 6. We understand that the enhancement of the sticking probability for water cluster ions compared with neutral clusters is caused by the values of $k_{d,i}$ smaller than those of $k_{d,h}$ as shown in Fig. 3.

5. Enhancement of the Rate of Water Vapor Condensation

When the enhancement factor, $F_e$, for rates of water vapor condensation on water clusters is defined as the ratio of the vapor condensation rate for water cluster ions, $r_{v,c,i}$, to that for neutral water clusters, $r_{v,c,h}$, $F_e$ is given as the ratio of the product $P_{s,i}\sigma_{coll,i}$ to $P_{s,h}\sigma_{coll,h}$ from the definition of the vapor condensation rate given by Eq. (4). Fig. 7 shows $F_e$ as a function of cluster size $n$ at 273 K. $F_e$ was as large as approximately 6 at $n$ = 3, decreased with increasing $n$, and was about 1.1 at $n$ > 20. The reason for the large $F_e$ values in the small cluster-size region was found to be large values of both $\sigma_{coll,i}/\sigma_{coll,h}$ and $P_{s,i}/P_{s,h}$ in this size region as shown in Figs. 2 and 6, respectively. Since the value of $P_{s,i}/P_{s,h}$ at $n$ = 3 is larger than that of $\sigma_{coll,i}/\sigma_{coll,h}$ at $n$ = 3, it was found that the large value of $F_e$ at $n$ = 3 was caused mainly by the large value of $P_{s,i}/P_{s,h}$.

6. Conclusions

In this paper, the calculation of the rate of water vapor condensation on a water cluster ion by using the described models quantified the effect of the cluster charge on the enhancement of the vapor condensation rate.
condensation rate as a function of cluster size. The rate of water vapor condensation on a water cluster ion was found to be enhanced, depending on the cluster size, compared with that on a neutral water cluster. The enhancement factor was large in the small cluster-size region, as large as approximately 6 at the cluster size of 3, and decreased with increasing the cluster size. We found that this enhancement effect was caused by the increases in the two variables, \( \sigma_{\text{coll}} \) and \( P_{s} \). In the case of water cluster ions, the attractive force between \( \text{H}_{2}\text{O} \) and the water cluster is stronger because of the electrostatic attractive force and consequently the collision cross section \( \sigma_{\text{coll}} \) increases. As a result a larger number of water molecules collide with water clusters and stick to the clusters. In addition, the water molecules which have stuck to positively charged water cluster ions are not as easily dissociated as the water molecules which have stuck to neutral water clusters, because of the larger dissociation energies of \( \text{H}_{2}\text{O} \) from water cluster ions.

As a result of this increase in sticking probability \( P_{s} \), the growth of water clusters is enhanced.

**Nomenclature**

\[ v_{m} : \text{monomer concentration} \quad (\text{m}^{-3}) \]
\[ F_{e} : \text{enhancement factor for rates of water vapor condensation} \quad \text{on water cluster} \quad (-) \]
\[ k_{d} : \text{dissociation rate constant} \quad (\text{s}^{-1}) \]
\[ k_{i} : \text{incorporation rate constant} \quad (\text{m}^{3}\text{s}^{-1}) \]
\[ k_{a} : \text{stabilization rate constant} \quad (\text{s}^{-1}) \]
\[ n : \text{cluster size} \quad (-) \]
\[ p_{i} : \text{incorporation probability} \quad (-) \]
\[ p_{s} : \text{sticking probability} \quad (-) \]
\[ r_{v} : \text{vapor condensation rate} \quad (\text{s}^{-1}) \]
\[ V_{n} : \text{dissociation energy of vibrationally excited water cluster} \quad \text{of cluster size } n \quad (\text{J}) \]
\[ v_{r} : \text{relative velocity between cluster and monomer} \quad (\text{ms}^{-1}) \]

**Greek Symbols**

\[ \nu : \text{vibrational frequency of the bond which is lost in the vibrationally excited cluster} \quad (\text{s}^{-1}) \]
\[ \sigma_{\text{coll}} : \text{collision cross section between cluster and monomer} \quad (\text{m}^{2}) \]

**References**


13) Nakai, H. and Ichikawa, T.: private communication