Calculation of the Sticking Probability of a Water Molecule to a Water Cluster†

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Abstract — The sticking probabilities of a water molecule to a water cluster at several temperatures are calculated as a function of cluster size by using the models proposed for dissociation and stabilization rate constants of vibrationally excited clusters. The model for dissociation is built from RRK theory, while the model for stabilization is based on the general equation describing $V \rightarrow T$ relaxation rates of diatomic molecules. The sticking probabilities calculated are strongly dependent on the size of the water clusters. They increase from zero to levels close to unity in the cluster-size region of 3 through approximately 20 and keep constant at levels close to unity at a cluster size larger than 20 at 253, 273, and 300 K.

Key Words : Sticking Probability, Water Cluster, Cluster Size.

1. Introduction

Water clusters have been studied extensively in an attempt to understand the nature of hydrogen-bonded systems and the chemistry of aqueous solutions1). Atmospheric chemistry is one of the most interesting fields of application, as water clusters play important roles in various serious atmospheric issues2, 3), including ozone depletion4).

The nucleation dynamics of water clusters depend on the rate of water molecule condensation on a water cluster. The rate is given by the product of the sticking probability, the collision cross section, the relative velocity between the cluster and the condensing water molecule, and the concentration of the condensing water molecules. The relative velocity is calculated 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. To date, however, no general theory exists that can predict the sticking probability depending on the cluster size.

This paper describes a new model for calculating the sticking probability of a water molecule to a water cluster in cluster formation. This model can be used to quantify the dependence of the sticking probability on the cluster size and temperature. The model is therefore applicable to general nucleation theory for evaluation of vapor condensation rates.

2. Dynamics of Cluster Growth

In the early stages of cluster formation, the monomer, $A_1$, attachment produces, at an incorporation rate constant $k_i$, unstable clusters which possess sufficient energy for dissociation as expressed by Eq. (1). The dissociation of a monomer $A_1$ 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 atoms, M, results in the formation of a stable cluster, A<sub>n</sub>, at a stabilization rate constant k<sub>s</sub>, as given by Eq. (3)<sup>6,7</sup>.

\[ k_f \]

\[ A_{n-1} + A_1 \rightarrow A_n^* \]  

(1)

\[ k_d \]

\[ A_n^* \rightarrow A_{n-1} + A_1 \]  

(2)

\[ k_s \]

\[ A_n^* + M \rightarrow A_n \ \ (n = 2, 3, 4 \ldots) \]  

(3)

The sticking probability \( P_s \) is defined as the ratio of the production rate of A<sub>n</sub> as expressed by Eq. (3) to the collision rate between A<sub>n-1</sub> and A<sub>1</sub> as expressed by the lefthand side of Eq. (1). According to the pseudo steady state assumption for the concentration of A<sub>n</sub>, \( P_s \) is given by

\[ P_s = |k_s / (k_d + k_s)| P_i, \]  

(4)

where \( P_i \) is the incorporation probability defined as the ratio of the production rate of A<sub>n</sub> to the collision rate between A<sub>n-1</sub> and A<sub>1</sub>. From Eq. (4), 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<sup>8</sup>, the incorporation probability of a water molecule into a water cluster was found to be equal to unity below approximately 1,000 K for the investigated cluster sizes, ranging from 2 to 10<sup>4</sup>.

3. Rate Constant for Dissociation \( k_d \) of Vibrationally Excited Clusters

The value of \( k_d \) is estimated using the difference between the vibrational energy of A<sub>n</sub>* and the dissociation threshold of the cluster based on the Rice-Ramsperger-Kassel (RRK) theory,

\[ k_d = v |(E_n - V_n) / E_n| \cdot L_n \]  

(5)

where \( v \) is the vibrational frequency of the bond that is lost in cluster A<sub>n</sub>*, \( E_n \) is the vibrational energy of A<sub>n</sub>*, \( V_n \) is the dissociation energy, and \( L_n \) is the number of degrees of vibrational freedom \( (= 3n-6 \) in water, where \( n \) is the cluster size). The vibrational energy of A<sub>n</sub>* includes the vibrational energy of A<sub>n-1</sub> before the incorporation of monomer A<sub>1</sub>, the bonding energy between A<sub>n-1</sub> and A<sub>1</sub> which is equal to \( V_n \), and the relative translational energy (collision energy) between A<sub>n-1</sub> and A<sub>1</sub>. The value of \( E_n \) is given by

\[ E_n = E_{n-1}' + V_n + E_c \]  

(6)

where \( E_{n-1}' \) is the vibrational energy of A<sub>n-1</sub> before the incorporation of monomer A<sub>1</sub> and \( E_c \) is the collision energy between A<sub>n-1</sub> and A<sub>1</sub>.

When we assume that the vibrational energy in the cluster is distributed only to intermolecular vibrations and no energy to intramolecular vibrations, and all the intermolecular vibration modes have the same vibrational frequency, then the vibrational energy of cluster A<sub>n-1</sub> is given by

\[ E_{n-1}' = h \nu \frac{3(n-1)-6}{|\exp(h \nu / k_B T)-1|} \]  

(7)

where \( h \) is Planck’s constant, \( \nu \) is the vibrational frequency for all intermolecular vibration modes in the cluster, \( k_B \) is the Boltzman constant, and \( T \) is the atmospheric temperature at which the monomers, stable clusters, and surrounding inert gas are present. The assumption, used for Eq. (7), that all of the vibrational energy concentrates on the intermolecular vibrations is not always applicable to general clusters. However, in the case of hydrogen bond clusters, as studied here, this assumption is realistic because the vibrational frequencies, indicating the vibrational energy levels, of the intermolecular vibration modes are much lower than those of intramolecular vibration modes and the vibrational energy is distributed to the intermolecular vibrations prior to the intramolecular vibrations. In using the Maxwell distribution law for the velocities of A<sub>1</sub> and A<sub>n-1</sub>, the kinetic energy of the relative motion between A<sub>1</sub> and A<sub>n-1</sub> gives the value of \( E_c \) as

\[ E_c = \frac{3}{2} \frac{8}{\pi} \frac{\sqrt{n-1}}{n} k_B T \]  

(8)

In this work, we used \( \nu = 2.68 \times 10^{12} s^{-1} \) obtained from the Stockmayer potential of H<sub>2</sub>O-H<sub>2</sub>O<sup>9</sup> independent of the water cluster size, since it is known that the vibrational frequencies for the intermolecular vibration modes in the soft clusters having weak intermolecular bonds as studied here do not strongly depend on the cluster size and cluster structure. We used \( V_2 = 4.23 \times 10^{-20} \) J, \( V_3 = 9.24 \times 10^{-20} \) J, \( V_4 = 9.74 \times 10^{-20} \) J, \( V_5 = 7.03 \times 10^{-20} \) J, \( V_6 = 6.90 \times 10^{-20} \) J, \( V_7 = 6.41 \times 10^{-20} \) J (i: \( \geq 7 \)) for the most stable structure of (H<sub>2</sub>O)<sub>n</sub> clusters obtained<sup>10</sup> by using the ab initio molecular orbital (MO) method, where the geometry optimization of the cluster was done by the B3LYP calculations with Dunning’s correlation consistent sets of the polarization plus valence triple-\( \xi \)-class (cc-pVTZ).

Fig. 1 shows the cluster-size dependence of the dissociation rate constant \( k_d \) of the vibrationally excited cluster (H<sub>2</sub>O)<sub>n</sub>* at 273 K. The dissociation
rate constant was strongly dependent on the cluster size. It dramatically decreased with increases in the cluster size. This decrease was found to be due to the index $L_n$ of Eq. (5) linearly increasing with the cluster size.

4. Rate Constant for Stabilization $k_s$ of Vibrationally Excited Clusters

Let us assume that the collisions of $A_n^*$ with inert gas molecules result in the deactivation of a part of $A_n^*$ due to the $V \to T$ relaxation. This part corresponds to the two molecules constituting $A_n^*$ close to the collision point, as shown in Fig. 2. The collision with inert gas molecules, first, induces the deactivation, due to the $V \to T$ relaxation, of the intermolecular bond between two molecules placed in the collision part. Subsequently, it induces the intermolecular-vibrational relaxation, which decreases the vibrational energy of the whole cluster. It is reasonable to believe that this assumption is realistic because of the following reasons. The vibrational energy in the water clusters is mainly distributed to the intermolecular vibrations as described above. The relaxation induced by the collisions, therefore, results in the deactivation of the intermolecular bonds mainly and almost no deactivation of the intramolecular bonds. This deactivation of the intermolecular bond is, then, restricted to one intermolecular bond between two molecules placed in the collision part, because all the intermolecular bonds are weak and the energy exchange between the cluster and inert gas molecule tends to occur in the local part of the cluster close to the collision point.

For estimation of $k_s$, the deactivation rate of the collision part of $A_n^*$ caused by the collisions with inert gas molecules is calculated using the following general equation describing the $V \to T$ relaxation rates of diatomic molecules.

$$p_T = \exp \left( \frac{(1.16 \times 10^{-3} \mu^{1/2} \theta^{1/2})}{T - \mu - 0.015 \mu^{1/4}} - 18.42 \right)$$

where $p$ is the inert gas pressure, $\tau$ is the vibrational relaxation time, $\mu$ is the reduced mass of the relaxed diatomic molecule and inert gas molecule, and $\theta$ is the characteristic temperature of the oscillator given as $\hbar^2 / k_B$. Suppose that a hypothetical situation is present in which one isolated intermolecular-bond between two molecules, corresponding to a water dimer, collides with inert gas molecules, $N_2$ in this case, at 1 atm many times. The vibrational relaxation time of this intermolecular bond can be calculated using Eq. (9). Then the value of the relaxation time gives the decreasing rate, $r_d$, of the vibrational energy of that intermolecular bond induced by an individual collision with $N_2$ from the frequency of collision between that intermolecular bond and $N_2$.

The decrease in the energy of the collision part of $A_n^*$ induced by the individual collision, $\Delta E_1$, is calculated from the vibrational energy of the intermolecular bond placed in the collision part, $E_d$, and the abovementioned value of $r_d$ at given temperature as

$$\Delta E_1 = r_d E_d.$$  \hspace{1cm} (10)

The intermolecular-vibrational relaxation subsequently induces the thermal equilibrium in the whole cluster. It achieves the decrease in the energy of the cluster, $\Delta E$, at the individual collision. The value of $\Delta E$ is then given by

$$\Delta E = \frac{\Delta E_1}{L_n}.$$  \hspace{1cm} (11)

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**Fig. 1** Dissociation and stabilization rate constants as functions of the cluster size of a vibrationally excited water cluster $\langle \text{H}_2\text{O} \rangle_n^*$ at 273 K.

**Fig. 2** Schematic of deactivation of a part of the vibrationally excited cluster due to the collision with surrounding cold molecule $N_2$ in the case of $\langle \text{H}_2\text{O} \rangle_3$ as an example.
The curve of the decreasing vibrational energy of the excited cluster after the collisions with N₂ as a function of time is then obtained from the values of $\Delta E$ and frequency of collision between the whole cluster and N₂, which is dependent on the cluster size and the cluster diameter. Thus the value of $k_s$ can be obtained from this curve at the given cluster size.

We used $\mu = 15.75$ given from the molecular weights of the H₂O dimer and N₂. The values of $k_s$ were estimated using the curves of the decreasing vibrational energy for various sizes of excited water clusters surrounded by N₂ at 1.01 × 10⁵ Pa.

Fig. 1 also shows the cluster-size dependence of the stabilization rate constant $k_s$ of vibrationally excited cluster (H₂O)$_n$ at 273 K surrounded by N₂ at 1.01 × 10⁵ Pa. The stabilization rate constant decreased with increases in the cluster size because of $L_n$ increasing, $\Delta E_1$ being almost size-independent, and consequently $\Delta E$ given as $\Delta E_1 / L_n$ decreasing. The decreasing rate of $k_s$ was smaller than that of $k_d$ with the cluster size. We found from Fig. 1 that the cluster-size dependences of $k_s$ and $k_d$ cross at cluster sizes of approximately 6, and that $k_d$ is larger than $k_s$ in the smaller size region and $k_s$ is larger than $k_d$ in the larger size region.

5. Sticking Probability in Cluster Formation

Fig. 3 shows the cluster-size dependences of the sticking probability $P_s$ calculated using Eq. (4) at 253, 273, and 300 K. The values of $P_s$ dramatically increased from zero to levels close to unity in cluster-size regions of 3 through approximately 20. At the lower temperature, $P_s$ was larger and approached unity at the smaller cluster sizes. As shown in Fig. 1, $k_s$ was much larger than $k_d$ at cluster sizes as large as 20. The tendency $k_s \gg k_d$ indicates that the stabilization (Eq. (3)) is dominant, and consequently most of A$_n^*$ are stabilized to form stable clusters A$_n$ without dissociation (Eq. (2)) after the incorporation of a monomer (Eq. (1)). We found that the tendency $k_s \gg k_d$ results in $P_s$ being close to unity at cluster sizes larger than 20, as shown in Fig. 3. In contrast, $P_s$ approaches zero with decreasing cluster size, as shown in Fig. 3, due to the tendency $k_d \gg k_s$, as shown in Fig. 1.

6. Conclusions

The technique for calculation of the sticking probability of a water molecule to a water cluster is proposed in this work on the basis of the models for the dissociation and stabilization rate constants of vibrationally excited water clusters. This technique and these models are in general applicable for van der Waals clusters and hydrogen bond clusters.

The dissociation and stabilization rate constants of vibrationally excited water clusters formed by the incorporation of water molecules into stable water clusters were found to be dependent on the water cluster size at 253, 273, and 300 K. At cluster sizes as small as approximately 3, since $k_d$ was much larger than $k_s$, the sticking probability, which is a function of $k_s / k_d$, was close to zero. In contrast, at large cluster sizes above 20, since $k_s$ was much larger than $k_d$, the sticking probability was close to unity.

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_n$</td>
<td>collision energy between A$_n$ and A$_1$ (J)</td>
</tr>
<tr>
<td>$E_n^*$</td>
<td>vibrational energy of vibrationally excited cluster A$_n^*$ (J)</td>
</tr>
<tr>
<td>$E_n-1^*$</td>
<td>vibrational energy of A$_{n-1}$ before the incorporation of monomer A$_1$ (J)</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant (J s)</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant (J K$^{-1}$)</td>
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<tr>
<td>$k_d$</td>
<td>dissociation rate constant (s$^{-1}$)</td>
</tr>
<tr>
<td>$k_i$</td>
<td>incorporation rate constant (cm$^3$ s$^{-1}$)</td>
</tr>
<tr>
<td>$k_s$</td>
<td>stabilization rate constant (s$^{-1}$)</td>
</tr>
<tr>
<td>$L_n$</td>
<td>number of degrees of vibrational freedom of A$_n^*$ (-)</td>
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<tr>
<td>$n$</td>
<td>cluster size (-)</td>
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<tr>
<td>$p$</td>
<td>inert gas pressure (atm)</td>
</tr>
<tr>
<td>$P_s$</td>
<td>incorporation probability (-)</td>
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<tr>
<td>$P_i$</td>
<td>sticking probability (-)</td>
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<td>$T$</td>
<td>atmospheric temperature at which the monomers, stable clusters and surrounding inert gas are present (K)</td>
</tr>
<tr>
<td>$V_n^*$</td>
<td>dissociation energy of A$_n^*$ (J)</td>
</tr>
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</table>
Greek Symbols

$\Delta E$: decrease in the energy of the cluster $A_n^*$ induced by the individual collision (J)

$\Delta E_1$: decrease in the energy of the collision part of $A_n^*$ induced by the individual collision (J)

$\theta$: characteristic temperature of the oscillator given as $\hbar \nu / k_B$ (K)

$\mu$: reduced mass of the relaxed diatomic molecule and inert gas molecule (kg)

$\nu$: vibrational frequency of the bond which is lost in the cluster $A_n^*$ (s$^{-1}$)

$\tau$: vibrational relaxation time (s)

References


