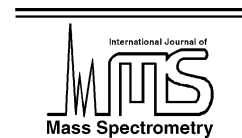




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Reactions of size-selected protonated water clusters $\text{H}^+(\text{H}_2\text{O})_n$ ($n = 2\text{--}6$) with an acetone molecule in a guided ion beam apparatus

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Abstract

The reactions of size-selected protonated water clusters, $\text{H}^+(\text{H}_2\text{O})_n$ ($n = 2\text{--}6$), with an acetone molecule were studied in a guided ion beam (GIB) apparatus. The collision energy dependence of the reaction cross-sections was investigated over the range of 0.05–2.0 eV in the center-of-mass frame. Water cluster beams with very narrow kinetic energy spreads, 0.02–0.04 eV, were generated to allow accurate measurement of the reaction cross-sections. We observed reaction products of incorporation and dissociation: the incorporation products are cluster ions having acetone whereas the dissociation products are protonated water clusters resulting from the evaporation of water molecule(s) from the parent cluster ions. Our results demonstrate that the incorporation process is dominant at low collision energies and that the proportion of the dissociation process increases as the collision energy increases. The incorporation cross-section at $n = 5$ is found to be the largest among the cluster sizes examined at the collision energy as low as 0.1 eV, which may be due to the water molecule in the second shell of the cluster. We also find that when the collision energy is larger than 0.5 eV, the dissociation cross-section has a maximum at $n = 5$, which is also probably due to the water molecule in the second shell of the cluster, and a minimum at $n = 3$, which may occur because the cluster ion core of the trimer, H_3O^+ , has one H-site that is not occupied by water molecules. (Int J Mass Spectrom 220 (2002) 375–383) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Protonated water clusters; Proton affinity; Acetone; Incorporation; Dissociation

1. Introduction

Water clusters have been studied extensively in an attempt to understand the nature of hydrogen-bonded systems and the chemistry of aqueous solutions [1]. Atmospheric chemistry is one of the most interesting applied fields, as water clusters play important roles in various serious atmospheric issues [2,3], including

ozone depletion [4]. The protonated water clusters $\text{H}^+(\text{H}_2\text{O})_n$ are considered to be the primary ions in the positive ion chemistry of the lower atmosphere, where n peaks around 4–6 [2]. These clusters react with many kinds of trace compounds that have a proton affinity higher than water, and these reactions may accelerate nucleation in the atmosphere [5]. Acetone, which plays an important role in atmospheric chemistry, is one of the significant trace compounds with a proton affinity greater than that

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of water. Acetone contributes to the formation of HO_x radicals and peroxyacetyl nitrate (PAN) [6,7]. It is interesting to study the reaction of protonated water cluster(s) and acetone to examine the behavior of acetone in detail. In previous studies of reactions of protonated water clusters and acetone, researchers have observed proton transfer, ligand exchange, and association [8–10]. Accurate reaction cross-sections at various collision energies that have not yet been measured may provide a deeper insight into the reaction mechanisms. The guided ion beam (GIB) method is appropriate to obtain accurate reaction cross-sections [11–13], because the reactions with walls are negligible, the ion collection efficiency is high and the reactions can be examined under single collision conditions.

In the present work, we studied the collision-induced reactions of protonated water cluster ions, $\text{H}^+(\text{H}_2\text{O})_n$ ($n = 2\text{--}6$), and acetone molecules at collision energies ranging from 0.05 to 2.0 eV with a narrow collision energy distribution of less than 0.05 eV by using a GIB apparatus. We observe a strong dependence of the incorporation cross-section on collision energy, especially at the low collision energies. We also describe the cluster size dependences of the reaction cross-sections.

2. Experimental setup

The experimental apparatus is schematically shown in Fig. 1. The apparatus is composed of a corona

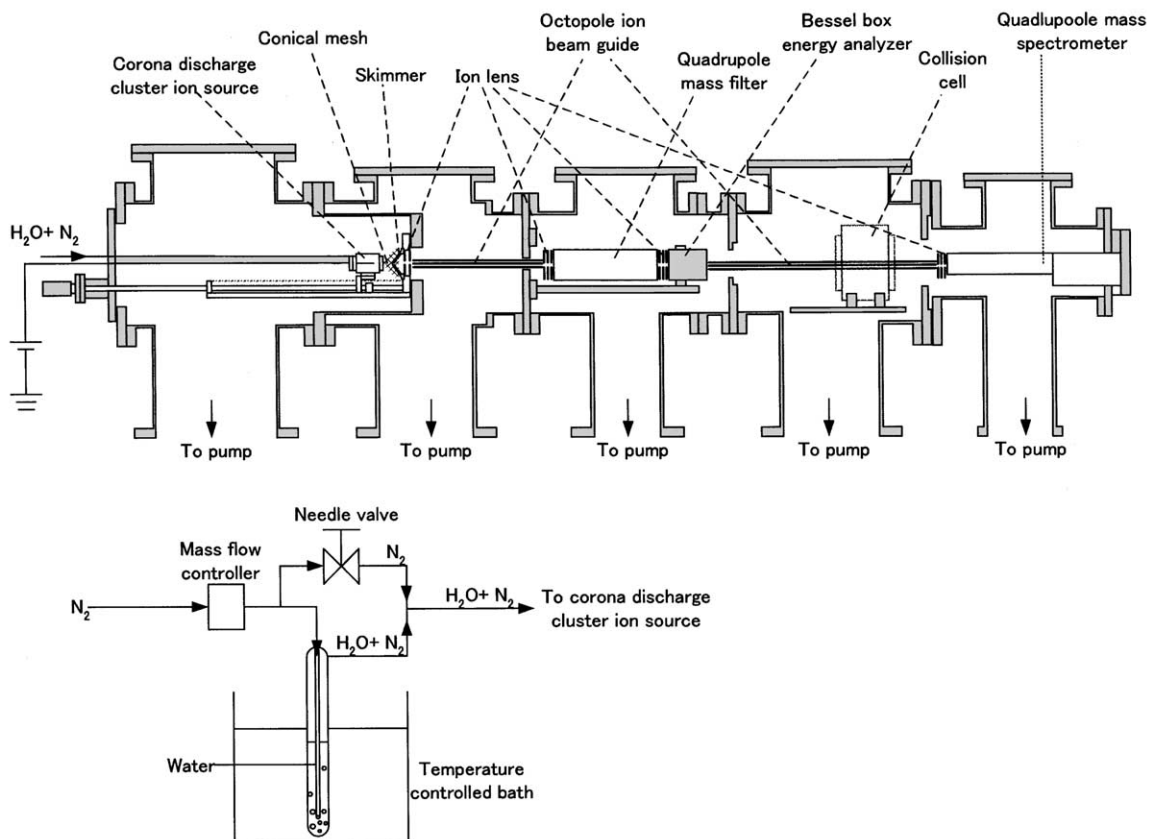


Fig. 1. Outline of the experimental apparatus.

discharge cluster ion source, two octopole ion beam guides, a quadrupole mass filter, a Bessel box energy analyzer, a collision cell, a quadrupole mass spectrometer, and a detector equipped with a secondary electron multiplier and an ion-conversion dynode. The details of the apparatus are described in a previous paper [14], except for a description of the water supply.

The protonated water cluster ions were formed in a supersonic expansion from the corona discharge cluster ion source through an aperture with a diameter of 100 μm . The water was supplied from a glass chamber in a bath maintained at 15 °C. Nitrogen was used as a carrier gas with a flow rate of 12–12.5 $\text{cm}^3 \text{min}^{-1}$. The partial pressure of water was controlled by changing the distribution of nitrogen flow through the water chamber. When the flow of nitrogen through the water chamber was increased, the partial pressure of water increased. The typical pressure in the discharge source was in the range of 4×10^4 to 5×10^4 Pa, and the discharge current was held constant at 3.0 μA . The generated cluster ions were guided into the mass filter for mass selection.

After optimization of the flow rate, the mixture ratio of nitrogen and water and the entire ion lens voltages, we made the kinetic energy distribution of the object water cluster narrower using the Bessel

box. The energy spreads of the cluster ions were set as low as 0.02–0.04 eV. Finally, we introduced acetone into the collision cell at the pressure of 6×10^4 to 7×10^{-4} Pa.

3. Data analysis

Fig. 2 shows typical mass spectra. Spectrum (a), the reference spectrum, was obtained without the target gas, and the mass spectrum (b), the collision spectrum, was obtained from the collision of $\text{H}^+(\text{H}_2\text{O})_4$ ($m/z = 73$) with CH_3COCH_3 at a collision energy of 0.1 eV in the center-of-mass frame. The suffix numbers indicate the number of water molecules contained in the cluster ions with the corresponding peaks. In the present case, one or two water molecules automatically evaporate from the parent clusters during the flight time from the mass filter to the detector, that is, unimolecular dissociation is taking place, as can be seen in Fig. 2a. Internal temperatures of the parent clusters estimated from the rates of unimolecular dissociations by using RRK model are 1.6, 1.2, 1.1, 0.93, and 0.98 eV at $n = 2, 3, 4, 5,$ and $6,$ respectively. As shown in Fig. 2b, there are many kinds of products resulting from the collision of $\text{H}^+(\text{H}_2\text{O})_n$ with an acetone molecule. These product cluster ions are formed in the following reactions:

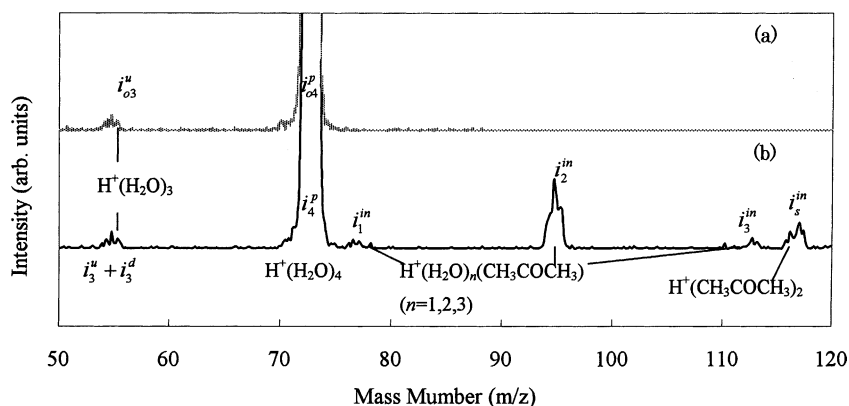
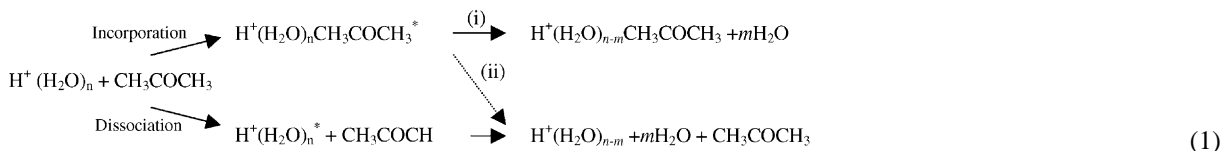


Fig. 2. Mass spectra at a collision energy of 0.1 eV. (a) Reference spectrum. (b) Collision spectrum of $\text{H}_2(\text{H}_2\text{O})_4 + \text{CH}_3\text{COCH}_3$.



where $\text{H}^+(\text{H}_2\text{O})_n\text{CH}_3\text{COCH}_3^*$ and $\text{H}^+(\text{H}_2\text{O})_n^*$ represent the intermediate vibrationally excited cluster ions. In the incorporation process, the parent cluster ion captures one acetone molecule and then subsequently releases one or more H_2O molecules. Thus, we classify all the products into the categories of incorporation and dissociation. Products of the secondary collision such as $\text{H}^+(\text{CH}_3\text{COCH}_3)_2$ were also observed at low collision energies (i_s^{in} in Fig. 2b), even though the pressure of acetone is low. This most likely indicates that the incorporation reaction is very fast. As a result, we classify the secondary products of $\text{H}^+(\text{H}_2\text{O})_{n-m}(\text{CH}_3\text{COCH}_3)_2$ as incorporation products.

The total reaction cross-section is given by:

$$\sigma_r = \frac{k_B T}{Pl} \ln \frac{I(0)}{I(l)} \quad (2)$$

where $I(0)$ and $I(l)$ are the intensities of the parent cluster ion at the entrance and at the exit of the collision cell, respectively; l is the effective path length of the collision cell; T and P are the temperature and the pressure of the target gas, respectively; and k_B is Boltzmann's constant. The incorporation cross-section σ_{in} and the dissociation cross-section σ_d are given by

$$\sigma_{\text{in}} = R_{\text{in}}\sigma_r \quad (3)$$

and

$$\sigma_d = R_d\sigma_r, \quad (4)$$

respectively, where R_{in} and R_d are the branching fractions. In general, the path (ii) must be taken into account, where the incorporated acetone is released, to obtain R_{in} . However, the dissociation cross-sections obtained without considering path (ii), which will be shown later, are very small at low collision energies. The fraction to path (ii) depends on the bond energies between acetone and the rest of the cluster, $[\text{CH}_3\text{CO}-\text{CH}_3]-[\text{H}^+(\text{H}_2\text{O})_n]$, and between water and the rest of

the cluster, $[\text{H}_2\text{O}]-[\text{H}^+(\text{H}_2\text{O})_{n-1}\text{CH}_3\text{COCH}_3]$. In the present case, the bond energy of acetone is larger than that of water [15]. The fraction to path (ii) estimated by RRK model is less than 5% when the internal energy of the intermediate is equal to that of the parent cluster plus the bond energy between acetone and the parent cluster. Even under an extreme condition that the internal energy of the intermediate is the sum of the initial internal energy of the parent cluster, the bond energy of acetone and the parent cluster, and the collision energy of 2.0 eV, the fraction to path (ii) is estimated less than 10%. These suggest that path (ii) may be negligible in the present case. The reduced intensity of dissociation products was obtained by subtracting the intensity corresponding to the daughter cluster ions produced by the unimolecular dissociation from the measured intensity of the dissociation products.

4. Results and discussion

4.1. Collision energy dependence

Fig. 3 shows the collision energy dependence of the reaction cross-sections in the collision of $\text{H}^+(\text{H}_2\text{O})_4$ with acetone. The error bars of x and y axes show the ion energy spread plus Doppler broadening and the probable error of the measured value average, respectively. The total reaction cross-section σ_r represented by open circles, decreases as the collision energy increases and then approaches a value of about 200 \AA^2 . Classical ion–molecule collision theories predict the enhancement of the collision cross-section by the electrostatic forces attributed to the polarizability and dipole moment at low collision energies [14,16]. When the collision cross-section is large, it is reasonable to assume that the reaction cross-section also becomes large, as in the present case.

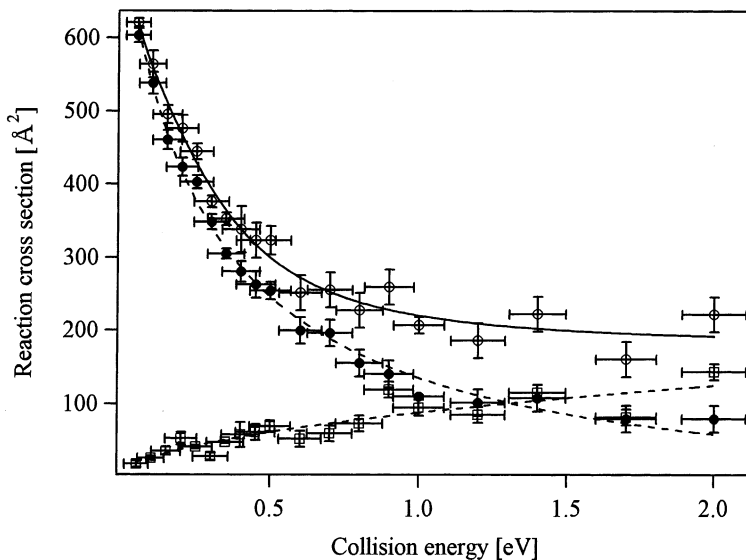


Fig. 3. Reaction cross-sections of $\text{H}^+(\text{H}_2\text{O})_4 + \text{CH}_3\text{COCH}_3$ as a function of collision energy in the center-of-mass frame. Open circles, solid circles, and open squares represent total cross-sections, incorporation cross-sections and dissociation cross-sections, respectively.

The collision energy dependence of the incorporation cross-section σ_{in} is similar to that of the total cross-section. The incorporation cross-section is nearly equal to the total cross-section at low collision energies and monotonically decreases as the collision energy increases. The incorporation cross-section at a

collision energy of 0.05 eV is about three times that of 2.0 eV. The incorporation cross-section is given by the product of incorporation branching fraction R_{in} and σ_r , as shown in Eq. (3). The collision energy dependence of the incorporation branching fractions R_{in} are shown in Fig. 4. The values of R_{in} are in the

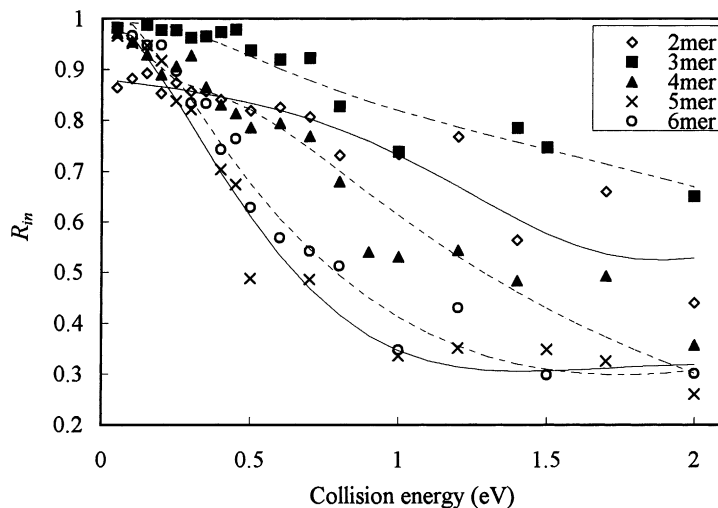


Fig. 4. The incorporation branching, R_{in} as a function of collision energy. Open diamonds, solid squares, solid triangles, crisscrosses, and open circles represent $n = 2, 3, 4, 5,$ and 6 , respectively.

range of 0.85–1 at 0.05 eV. The values of R_{in} monotonically decrease as the collision energy increases for all reactant cluster sizes examined. In our previous paper [14], we showed that small incident angle collisions (head-on-collisions) increase with decreasing collision energy in the low collision energy region. When orbiting occurs, the reaction probability between the cluster ion and incident molecule increases because of the long interaction time. In the case of head-on-collisions, the probability of incorporation of the acetone molecule by the cluster ion becomes high.

The reaction rate constants are given by the product of the incorporation cross-section multiplied by the relative velocity between the cluster and target molecule. The rate constants are estimated to be 2.5×10^{-9} , 3.2×10^{-9} , 3.3×10^{-9} , 3.4×10^{-9} , and $3.2 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$ at 500 K at $n = 2, 3, 4, 5,$ and 6 , respectively, and 1.9×10^{-9} , 2.4×10^{-9} , 2.6×10^{-9} , 2.6×10^{-9} , and $2.5 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$ at 300 K at $n = 2, 3, 4, 5,$ and 6 , respectively. These values are in agreement with the previously reported ones; 2.1×10^{-9} to $2.3 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$ ($n = 2-4$) at 300 K [8], 2.4×10^{-9} to $3.2 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$ at 300 K ($n = 2-4$) [9], and about 1.5×10^{-9} at 500 K ($n = 4$) [8]. At 300 K, the reaction rate constants for the incorporation of acetone are 1.1–2.3 times as large as those of water [17]. In addition, the reaction efficiencies relative to the calculated cross-section are about 70%, while it was about 44% in the case of water. Thus, acetone is one of the trace compounds that accelerate nucleation in the atmosphere.

The dissociation cross-section is, on the other hand, an increasing function of the collision energy in the case of the reaction of $\text{H}^+(\text{H}_2\text{O})_4$ with acetone, as shown in Fig. 3. The increasing trend of the dissociation cross-section with the collision energy was observed for the cases where $n = 3-6$. The reaction probabilities for dissociation in the collision of $\text{H}^+(\text{H}_2\text{O})_4$ with CH_3COCH_3 are nearly zero at ~ 0.05 eV collision energy, and gradually increase with collision energy. When $n = 2$, the dissociation cross-section appears to be almost independent of the collision energy under the experimental conditions employed here.

4.2. Size effects on the reaction cross-sections

The reaction cross-sections are plotted as functions of the parent cluster size, n , in Fig. 5. In Fig. 5a, the total reaction cross-sections are plotted together with the geometrical cross-sections taken as πr^2 , where r is estimated as the distance between the center of the mass of the reactant water cluster ion and the most distant H-atom under the most probable cluster structure [14] plus the distance between the center of the mass of acetone molecule and the hydrogen atom. Though water clusters are expected to have various isomers, the protonated water cluster is likely to have the core of $(\text{H}_5\text{O}_2)^+$ at $n = 2$ and 6 [14]. For $n = 3, 4,$ and 5 , the cluster ions are thought to have the core of $(\text{H}_3\text{O})^+$, and there would be a closed solvent shell structure at $n = 4$. In the case of $n = 5$, the fifth water molecule is probably located in the second solvent shell outside of the first closed shell. In the case of $n = 6$, the cluster ion may have another closed shell structure with the core of $(\text{H}_5\text{O}_2)^+$ surrounded by four water molecules. This closed shell structure may be the reason why the water cluster has a smaller total cross-sections at $n = 6$ than at $n = 5$. Calculated collision cross-sections by using density functional theory, B3LYP/cc-pVDZ, appears to support this discussion. The details of the calculations is described somewhere else [16].

In Fig. 5b, the incorporation cross-sections are plotted at collision energies of 0.1, 0.5, and 2.0 eV, respectively. As shown in this figure, the incorporation cross-section at the collision energy of 0.1 eV had a maximum at $n = 5$. The size dependence of the incorporation cross-section in the low collision energy region was similar to the size dependence of the geometrical collision cross-section. The branching fractions of incorporation, R_{in} at 0.1 eV, have values close to 1, as shown in Fig. 3. Therefore, the size effects on the total cross-section are reflected in the incorporation cross-section: the water molecule in the second shell of the water cluster at $n = 5$ may be the reason for the larger incorporation cross-section than that at $n = 6$. Due to the variation in the R_{in} at high collision energies, the size effects on the incorporation cross-section are not obvious at 0.5 and 2.0 eV.

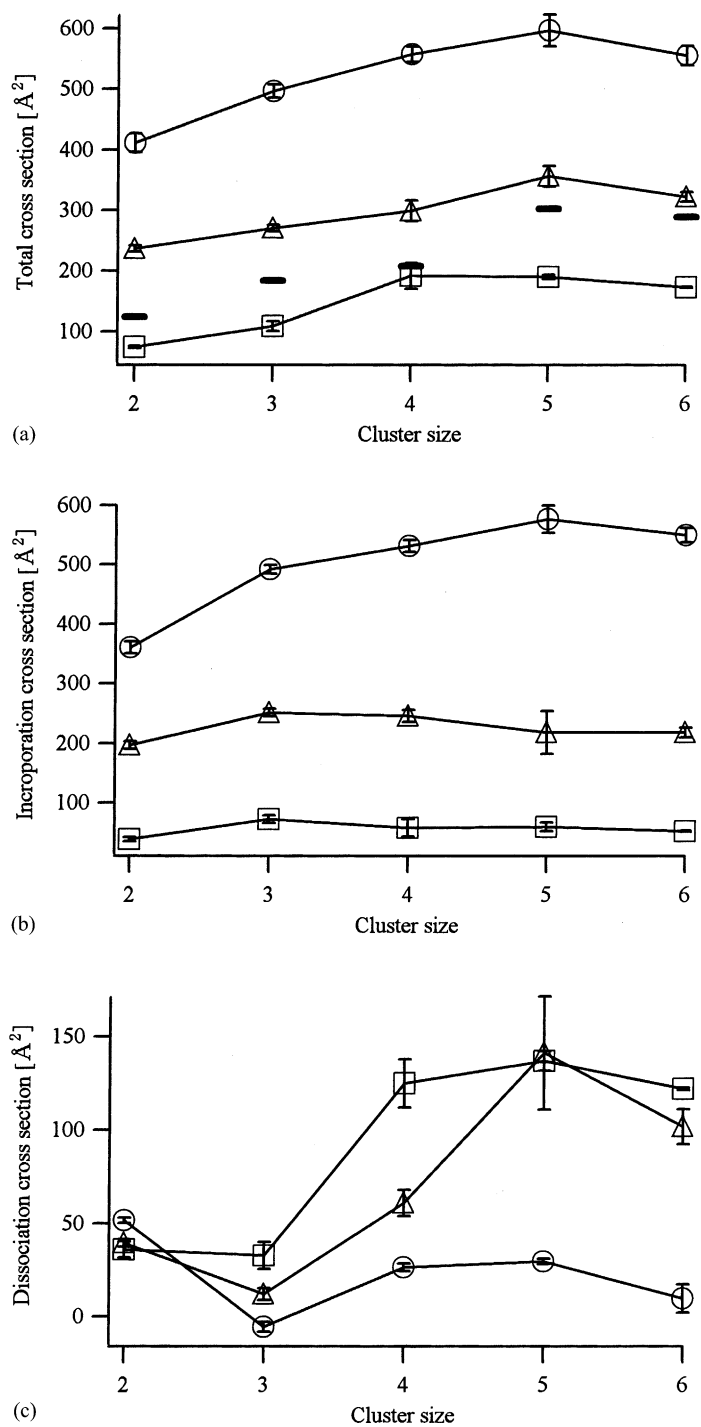


Fig. 5. The reaction cross-sections at a collision energy of 0.1, 0.5, and 2.0 eV, represented by circles, triangles, and squares, respectively. Total, incorporation, and dissociation cross-sections are shown in (a), (b), and (c), respectively.

In Fig. 5c, the dissociation cross-sections are plotted. It is noted that the dissociation cross-section at $n = 5$ are greater than that at $n = 6$. When the collision energy increases, the size effects are enhanced. It is very obvious at 0.5 eV that the dissociation cross-section has its maximum at $n = 5$. This is probably attributed to the water molecule present in the second shell of the water cluster at $n = 5$. A significant difference between the dissociation cross-section at $n = 3$ and 4 appears at the collision energy of 2.0 eV. When it is easy for acetone to directly stick to the proton, where the binding energy of the cluster and acetone is relatively strong, the probability of the incorporation may become high and the R_d may become small. In the case of a trimer, the core of the cluster ion (H_3O^+) does not have a closed shell around it. Therefore, the acetone molecule, by sticking to the ion core, can easily be incorporated rather than lead to the dissociation process. The small dissociation cross-section of the trimer may arise from the open site available at the ion core, H_3O^+ , allowing a bond between the core and the incident acetone molecule to be formed.

5. Conclusions

We have investigated the reactions of the size-selected protonated water $\text{H}^+(\text{H}_2\text{O})_n$ ($n = 2\text{--}6$) cluster ion with a CH_3COCH_3 molecule. The reaction cross-sections were measured at collision energies of 0.05–2.0 eV in the center-of-mass frame with narrow collision energy distributions in the range of 0.02–0.04 eV.

The incorporation cross-section had the largest value at the lowest collision energies. In the case of the collision of $\text{H}^+(\text{H}_2\text{O})_4$ with CH_3COCH_3 , for example, the incorporation cross-section at 0.05 eV collision energy is about three times as large as that at 2.0 eV collision. We hypothesized that the large reaction cross-section at a very low collision energies occurs mainly because the collision cross-section is enhanced by the electrostatic attractive force between the protonated water cluster ion, $\text{H}^+(\text{H}_2\text{O})_n$ ($n =$

2–6), and the CH_3COCH_3 molecule. The probability for incorporation increases with decreasing collision energy. Thus, we conclude that the increases in both the collision cross-section and the probability for incorporation accelerate the nucleation of the cluster ion at low collision energies.

The incorporation cross-section as well as the total reaction cross-section are found to have a maximum at the cluster size $n = 5$ at the collision energy as low as 0.1 eV. This is probably due to the effect of the water molecule located in the second shell. The dissociation cross-section is also found to have its maximum at $n = 5$ at collision energies above 0.5 eV. This is also attributed to the effect of the water molecule in the second solvent shell. The dissociation cross-section is found to have its minimum at $n = 3$. This phenomenon may be attributed to the open site of the trimer's core, H_3O^+ : water molecules in the case of a trimer occupy only two of the three hydrogen atoms of the cluster ion core.

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