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Electron-stimulated desorption of positive ions from Na nanoclusters adsorbed on Pt(111) and Ar, H_2O, and SF_6 spacer layers

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Electron-stimulated desorption of positive ions from supported Na nanoclusters has been investigated in terms of the localization or delocalization of valence holes, as well as the reaction of Na with the substrate or coadsorbed molecules. On the Ar substrate, the Na^+ yield is enhanced markedly at the smallest coverage and decay steeply with increasing coverage. We interpret that Na^+ is emitted via Coulomb explosion of the adsorbed Na nanoclusters in which valence holes are confined, i.e., localized. Very few Na^+ ions are emitted from the Na nanoclusters adsorbed on the Pt(111) and H_2O substrates. The complete suppression of the Na^+ emission is interpreted as a result of neutralization of nanoclusters due to electron transfer from the substrate, i.e., the delocalization of valence holes. Na tends to interact with the H_2O nanoclusters on the Ar substrate as revealed from the evolution of hydrated Na^+ ions prior to bare Na^+ ions. The formation of Na nanoclusters is suppressed on the SF_6 substrate due to reactions, resulting in a much smaller Na^+ yield than that from the Ar substrate.

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I. INTRODUCTION

Electronic excitations of small clusters induced by electron and photon irradiation result in sequential desorption of neutrals and ions. Small multiply charged clusters are often unobservable in mass spectra as a consequence of Coulombic fission [1], which occurs when repulsive energy between positive holes exceeds the binding energy of molecules in clusters. Such fragmentation (fission) is of importance for understanding the intrinsic stability and binding forces of these objects. So far, a considerable research effort has been devoted to alkali-metal clusters [2–6], where energetics and dynamics of Coulombic fission of small doubly charged sodium and potassium clusters have been investigated both experimentally and theoretically. The critical size n_c of doubly charged clusters Na_n^{2+} which do not fission into singly charged fragments is determined to be about 27 [3]. Around this critical size, the singly charged fragments, Na_{n-p}^+, $p=1,3,5,7,9$, were observed. It is also revealed theoretically that smaller-sized Na_n^{2+} $(n<12)$ clusters undergo asymmetric fission with Na_3^+ being the most preferred products [6], the validity of which was confirmed experimentally from the predominant fission of K_n^{2+} into $K_{n-3}^+ + K_3^+$ $(5<n<12)$ [4].

As mentioned above, suspended metal clusters possess many interesting features, but the physics of the cluster-on-surface system is of fundamental importance in that they might have an advantage to investigate the size dependent evolution toward bulk properties, such as phase transitions, electronic bands, propagating excitations, etc., with increasing the cluster size. Also of interest is that the interaction with the contact medium might change their distinctive characteristics. The idea of Coulomb explosion, proposed originally for the gas-phase molecular dissociation [7], was imported to elucidate photon and electron stimulated desorption (PSD, ESD) of positive ions from highly ionic-compound surfaces [8], as well as physisorbed and chemisorbed molecules on metal surfaces [9]. However, very few works have so far been done regarding Coulomb explosion of adsorbed nanoclusters. The bottleneck of investigating cluster-on-surface systems in this respect arises from the competition with very efficient decay channels of charged molecules and clusters due to the interaction with a metal substrate. This difficulty would be overcome by using an appropriate spacer layer of physisorbed atoms and molecules formed on the metal substrate [10], thereby enabling us to explore the dynamical properties of adsorbed metal clusters, together with the role of the spacer layers in the confinement of valence holes. In this paper, we investigate ESD of positive ions from Na nanoclusters adsorbed on the Pt(111) surface, as well as Ar, SF_6, and H_2O spacer layers formed on it, in order to gain more insight into the localization or delocalization of valence holes on condensed-matter surfaces.

II. EXPERIMENT

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure of 1×10^{-10} mbar) equipped with facilities for standard surface characterization. The electron beam was chopped by an electrostatic deflector into pulses with width of 100 ns and frequency of 40 kHz, so that the emitted ions were detected by the time-of-flight (TOF) technique. The TOF-ESD measurements were made in such a manner that the sample, floated with a bias voltage of $+500$ V, was irradiated with a primary electron beam of 500 eV through a grounded stainless-steel mesh placed 4 mm above the sample (the electron-impact energy was 1.0 keV), and the positive-ions extracted into the field-free region of the TOF

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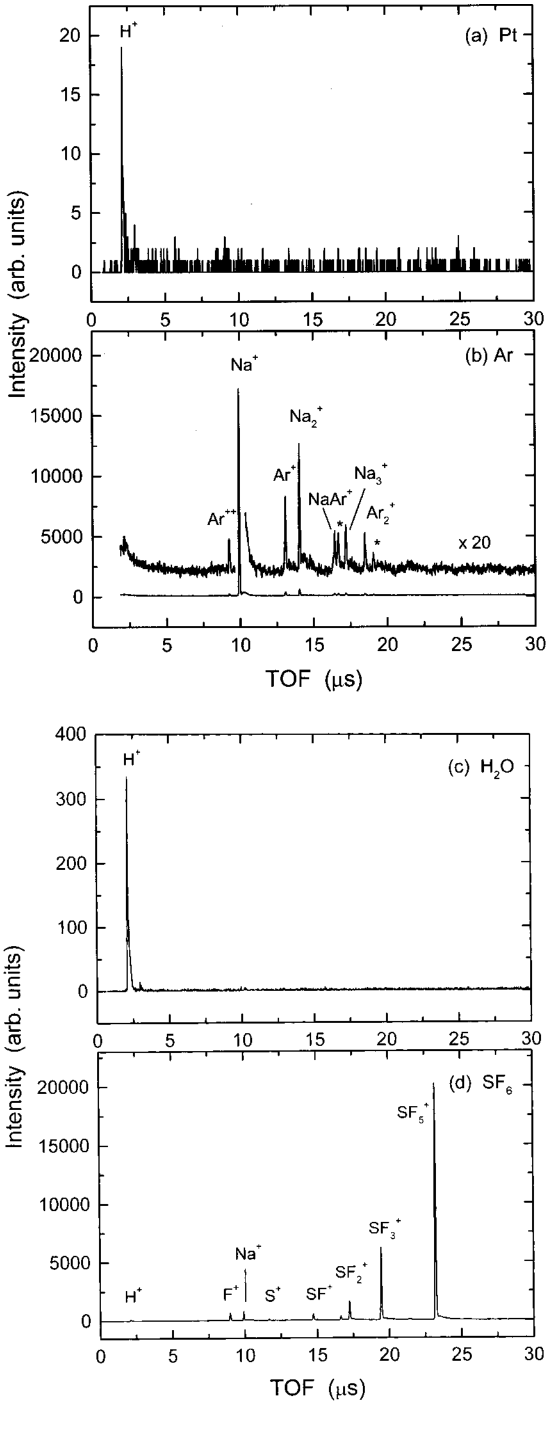

FIG. 1. TOF-ESD spectra of positive ions from Na (0.07 ML) adsorbed on (a) the Pt(111) substrate and the spacer layers of (b) Ar (15 ML), (c) H_2O (30 ML), and (d) SF_6 (20 ML) formed on Pt(111). The temperature of the Pt(111) substrate was 10 K. The TOF peaks indicated with asterisks are due to contaminants assignable to Zn ($m=65$) and Rb (86) from the dispenser.

tube were detected with a channel electron multiplier. To minimize charging and damage of a surface, a pulsed electron beam with a low incident flux (0.5 nA/cm^2) was used. The substrate was the Pt(111) surface mounted on a sample holder cooled to 10 K by means of a closed-cycle He refrigerator. The substrate was cleaned by He$^+$ sputtering and annealing around 1200 K. The cleanliness of the Pt(111) surface was confirmed from the low-energy He$^+$ ion scattering (LEIS) which revealed no peaks other than Pt. Thin layers of Ar, H_2O, and SF_6 were condensed on the Pt(111) surface at 10 K. The one monolayer (1 ML) coverage of these gas molecules was determined from the decay curve of the Pt surface-peak intensity in LEIS (using a $E_0=100$ eV He$^+$ beam to minimize the sputtering effect) as a function of adsorption time, and the thickness of the spacer layers was estimated on the basis of this value. Na was deposited on these substrates from a thoroughly outgassed Na dispenser (SAES Getters). The coverage of Na adatoms was estimated from the changes in work function of the Pt(111) surface.

III. EXPERIMENTAL RESULTS

Figure 1 shows typical TOF-ESD spectra of positive ions from Na adsorbed on (a) the clean Pt(111) substrate and the spacer layers of (b) Ar (15 ML), (c) H_2O (30 ML), and (d) SF_6 (20 ML) formed on it; the coverage of adsorbed Na was about 0.07 ML and all measurements were made at 10 K. Very few ions were emitted from Na adsorbed on the Pt(111) substrate. This is because electronic excitations or valence holes created in the Na adatoms have a short lifetime (<1 fs) due to the resonance electron transition between the Na 3s state and valence-band state of the Pt(111) substrate. In this paper, we define such a phenomenon as delocalization of valence holes. In contrast, the Ar spacer layer formed on Pt(111) is very effective for preventing the holes diffusion into the substrate so that positive ions are emitted from adsorbed Na efficiently; the Na$^+$ ion is the dominant species and cluster ions, such as Na_n^+ ($n \leqq 3$) and NaAr$^+$, are clearly discernible. We tentatively assume that the Na$^+$ ion is emitted via Coulomb explosion of multiply charged Na nanoclusters formed on Ar, in analogy with the results of free Na nanoclusters (a detailed discussion is presented in the following section). The Na$^+$ yield is much higher than the ion yields from the Ar spacer layer (Ar$^+$, Ar_2^+, and Ar^{2+}) in spite of a much smaller amount of adsorbed Na. The emission of Ar$^+$ and Ar^{2+} ions has been ascribed to the Coulombic repulsion [11] or cavity expulsion mechanism [12,13] associated with the doubly excited states.

In Fig. 1, it should be noticed that the yields of the Na$^+$ ions are largely dependent on the spacer layers. Protons are the dominant species from the H_2O layer with and without the Na adatoms; the ions from adsorbed Na, as well as heavier ions including O atoms, are negligibly small in intensity. The spacer layer of SF_6 itself yields a variety of fragment ions with a considerable intensity. However, the Na$^+$ intensity from Na/SF_6 is at most about 1/30 of that from Na/Ar. The TOF peaks of Na$^+$ and SF_n^+ are accompanied by a small hump or a tail in their longer TOF side. The origin of such structures will be discussed elsewhere.

In the case of H_2O, it is revealed that the morphology of adsorbed layers largely depends on the way of gas dosage [14]. In the background dosing at 10 K, a porous water film is grown on the Pt(111) substrate because of the highly oriented hydrogen bonds. On the other hand, Ar and SF_6, condensed via isotropic van der Waals force, should form a

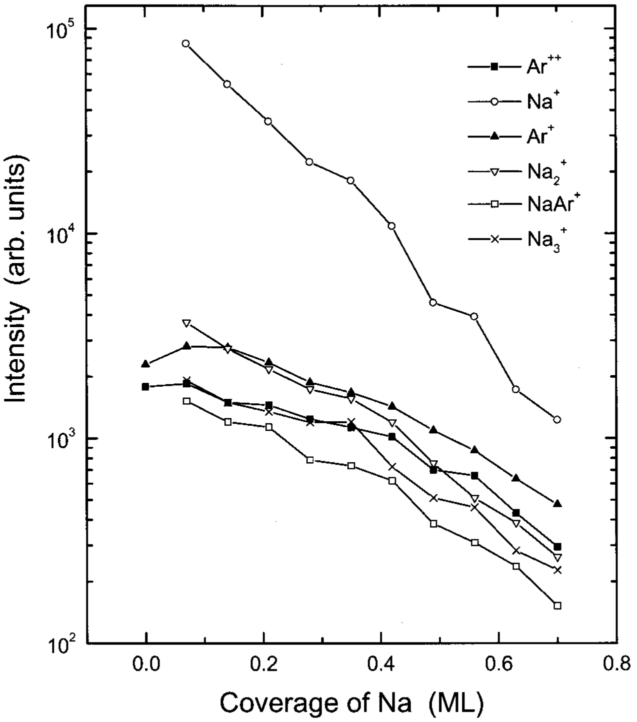

FIG. 2. Evolutions of ESD ions from Na adsorbed on the Ar (15 ML) substrate as a function of Na coverage.

much smoother layer [15]. Regarding the morphology of adsorbed Na adatoms, two factors may determine the size of islands or the formation of either two-dimensional or three-dimensional clusters: (a) roughness of the substrate film and (b) the diffusion length of Na adatoms on a surface to nucleation sites. A larger number of Na nanoclusters would be formed on such a rough layer as porous water ice than the smoother Ar layer. Therefore, the absence of the Na^+ ions from Na/H_2O should not be ascribed to the size or morphology of the adsorbed Na clusters but is due to the shorter lifetime (or delocalization) of valence holes in the Na adatoms on the water substrate.

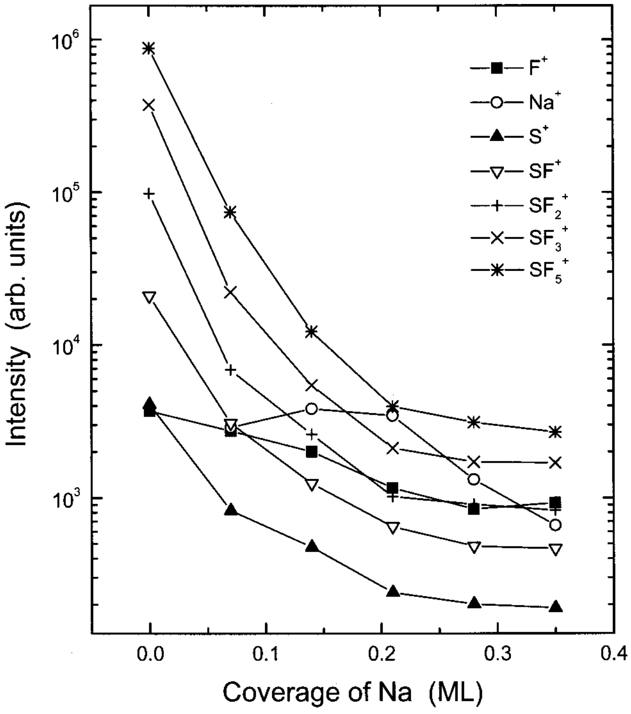

FIG. 3. Evolutions of ESD ions from Na adsorbed on the SF_6 (20 ML) substrate as a function of Na coverage.

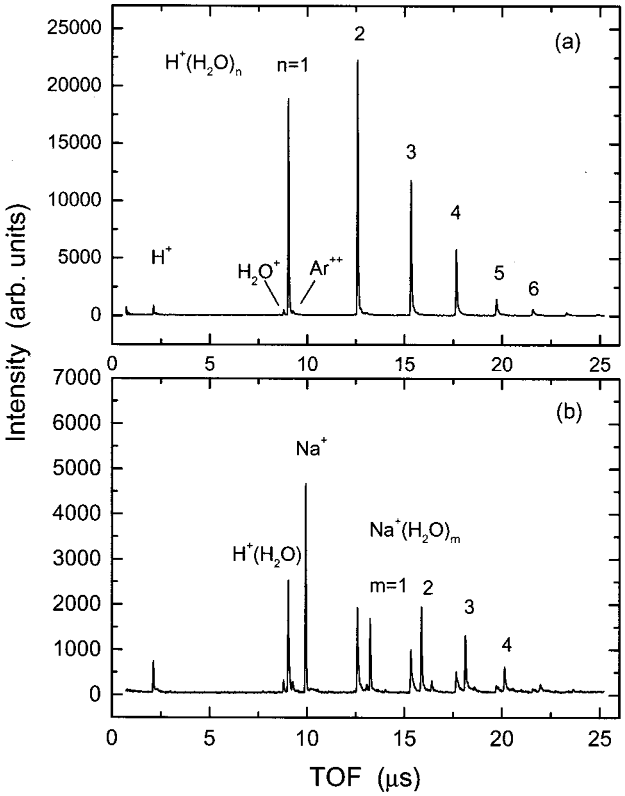

FIG. 4. (a) TOF-ESD spectra of positive ions from H_2O (0.05 ML) adsorbed on the Ar substrate (15 ML). The change in TOF-ESD spectra upon subsequent deposition of Na atoms (0.21 ML) on this surface is shown in (b).

Figure 2 shows evolutions of the ESD ion yields from Na adsorbed on the Ar spacer layer as a function of Na coverage. The Na^+ yield is highest at the smallest coverage and then decays almost exponentially with increasing coverage. The same tendency is observed in the evolutions of the cluster ions such as Na_2^+, Na_3^+, and $NaAr^+$. The Ar spacer layer is quite effective for the emission of positive ions from the adsorbed Na nanoclusters, and the decay of the ion yields with coverage can be ascribed to the formation of larger-sized Na clusters in which Coulomb explosion is quenched.

In Fig. 3 are shown evolutions of the ESD positive ions from the Na/SF_6 surface as a function of coverage. The Na^+ yield is rather small and decreases with increasing coverage. The yields of fragment ions from the SF_6 substrate, SF_n^+ $(0<n<5)$, decay more steeply than the Ar^+ yield from the Ar substrate with increasing Na coverage. Moreover, it should be noted that the decay curve of F^+ is apparently more gradual than that of the SF_n^+ ions. These experimental results may be related to the occurrence of chemical reactions between Na and SF_6 [16].

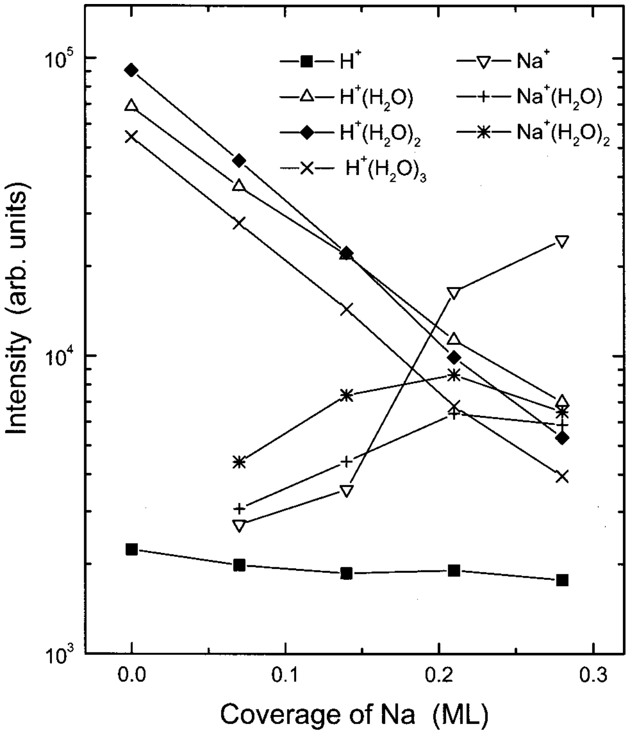

FIG. 5. Evolutions of ESD ions upon Na adsorbed on the H_2O (0.05 ML) precovered solid Ar (15 ML) substrate as a function of Na coverage.

Figure 4(a) shows the TOF spectra of positive ions from H_2O (0.05 ML) adsorbed on the Ar substrate (15 ML). As has already revealed in the previous paper [10], the protonated water-cluster ions are emitted predominantly from the water nanoclusters adsorbed on the Ar substrate. The cluster ion yields decay steeply with increasing coverage. This result is almost identical to that of the Na nanoclusters discussed here. It would be of interest to investigate whether or not chemical interactions occur between the Na and H_2O adatoms on the Ar substrate. Figure 4(b) shows the change in the TOF-ESD spectra upon successive Na deposition (0.2 ML) on the H_2O-preadsorbed Ar substrate [Fig. 4(a)]. In addition to bare Na^+ ions, the hydrated Na^+ ions are emitted with considerable intensity.

Figure 5 shows evolutions of the positive-ion yields from the water-adsorbed Ar surface as a function of Na coverage; the coverage of preadsorbed H_2O molecules was around 0.05 ML. With increasing Na coverage, the yields of hydrated Na^+ ions (hydrated H^+ ions) increase (decrease). Thus, the proton is replaceable by Na^+ as far as the cluster-ion formation is concerned. This is because the underlying mechanism for the formation of cluster ions is ion-dipole interactions, which may be reinforced by the hydrogen bond of H_2O. Note that the yields of the $H^+(H_2O)_n$ ions decay much steeper than the H^+ yield and that the Na^+ yield increases relative to the $Na^+(H_2O)_n$ yield for coverage above 0.15 ML. Probably, the latter suggests that the agglomeration of Na nanoclusters occurs after the Na adatoms react with the preadsorbed H_2O nanoclusters.

IV. DISCUSSION

It might be presumed that the efficient ion emission from Na adatoms formed on the Ar substrate is caused by the gas-phase ionization following the neutrals desorption via electron-induced local heating or direct electronic excitation (Menzel-Gomer-Redhead mechanism [17,18]). The neutrals desorption occurs more preferentially from the spacer layers than Na adatoms because of the smaller cohesive energy. Therefore, if the ionization occurred in the gas phase, the yield of Ar^+ would be much higher than that of Na^+. Moreover, no detectable increase in the background pressure occurred during the TOF-ESD measurements, indicating that all of the detected ions are emitted directly from the surface via the electronic process. The marked enhancement of the Na^+ yield at smallest coverage, as typically observed on the Ar substrate, is explicable in terms of Coulomb explosion of adsorbed Na nanoclusters in which multiple valence holes are confined. The valence holes are created as a consequence of the Auger decay of a deep core hole or multiple valence excitation by a primary electron beam. It is also likely that the excited Ar atoms formed in the substrate contribute to the ionic emission as a consequence of the charge transfer. The presence of mixed $NaAr^+$ ions might suggest such possibilities. Because of the highly localized nature of valence holes in the Ar layer [19], the excited Ar atoms formed in the interface region should be considered. Since the first ionization potentials of Na and Ar, respectively, are 5.1 and 15.8 eV, the Ar^+ ion can create two valence holes in the Na adatoms via the Auger process. The interaction between doubly excited Ar^{+*} (Ar^{2+}) and Na also results in the Ar^+-Na^+ pair. In any case, the Coulombic repulsion between the localized ion pairs is thought to be prerequisite for the emission of energetic ions from the surface.

As described in the Introduction, the suspended Na nanoclusters exhibit a critical size for the Coulombic fission and a magic number in the daughter cluster-ions distribution [2–6]. In the present experiment, no preference of the emitted Na_n^+ ions with the closed-shell electronic structures was observed. Probably, this is because the barrier for desorption of Na_n^+ ions from the surface determines the relative yields; it might be higher than the fission barrier due to the image charge effect. Although the size distributions of adsorbed Na clusters are unknown, the Na^+ ion desorption may occur preferentially from smaller-sized clusters ($n \ll 27$) in order to gain higher kinetic energy during the Coulombic fission.

Of particular interest in the present study is that the desorption probability of Na_n^+ is sensitively dependent on the substrate. In this respect, we have already investigated the ESD of positive ions from H_2O nanoclusters adsorbed on Pt(111), NaCl, and TiO_2(110) substrates, as well as thin layers of condensed Ar, Xe, SF_6, O_2, CO, CH_4, and CH_3OH [10]. The emission of the $H^+(H_2O)_n$ ion occurs most efficiently from the Ar and SF_6 substrates via Coulomb explosion of a water nanocluster including multiple valence holes or hydrated protons. However, very few or almost no $H^+(H_2O)_n$ ions are ejected from water nanoclusters adsorbed on Pt(111), TiO_2, and NaCl. These results clearly show that the electronic properties of the substrates, especially the lifetime of valence holes on it, are of importance for the occurrence of Coulombic fission, since charged nanoclusters should survive for considerably long time (10–100 fs) corresponding to the ion desorption time. This is realized on the Ar substrate because valence holes created in the charged Na nanoclusters hardly diffuse into the physically condensed Ar substrate [19]. On the other hand, the charged Na nanoclusters on the Pt(111) substrate has a short lifetime due to the delocalization of valence holes in the metal substrate, resulting in no Na^+ desorption. The same is true for the charged Na nanoclusters adsorbed on the water substrate. The delocalized nature of valence holes in solid water manifests itself in the absence of the ESD $H^+(H_2O)_n$ ions from the multilayer water, as well as the efficient neutralization of H^+ ions ($E_0 = 100$ eV) scattered from the water ice surface [20]. The Na and H_2O nanoclusters, respectively, adsorbed on the Ar layer exhibit quite similar behaviors in terms of the Na_n^+ and $H^+(H_2O)_n$ ions desorption; a marked decay of the ion yields with increasing coverage, following the enhanced ion yields from Na and H_2O nanoclusters, can be ascribed to the delocalization of valence holes in multilayers of these adsorbates.

The yield of H^+ is considerably small from the H_2O nanocluster. This is related to the fact that bare protons hardly exist in water due to strong ion-dipole interactions. In contrast to the evolution of Na^+ shown in Fig. 2, moreover, the H^+ yield from water increases monotonically with increasing coverage [10]. This behavior is apparently inconsistent with the Coulombic fission; the H^+ ion originates from localized electronic excitation, created in the dangling O—H bond at the topmost surface layer. The H^+ emission results from the creation of a hole in the $2a_1$ orbital (with the O $2s$ character) or the two-holes creation in the $1b_1$ and $3a_1$ orbitals [21]. The latter is less likely for thick water ice since holes in the valence $1b_1$ and $3a_1$ orbitals, taking part in the hydrogen bond, should be delocalized [20].

The fact that the yield of Na_n^+ from the SF_6 layer is about 1/30 of that from the Ar layer is rather remarkable by considering that the abilities for the confinement of valence holes in adsorbates are thought to be almost identical between Ar and SF_6 as inferred from the $H^+(H_2O)_n$ emission efficiencies from the adsorbed water nanoclusters [10]. This result may be related to the occurrence of chemical reactions between Na and SF_6. On the basis of the ultraviolet and x-ray photoelectron spectroscopy [16], it is shown that SF_6 molecules are physisorbed on the Ni(111) substrate but a significant chemical reaction occurs when the surface is precovered with Na adatoms; the reaction occurs even at temperature of 20 K due to the transfer of a Na $3s$ electron to the empty SF_6 $6a_{1g}$ orbital, and the dissociation products such as SF_4, S, F, and possibly NaF may be formed on the surface. In Fig. 3, the slowly decaying F^+ yield, relative to the others, would be an indication of such a chemical reaction and formation of the Na—F bond. The quenching of the Na nanoclusters formation may be responsible for the smaller yield of the Na^+ ions. In fact, Na adatoms on the SF_6 layer exhibit no metallic character as revealed by metastable impact electron spectroscopy (MIES).

Recently, the reaction of Na adatoms with thick water ice layers has been explored with MIES [22,23]. Upon Na adsorption at 100 K, it is found that the 3σ and 1π orbitals, which are characteristic of hydroxide group, evolve instead of the $1b_2$, $3a_1$, and $1b_1$ orbitals of H_2O, indicating that the Na adatoms react with the water substrate and form NaOH-like species at the interface [22]. At 10 K, however, metallic Na layers grow more preferentially than NaOH, but the Na adatoms tend to cover the water nanoclusters [23]. As seen in Fig. 5, the evolution of the $Na^+(H_2O)_n$ species, together with a marked decay of $H^+(H_2O)_n$ ions, suggests that Na is adsorbed close to the H_2O nanocluster, where some chemical interactions might be induced or precursors for the reaction would be formed. In the present case, the formation of sodium hydroxide, as well as the hydration of the Na^+ ions, can be induced even at 10 K by the kinetic energy of the Na^+ ions released as a result of the Coulombic fission. The delayed evolution of the Na^+ ion relative to the $Na^+(H_2O)_n$ ions indicates that the metallic Na cluster grows after saturation of possible adsorption sites around the H_2O nanocluster. The preferential interactions between Na and H_2O may create a larger number of nucleation sites for Na nanoclusters and, therefore, the Na^+ yield increases till higher coverage (see Fig. 5). On the other hand, Na adatoms can migrate on the inert Ar substrate for a longer distance to form a larger cluster, so that the Na^+ yield decays more steeply than that from the water-precovered Ar substrate.

V. SUMMARY

The electron stimulated positive-ion desorption has been investigated from Na nanoclusters adsorbed on the Pt(111), Ar, SF_6, and H_2O substrates. On the Ar substrate, the Na^+ yield is highest at the smallest coverage (0.07 ML) and then decays steeply with increasing coverage. This behavior is explicable in terms of Coulomb explosion of adsorbed Na nanoclusters, in which valence holes are confined, as well as the delocalization of holes in multilayer Na. In contrast to the suspended Na nanoclusters, the relative yield of Na_3^+ is small and no preference for the emission of closed-shell Na_n^+ ($n = 1,3,5\ldots$) ions is observed. Probably, this is because only smaller-sized ions with a higher kinetic energy can escape from the image-charge attractive force. In contrast, the $H^+(H_2O)_n$ ions are the dominant species relative to H^+ from water nanoclusters adsorbed on the Ar substrate, where the hydrogen bond associated with the ion-dipole interactions plays a role in the formation of protonated water-cluster ions. Very few or no Na^+ ions are emitted from the Na nanoclusters adsorbed on the Pt(111) and H_2O substrates due to the delocalization of valence holes. The Na and H_2O nanoclusters coadsorbed on the Ar substrate are found to interact with each other as evidenced by the desorption of $Na^+(H_2O)_n$ ions prior to the evolution of the Na^+ ion. The Na^+ yield is considerably small from Na adatoms on the SF_6 layer relative to that on the Ar layer since the Na adatom reacts with the F atom of SF_6, thereby preventing the formation of metallic Na nanoclusters.

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