Collision-Induced Dissociation Study of Strong Hydrogen-Bonded Cluster Ions Y\(^{-}\)(HF)_\(n\) (Y=F, O\(_2\)) Using Atmospheric Pressure Corona Discharge Ionization Mass Spectrometry Combined with a HF Generator

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Hydrogen fluoride (HF) was produced by a homemade HF generator in order to investigate the properties of strong hydrogen-bonded clusters such as (HF)_\(n\). The HF molecules were ionized in the form of complex ions associated with the negative core ions Y\(^{-}\) produced by atmospheric pressure corona discharge ionization (APCDI). The use of APCDI in combination with the homemade HF generator led to the formation of negative-ion HF clusters Y\(^{-}\)(HF)_\(n\) (Y=F, O\(_2\)), where larger clusters with \(n\geq 4\) were not detected. The mechanisms for the formation of the HF, F\(^{-}\)(HF)_\(n\), and O\(_2\)(HF)_\(n\) species were discussed from the standpoints of the HF generator and APCDI MS. By performing energy-resolved collision-induced dissociation (CID) experiments on the cluster ions F\(^{-}\)(HF)_\(n\) (\(n=1–3\)), the energies for the loss of HF from F\(^{-}\)(HF)_\(n\), F\(^{-}\)(HF)_\(n\), and F\(^{-}\)(HF)_\(n\) were evaluated to be 1 eV or lower, 1 eV or higher, and 2 eV, respectively, on the basis of their center-of-mass energy (\(E_{CM}\)). These \(E_{CM}\) values were consistent with the values of 0.995, 1.308, and 2.048 eV, respectively, obtained by \(ab\ initio\) calculations. The stability of [O\(_2\)(HF)_\(n\)]\(^{-}\) (\(n=1–4\)) was discussed on the basis of the bond lengths of O\(_2\)H–F–F(HF)_\(n\) and O\(_2\)H–F(HF)_\(n\) obtained by \(ab\ initio\) calculations. The calculations indicated that [O\(_2\)(HF)_\(n\)]\(^{-}\) is separated into O\(_2\)H and F\(^{-}\)(HF)_\(n\).

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INTRODUCTION

Mass spectrometry (MS) provides data on the hydrogen bond dissociation characteristics of complex gaseous ions such as hydrated cluster ions H\(_2\)O\(^{+}\)(H\(_2\)O)_\(n\) and Y\(^{-}\)(H\(_2\)O)_\(n\) (Y=OH, O\(_2\), CO\(_2\)),\(^{1–3}\) and it also gives experimental evidence of the thermodynamic stabilities of small clusters.\(^{4,5}\)

Although it is difficult to apply the collision-induced dissociation (CID) method to weakly bound hydrogen-bonded systems, it is possible to use it to examine strong hydrogen-bonded systems such as the fluoride ion complex F\(^{-}\)(HF).\(^{6,7}\) A strong-hydrogen bonding (SHB) can be distinguished from a weak-hydrogen bonding (WHB) by means of the bond energy (WHB <30kJ/mol, SHB >50 or 100 kJ/mol).\(^{7}\) SHB is often indicated as A–H–B or A⋯H⋯B, while normal or WHB is expressed by A–H⋯B. Another method for representing WHB and SHB is based on the use of the potential profile, i.e., WHB and SHB are denoted by a symmetric or asymmetric double-minimum potential with a high energy barrier and a symmetric double- or single-minimum potential with a low energy barrier, respectively.\(^{7}\) Hydrogen fluoride (HF), its clusters (HF)_\(n\), and related chemicals have attracted both theoretical and experimental interest as hydrogen-bonded systems owing to their strong binding energies, i.e., 150–240 and 160–230 kJ/mol from the thermochemical and theoretical data, respectively, of F\(^{-}\)(HF)X (X=N\(^{+}\)Me\(_4\) and alkali-metal cations),\(^{7}\) in contrast to the WHB energy of the neutral cluster HF–HF that is 25.09 kJ/mol.\(^{9}\) The HF cluster negative ions have been studied from the standpoints of the electron and hydrogen transfer\(^{9}\) as well as complex formation with heterocyclic organic cations in solution.\(^{10}\)

Wenthold and Squires have estimated the hydrogen-bonding energy of a hydrogen fluoride anion F\(^{-}\)(HF) by means of the center-of-mass energy (\(E_{CM}\)) that was determined by low-energy CID experiments.\(^{9}\) Here, in order to study the properties of strong hydrogen-bonded systems,
we focused on the CID analysis of hydrogen fluoride cluster anions of the type F(HF)_n. The energy for the loss of HF from F(HF)_n (n=1–3) was estimated on the basis of the E_CM energy. In order to produce HF clusters, a generator of hydrogen atoms H and HF molecules was assembled and the resulting HF molecules were ionized as complexes associated with the negative core ions Y^− (Y=F, O_2) produced by atmospheric pressure corona discharge ionization (APCDI). The dissociation energy of F(HF)_n estimated from the CID experiments was compared with the energy calculated by ab initio methods combined with density functional theory (DFT). The stability of other complex ions such as O_2(HF)_n (n=1–4) was discussed on the basis of the results of ab initio calculations.

MATERIALS AND METHODS

Generation of hydrogen fluoride

Gaseous HF molecules were produced by using a homemade generator for H/HF species. The H/HF generator consisted of a deuterium lamp D200F (Heraeus, Tokyo, Japan), a reaction tube made of polycarbonate (PC tube), and a polytetrafluoroethylene (PTFE) tape, as shown in Fig. 1. The deuterium lamp generated UV photons over a wavelength range of 160–400 nm (3.8–7.7 eV). Upon supplying hydrogen gas (H_2) to the reaction tube, the H molecules dissociated into hydrogen atoms H^+ owing to the lower dissociation energy of the H–H bond (4.5 eV) compared to the UV photon energy (7.7 eV, reaction 1). The UV photons may produce fluoride atoms F^− from the PTFE tape (reaction 2). Although it is expected that the HF molecules are mainly formed according to reaction 3, another minor reaction 4 may occur following the fluorine atom abstraction with H from the PTFE tape in view of the dissociation energies of C–F (5.07 eV) and H–F (5.89 eV).

H_2 + hv → 2H

⋯(C_2F_2)n⋯ + hv → F

H_2 + F → HF + H

H + ⋯(C_2F_2)n + 1→ HF + ⋯(C_2F_2)(C_2F_2)⋯

The resulting HF molecules were transferred using N_2 as carrier gas to the drift region adjusted to a gap length of 3 mm between the tip of the corona needle and the orifice of the mass spectrometer (Fig. 1).

Atmospheric pressure corona discharge ionization

The detailed schematic illustration of the APCDI apparatus used in this study has been described elsewhere. The corona discharge experiments for generating negative atmospheric core ions Y^− (Y=F, O_2, HO_2, NO_2, CO_3)^11,12 were performed under ambient laboratory conditions in the presence of nitrogen (N_2), oxygen (O_2), water vapors (H_2O), and minor amounts of other species, such as CO_2 and Ar. The laboratory temperature and relative humidity were 298 K and 40–70%, respectively. The corona needle used as point electrode with a tip radius of ca. 1 μm was a headless insect pin (Shiga, Tokyo, Japan), made of stainless steel with a diameter and length of 200 μm and 20 mm, respectively. The discharge gap between the needle tip and the orifice plate of the mass spectrometer was adjusted to 3 mm with a π/2 rad needle angle with respect to the orifice plate axis (Fig. 1). A DC voltage of ~2.0 kV was applied to the needle relative to the orifice plate.

Mass spectrometry

The mass spectra were obtained with a TSQ7000 triple-quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). The resulting ions were introduced into an orifice hole with a diameter and length of 320 μm and 114 mm, respectively. The orifice was heated at 70°C to prevent the generation of large water cluster ions. The ions introduced into the orifice hole were focused onto a skimmer opening by the tube lens, and they were then transported to the ion guide. The voltages applied to the skimmer and tube lens were 0 and 67.8 V, respectively. The applied rf voltage on the ion guide was 3 V. The transported ions were accelerated to 20 V at the focusing lens electrode. The assignment of the negative ion species generated by the corona discharge and the ion/molecule reactions in the atmospheric pressure drift region (3 mm) between the needle tip and the orifice plate was performed by using CID experiments. Thus, the precursor ion selected by the first quadrupole (Q1) was injected into the rf-only second quadrupole (Q2) collision cell, and the product ions were mass-analyzed by the third quadrupole (Q3). The target collision gas and laboratory frame collision energy (E_CM) used were argon at 2.2×10^{-3} Torr and 1–25 eV, respectively. For the energy-resolved CID experiments, the laboratory frame axial collision energy (E_ab) was set by the Q2-rod offset voltage, and then the E_CM was determined according to the equation E_CM=E_ab[m_i(m_i+m_p)], where m_i and m_p represent the masses of the target gas and precursor ion, respectively.

Ab initio calculations

All calculations were performed using ab initio methods combined with the DFT unrestricted B3LYP13,14 level of

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Fig. 1. Schematic illustration of APCDI mass spectrometer (upper) combined with a generator of hydrogen atoms H and hydrogen fluoride HF under atmospheric pressure conditions (lower).
theory and 6-311+G(2d,p) basis set in the Gaussian 09 suite of programs. The initial structures of HF, F(HF)$_n$, and O$_2$(HF)$_n$ were generated using CS Chem3D Ultra (Cambridge Soft, Cambridge, MA, USA). The input file was minimized under a semi-empirical MO (PM7) run through a Winmoster interface using MOPAC2012.

RESULTS AND DISCUSSION

Formation of hydrogen fluoride anion clusters F$^-(\text{HF})_n$ using APCDI MS

The negative-ion APCDI mass spectra of the background in the absence of HF supply and HF molecules associated with the preformed core ions are shown in Fig. 2. The background spectrum (Fig. 2a) exhibited peaks corresponding to the negative atmospheric core ions Y$^-$ (Y=O$_2$, CO$_3$, CO$_4$, HCO$_3$, and HCO$_4$) and those of the water clusters Y$^-$(H$_2$O)$_n$, although the source of the carbon atoms of CO$_x$ and HCO$_x$ ions has not yet been clarified. The spectrum obtained in the presence of the HF supply (Fig. 2b) displayed peaks corresponding to the HF clusters F$^-$(HF)$_n$ ($n=2, 3$) at $m/z$ 59 and 79, respectively, while clusters larger than $n=3$ could not be observed. A weak peak corresponding to the hydrogen-bonded ion F(HF) at $m/z$ 39 was also observed.

Other HF cluster ions were observed, such as O$_2$(HF)$_n$ ($n=1$ to 3), O$_2$(HF)$_n$+HCOOH$^-$ ($n=1$ to 2), and HCO$_2$(HF)$_n$ ($n=1$ to 2). From the viewpoint of the stability of cluster ions, it is worth mentioning that F(HF)$_n$ and O$_2$(HF)$_n$ with $n \geq 4$ were not detected, as shown in Fig. 2b. The HF clusters associated with ions Y$^-$ and/or neutral byproducts B (such as H$_3$CO$_n$, HCO$_3$, HO$_x$, and HNO$_3$) can be formed according to the gas-phase reactions (5) and (6) in the drift regions and/or adiabatic expansion cooling in the orifice vacuum region.

Considering the hydrogen-bonding energies of 0.141 and 0.211 eV calculated for the neutral clusters HF–HF and HF–(HF)$_2$, respectively, it is reasonable to assume that the HF molecules form hydrogen-bonded cluster (HF)$_n^-$.

$\text{HF} + \text{Y}^- \rightarrow \text{Y}^-(\text{HF})$  \hspace{1cm} (5)

$\text{HF} + \text{B} + \text{Y}^- \rightarrow \text{Y}^-[\text{HF} + \text{B}]$  \hspace{1cm} (6)

Regarding the formation of fluoride anion clusters F$^-(\text{HF})_n$, it may be possibly due to the proton abstraction by the negative ions Y$^-$ from the HF molecules. On the basis of the strong proton affinity of superoxide O$_2^-$ (PA=15.3 eV), higher stability of the cluster ion F(HF)$_n$ than (HF)$_n^+$ and (HF)$_n^-$, and thermochemical data (16.12 eV for HF$\rightarrow$F$^-+$H$^+$, 1.99 eV for F(HF)$\rightarrow$F$^-+$HF$^-$), the overall process (7a and 7b) may occur as an exothermic reaction to

Fig. 2. Negative-ion APCDI mass spectra of (a) background (without HF supply) and (b) hydrogen fluoride molecules (HF)$_n$ associated with preformed core ions Y$^-$ generated with corona discharge.
form the strong hydrogen bonded ion \(F^-(HF)\). Larger cluster ions may be formed by the interaction of \(F^-(HF)\) with the HF molecules in the drift region and/or adiabatic expansion cooling in the orifice vacuum, as expressed by equation (7c):

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\begin{align*}
O_2^- + HF & \rightarrow O_2H + F^- \quad (7a) \\
F^- + HF & \rightarrow F^- (HF) \quad (7b) \\
F^- (HF) + (n-1)HF & \rightarrow F^- (HF)_n \quad (7c)
\end{align*}
\]

Estimation of the energy for the loss of HF from the anion clusters \(F^- (HF)_n\)

The CID spectra of the cluster ions \(F^- (HF)_n\) \((n=1–3)\) obtained with laboratory frame collision energies \((E_{\text{lab}})\) of 5 and 15 eV, are shown in Fig. 3. All the spectra showed the peaks relative to the product ions \(F^-\) at \(m/z\) 19, \(F^- (HF)\) at \(m/z\) 39, and/or \(F^- (HF)_2\) at \(m/z\) 59 originated from the loss of neutral HF from the precursor ions \(F^- (HF)_n\) \((n=1–3)\). The CID spectra of the cluster ions \(F^- (HF)\) and \(F^- (HF)_2\) obtained with a 15 eV/\(E_{\text{lab}}\) exhibited a peak corresponding

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Fig. 3. The CID spectra of fluoride anion clusters \(F^- (HF)_n\), obtained with laboratory frame collision energies 5 and 15 eV for the precursor ions of (a) \(F^- (HF)\) at \(m/z\) 39, (b) \(F^- (HF)_2\) at \(m/z\) 59, and (c) \(F^- (HF)_3\) at \(m/z\) 79.
Fig. 4. Breakdown diagrams obtained with CID experiments of F\(^+(HF)_n\) \((n=1-3)\) for the precursor ions of (a) F\(^+(HF)\) at \(m/z\) 39, (b) F\(^+(HF)_2\) at \(m/z\) 59, and (c) F\(^+(HF)_3\) at \(m/z\) 79. Right hand side represents enlarged diagram in intensity.

Table 1. Energies for the loss of HF from the fluoride cluster ions F\(^+(HF)_m\) \(F\(^-(HF)n\) and F\(^-(HF)n\), estimated from the CID experiments, \textit{ab initio} calculations and other reports.

| Precursor | Products | \(E_{CM}\) \(^a\) (eV) | Calc. \(^b\) \(E(z)\) (eV) | Other report |
|-----------|----------|-----------------------------|-----------------------------|--------------|
| F\(^+(HF)_1\) | F\(^+(HF)_2\)+HF | 1 or lower | 0.995 | 0.82–1.0\(^{14}\) |
| F\(^+(HF)_2\) | F\(^+(HF)_3\)+HF | 1 or higher | 1.308 | |
| F\(^+(HF)_3\) | F\(^+(HF)\)+HF | 2 | 2.048 | 1.99\(^{15}\) |

\(^a\)\(E_{CM}\) estimated from the CID experiments performed in this study.
\(^b\)\(E(z)\) calculated in the course of this study.

to the fluoride anion F\(^-\), while those with 5 eV/\(E_{lab}\) did not show such peak (Figs. 3a and 3b). The peak corresponding to the fluoride ion F\(^-\) was also absent in the CID spectrum of F\(^+(HF)_1\) (Fig. 3c), suggesting an insufficient internal energy of the precursor ion F\(^-(HF)_1\). With regard to this, the internal energy deposited in the precursor ions can be roughly estimated from the \(E_{CM}\).

In order to estimate the dissociation energy from the \(E_{CM}\) of the F\(^-(HF)_n\) ions \((n=1-3)\), breakdown diagrams were extrapolated from the CID data, as shown in Fig. 4. The breakdown diagram for the hydrogen-bonded cluster F\(^-(HF)\) indicated that the appearance energy for the F\(^-\) ion was about 2 eV/\(E_{CM}\) or higher (Fig. 4a). The estimated energy was consistent with the \(E_{CM}\) value of 1.99 eV reported by Wenthold and Squires.\(^{62}\) On the other hand, the \(E_{CM}\) data for F\(^-(HF)_2\) and F\(^-(HF)_3\) showed that the first loss of HF from these precursor ions occurred at 1 eV/\(E_{CM}\) or lower to form the product ions F\(^-(HF)_2\) and F\(^-(HF)_3\), respectively (Figs. 4b and 4c). Furthermore, it can be seen in Fig. 4c that the second loss of HF from F\(^-(HF)_2\) at \(m/z\) 59 to form the product ion F\(^+(HF)\) at \(m/z\) 39 occurred at about 1 eV/\(E_{CM}\) or higher. The results discussed above indicate that the energy for the loss of HF from F\(^-(HF)_n\) \((n=1-3)\) is dependent on the first, second, and third loss, as summarized in Table 1. The \(E_{CM}\) order for the loss of HF was F\(^-(HF)\)\(_{2}\)<F\(^+(HF)\)\(_{2}\)<F\(^+(HF)\)\(_{1}\).

\textit{Ab initio} calculations for F\(^+(HF)_n\) \((n=1-3)\)

The structure of the cluster ions F\(^+(HF)_n\) has been examined by low-temperature solid-state infrared (IR) spectroscopy,\(^{16}\) nuclear magnetic resonance (NMR) in the liquid state,\(^{19}\) and \textit{ab initio} calculations under vacuum.\(^{9}\) The IR solid-state study suggested that the F\(^+(HF)_1\) species possesses the highest clustering number \(n=3,18\) The NMR liquid-state study indicated the presence of a central fluoride ion involved in multiple hydrogen bonds of the HF molecules to form F\(^-(HF)_n\) \((n=2-4)\), although the F\(^+(HF)_4\) was only tentatively assigned.\(^{19}\) On the other hand, the \textit{ab initio} calculations indicated that limited zig-zag chains such as FH\(_{2}\)–F\(_{2}\)⋯HF and FH\(_{2}\)–F\(_{2}\)⋯HF⋯HF are more stable than (HF\(_{1}\))\(_{2}\) and (HF\(_{2}\))\(_{2}\), respectively.\(^{9}\) With regard to the structure of the cluster F\(^+(HF)_n\), Groenewold \textit{et al.} reported that the average binding energy of the first, second, and third step addition of HF to the central F\(^-\) ion was 1.3 eV, while the binding energy for the third step addition of HF to F\(^-(HF)_2\) was 0.82–1.0 eV on the basis of \textit{ab initio} calculations.\(^{16}\) The authors emphasized that the further addition of HF to F\(^-(HF)_2\) could not be observed in the gas-phase owing to a
weak binding energy. Actually, the cluster ion F\(^{-}\)(HF)\(_n\) as well as larger clusters could not be detected in the present study. The \(E_{\text{CM}}\) estimated here (Table 1) were well consistent to the reports of Wenthold and Squires\(^{6}\) and Groenewold et al.,\(^{10}\) although the \(E_{\text{CM}}\) just only gives maximum energy contents or rough values.

Herein, we calculated the binding energies of F–HF, F(HF)\(_2\), and F(HF)\(_3\) by using an \textit{ab initio} method, as summarized in Table 1. The \(E_{\text{CM}}\) values estimated from the CID experiments were qualitatively in agreement with the calculated values (Table 1). The H–F and F–HF bond lengths for the cluster ions F\(^{-}\)(HF), F\(^{-}\)(HF)\(_2\), and F\(^{-}\)(HF)\(_3\) were calculated for the D\(_{\text{sh}}\) and D\(_{\text{sh}}\) symmetries of F\(^{-}\)(HF)\(_2\) and F\(^{-}\)(HF)\(_3\) respectively (Scheme 1), as summarized in Table 2. The length of the covalent bond of the neutral H–F decreased with increases of the size of the clusters F\(^{-}\)(HF)\(_n\), while the length of the hydrogen bond between F\(^{-}\) and HF increased with increasing cluster sizes. The results of the binding energy and bond length calculated in this study support the \(E_{\text{CM}}\) values and the order of the energy for the loss of HF from the cluster ions F\(^{-}\)(HF)\(_n\), i.e., F\(^{-}\)(HF)\(_3\)>F\(^{-}\)(HF)\(_2\)>F\(^{-}\)(HF)\(_2\)>F\(^{-}\)(HF).

**Stability of O\(_{2}^{-}\)(HF)\(_n\) (n=1–4) based on \textit{ab initio} calculations**

As described above, the APCDI mass spectrum of the HF cluster associated with F\(^{-}\) and O\(_{2}^{-}\) ions did not exhibit any peak corresponding to cluster ions of the Y\(^{-}\)(HF)\(_n\) (Y=F, O\(_2\)) type larger than \(n=3\) (Fig. 2a), although Groenewold et al. have suggested that F\(^{-}\)(HF)\(_n\) could not be observed owing to the weak binding energy of HF to F\(^{-}\)(HF)\(_n\).\(^{10}\) In order to examine the stability of the superoxide/HF cluster ions O\(_{2}^{-}\)(HF)\(_n\) (n=1–4), we calculated the bond length of O\(_{2}^{-}\)(HF)\(_n\) and O\(_2\)H–F using DFT calculations. The most stable structures of each cluster for \(n=2\) and 3 were zig-zag forms; thus, the bond lengths were calculated on the basis of the zig-zag structures (Scheme 2), and they are summarized in Table 3.

The calculated bond length of O\(_2\)H–F decreased upon increasing of the cluster size \(n\), while that of O\(_2\)H–F increased with increasing cluster sizes. The short bond length equal to 1.007 Å for O\(_2\)H–F(HF)\(_3\) and the long bond length of 1.562 Å for O\(_2\)H–F(HF)\(_n\) suggested that neutral O\(_2\)H detaches from the cluster ion O\(_2\)H–F(HF)\(_n\), since the bond length (1.562 Å) of O\(_2\)H–F(HF)\(_n\) is much longer than that of neutral H–F (0.922 Å). The absence of the peak corresponding to the cluster ion O\(_2\)H–F(HF)\(_n\) in Fig. 2b may be due to a less stable structure of the ion, which may be separated into O\(_2\)H and F\(^{-}\)(HF)\(_3\) under the present experimental conditions.

**CONCLUSION**

In order to study the properties of strong hydrogen-bonded systems, a homemade generator of HF was assembled and its use was combined with atmospheric pressure corona discharge ionization mass spectrometry. The negative-ion APCDI MS combined with the H/HF generator allowed the formation of complex cluster ions such as F\(^{-}\)(HF)\(_n\) (n=1–3), O\(_2\)H–F(HF)\(_n\) (n=1–3), HCO\(_2\)H–F(HF)\(_n\) (n=1, 2), and O\(_2\)H–F(HF)\(_n\)+HCOOH\(_n\) (n=1, 2). The CID spectra of hydrogen-bonded HF cluster anions F\(^{-}\)(HF)\(_n\) (n=1–3) indicated the formation of product ions F\(^{-}\) at \(m/z\) 19, F\(^{-}\)(HF) at \(m/z\) 39,
and F(HF) at m/z 59, depending on the collision energy and the size of the HF clusters. The $E_{\text{CM}}$ values for the loss of HF from F(HF)$_n$, F(HF)$_2$, and F(HF) ions were 1 eV or lower, 1 eV or higher, and 2 eV, respectively. The $E_{\text{CM}}$ energies estimated above were in good agreement with the energy and bond length data obtained by ab initio calculations. The ab initio calculations of the cluster ions O$_2$(HF)$_n$ (n = 1–4) indicated that the ion [O$_2$(HF)$_3$]$^-$ possessed the structure O$_2$H⋯F⋯(HF)$_3$, while the absence of the F(HF)$_4$ ion peak in Fig. 2b was due to the weak bonding energy of HF to F-(HF)$_3$.^10^}

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