

Original Article

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 $F^-(HF)_3$, $F^-(HF)_2$, and $F^-(HF)$ 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 $O_2H-F^-(HF)_n$ and $O_2^-(HF)_n$ obtained by *ab initio* calculations. The calculations indicated that $[O_2(HF)_4]^-$ separated into O_2H and $F^-(HF)_3$.



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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 $H_3O^+(H_2O)_n$ and $Y^-(H_2O)_n$ ($Y=OH, O_2, CO_2$),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 A strong-hydrogen bonding (SHB) can be distinguished from a weak-hydrogen bonding (WHB) by means of the bond energy (WHB <30 kJ/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 asym-

metric 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.⁸ The HF cluster negative ions have been studied from the standpoints of the electron and hydrogen transfer⁹ 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.⁶ Here, in order to study the properties of strong hydrogen-bonded systems,

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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^\cdot 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 home-made generator for H^\cdot /HF species. The H^\cdot /HF generator consisted of an ultraviolet (UV) light source incorporating 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_2 molecules dissociated into hydrogen atoms H^\cdot 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^\cdot 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^\cdot from the PTFE tape in view of the dissociation energies of C–F (5.07 eV) and H–F (5.89 eV).

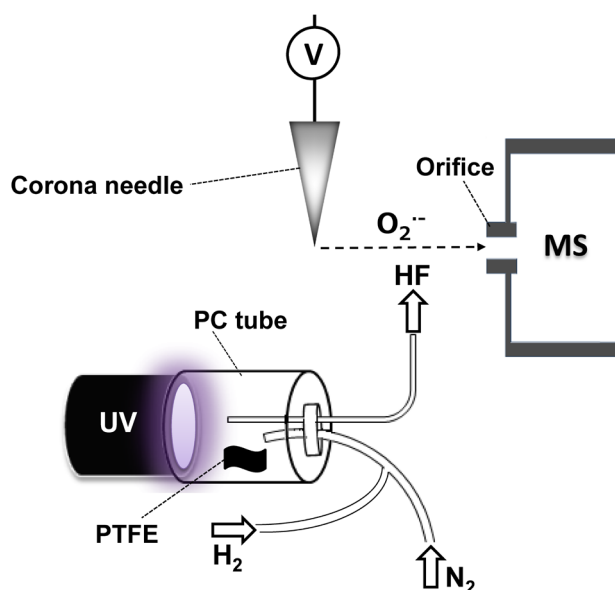
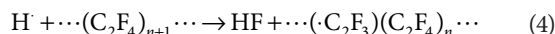
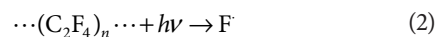


Fig. 1. Schematic illustration of APCDI mass spectrometer (upper) combined with a generator of hydrogen atoms H^\cdot and hydrogen fluoride HF under atmospheric pressure conditions (lower).



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.¹¹ The corona discharge experiments for generating negative atmospheric core ions Y^- ($Y=O_2, HO_x, NO_x, CO_x$)^{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 $\pi/2$ 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_{lab}) 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_{lab}) was set by the Q2-rod offset voltage, and then the E_{CM} was determined according to the equation $E_{CM} = E_{lab} [m_t / (m_t + m_p)]$, where m_t 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 B3LYP^{13,14} level of

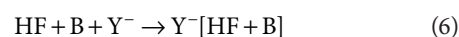
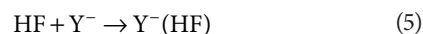
theory and 6-311++G(2d,p) basis set in the Gaussian 09¹⁵ suite of programs. The initial structures of HF, $F^-(HF)_n$, and $O_2^-(HF)_n$ were generated using CS Chem3D Ultra (Cambridge Soft, Cambridge, MA, USA). The input file was minimized under a semi-empirical MO (PM7) run through a Winmoster interface using MOPAC2012.

RESULTS AND DISCUSSION

Formation of hydrogen fluoride anion clusters $F^-(HF)_n$ 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 $Y^-(H_2O)_n$,¹¹ although the source of the carbon atoms of CO_x and HCO_x ions has not been yet 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 $O_2^-(HF)_n$ ($n=1-3$), $O_2^-[(HF)_n+HCOOH]$ ($n=1, 2$), and $HCO_2^-(HF)_n$ ($n=1, 2$). 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_2CO_3, HCO_2, HO_2 , and HNO_3)¹² 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.¹² 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.



Regarding the formation of fluoride anion clusters $F^-(HF)_n$, 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),¹⁶ higher stability of the cluster ion $F^-(HF)_n$ than $(HF)_{n+1}$ and $(HF)_n$,⁹ and thermochemical data (16.12 eV for $HF \rightarrow F^- + H^+$,¹⁷ 1.99 eV for $F^-(HF) \rightarrow F^- + HF$),⁶ the overall process (7a and 7b) may occur as an exothermic reaction to

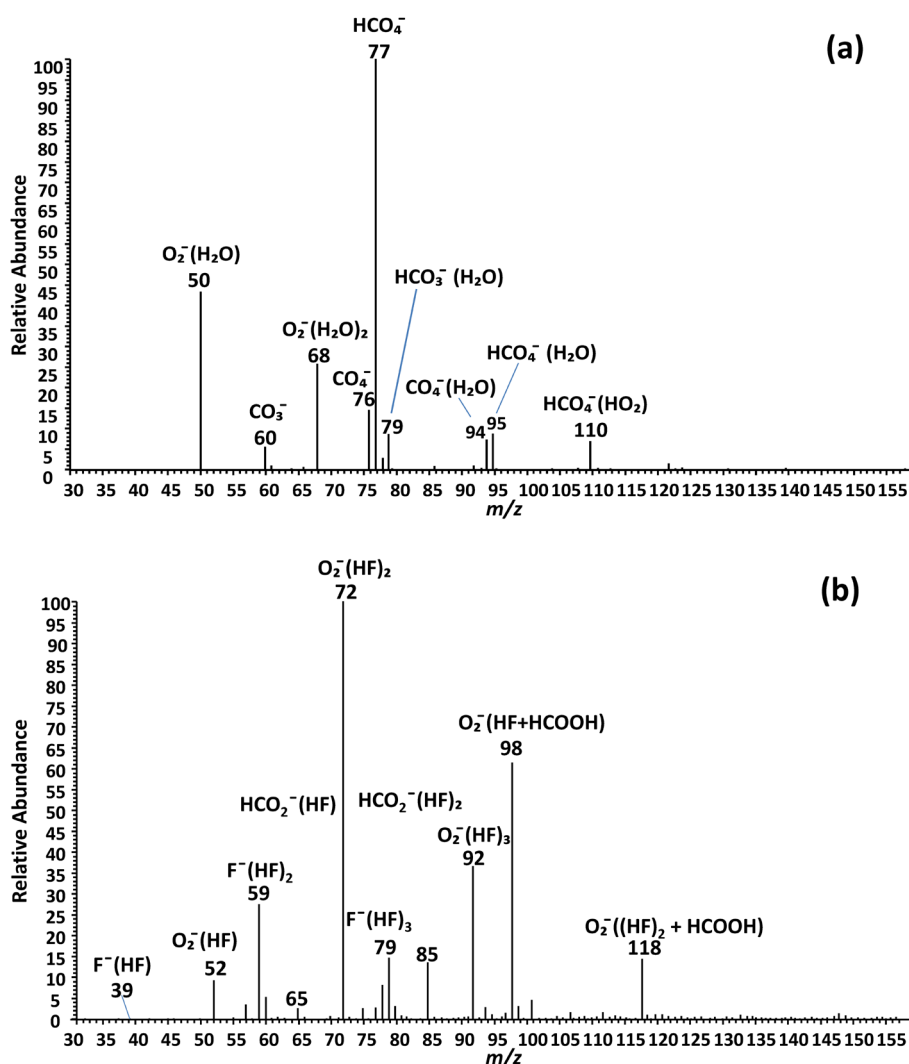
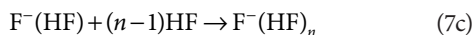
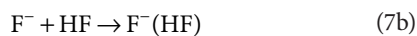
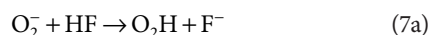


Fig. 2. Negative-ion APCDI mass spectra of (a) background (without HF supply) and (b) hydrogen fluoride molecules $(HF)_n$ associated with preformed core ions Y^- generated with corona discharge.

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).



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_{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 $15\text{ eV}/E_{lab}$ exhibited a peak corresponding

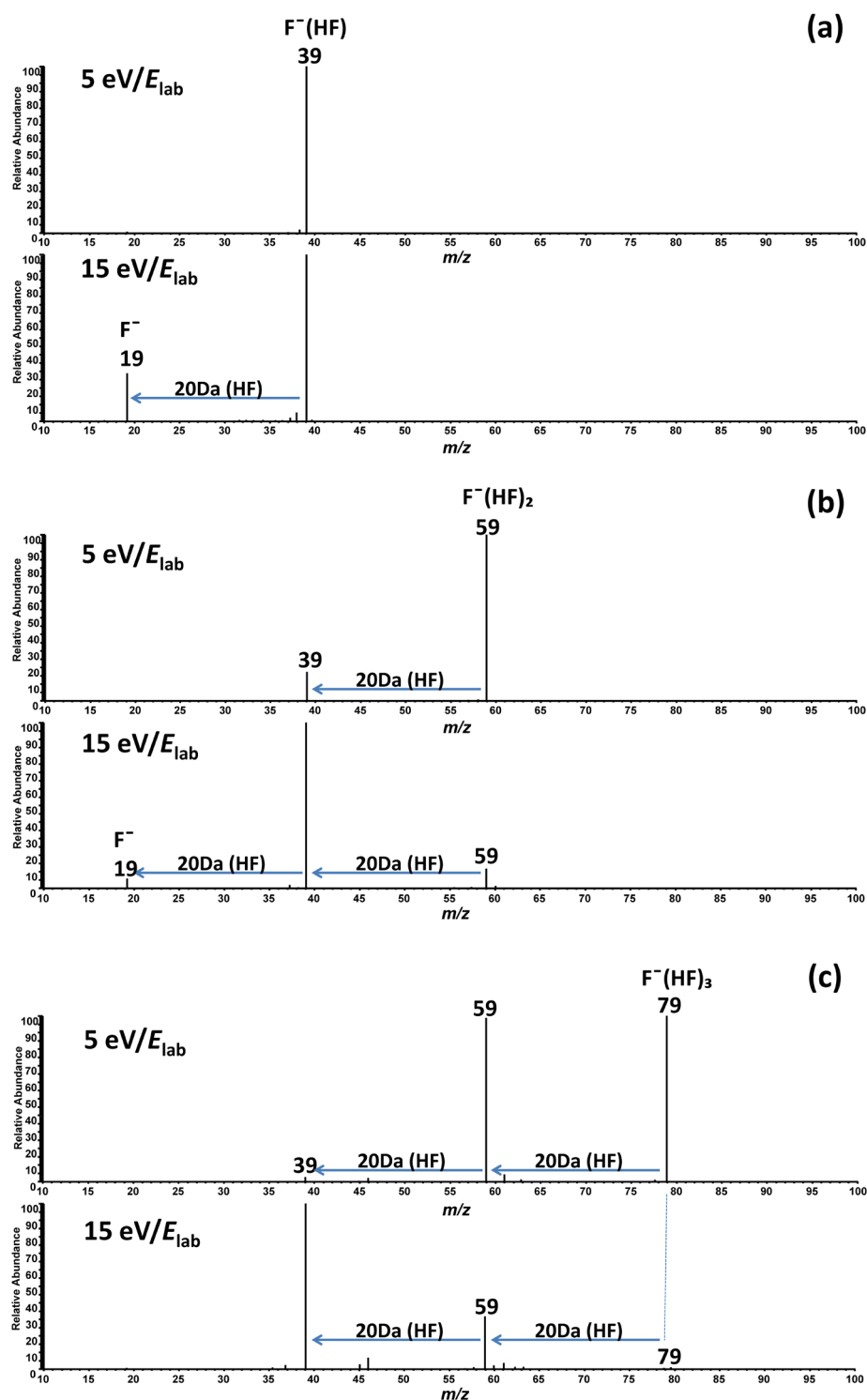


Fig. 3. The CID spectra of fluoride anion clusters $F^-(HF)_n$ obtained with laboratory frame collision energies 5 and 15 eV for the precursor ions of (a) $F^-(HF)$ at m/z 39, (b) $F^-(HF)_2$ at m/z 59, and (c) $F^-(HF)_3$ at m/z 79.

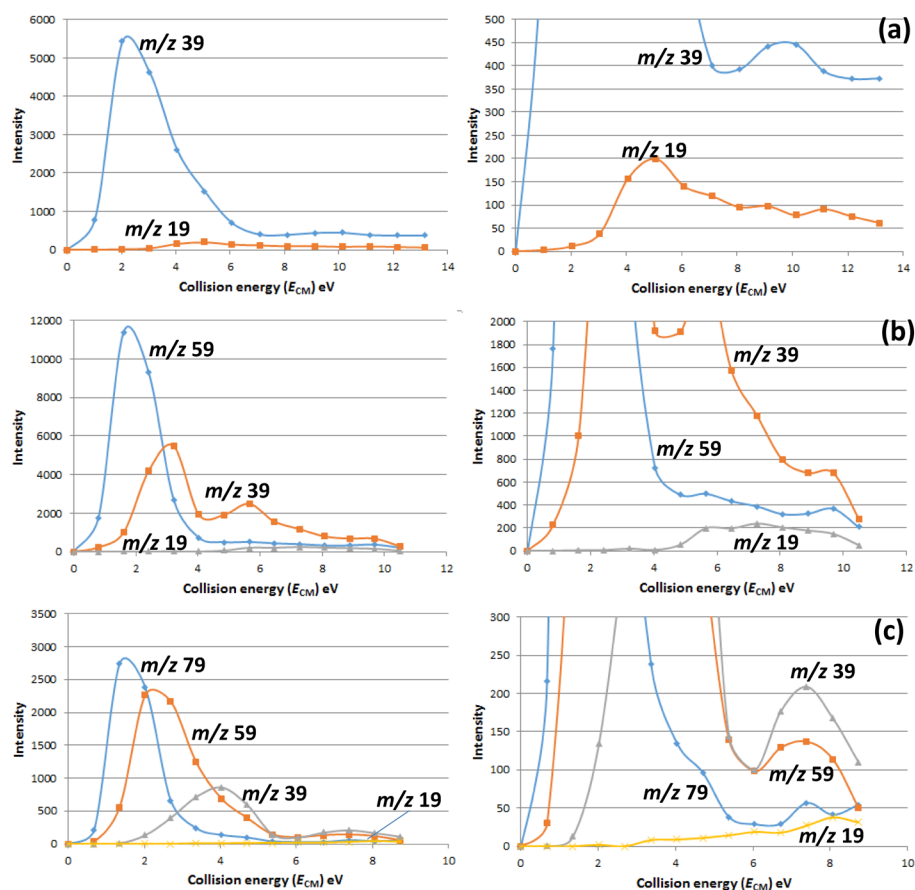


Fig. 4. Breakdown diagrams obtained with CID experiments of $F^-(HF)_n$ ($n=1-3$) for the precursor ions of (a) $F^-(HF)$ at m/z 39, (b) $F^-(HF)_2$ at m/z 59, and (c) $F^-(HF)_3$ at m/z 79. Right hand side represents enlarged diagram in intensity.

Table 1. Energies for the loss of HF from the fluoride cluster ions $F^-(HF)_3$, $F^-(HF)_2$, and $F^-(HF)$, estimated from the CID experiments, *ab initio* calculations and other reports.

Precursor	Products	E_{CM}^a (eV)	Calc. ^{b)} (eV)	Other report
$F^-(HF)_3$	$F^-(HF)_2+HF$	1 or lower	0.995	0.82–1.0 ⁽¹⁰⁾
$F^-(HF)_2$	$F^-(HF)+HF$	1 or higher	1.308	
$F^-(HF)_1$	F^-+HF	2	2.048	1.99 ⁽⁶⁾

^{a)} E_{CM} estimated from the CID experiments performed in this study.

^{b)}Dissociation energy calculated in the course of this study.

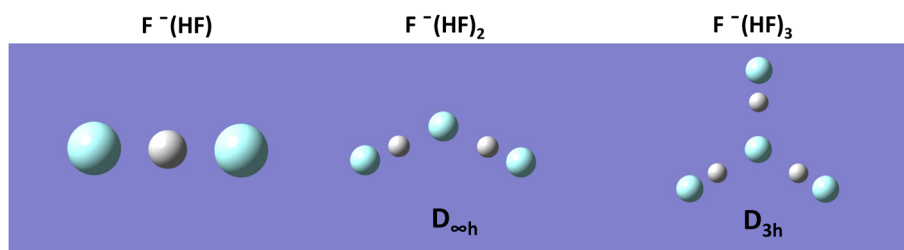
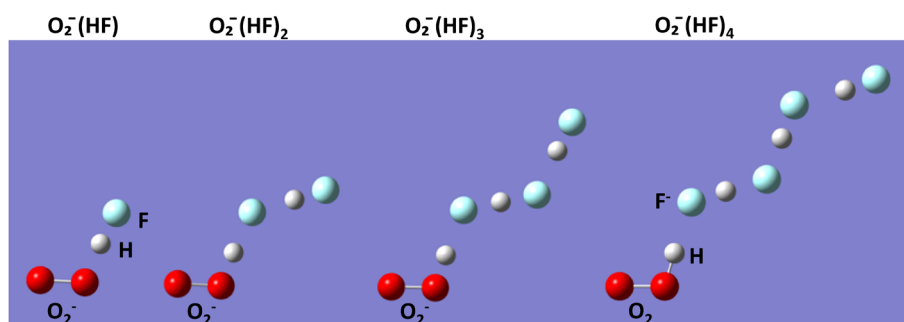
to the fluoride anion F^- , while those with $5\text{ eV}/E_{lab}$ did not show such peak (Figs. 3a and 3b). The peak corresponding to the fluoride ion F^- was also absent in the CID spectrum of $F^-(HF)_3$ (Fig. 3c), suggesting an insufficient internal energy of the precursor ion $F^-(HF)_3$. With regard 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 $2\text{ eV}/E_{CM}$ or higher (Fig. 4a). The estimated energy was consistent with the E_{CM} value of 1.99 eV reported by Wenthold and Squires.⁽⁶⁾ 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 $1\text{ eV}/E_{CM}$ or lower to form

the product ions $F^-(HF)$ and $F^-(HF)_2$, 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 $1\text{ eV}/E_{CM}$ 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 $F^-(HF)_3 < F^-(HF)_2 < F^-(HF)$.

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,⁽⁸⁾ nuclear magnetic resonance (NMR) in the liquid state,⁽⁹⁾ and *ab initio* calculations under vacuum.⁽⁹⁾ The IR solid-state study suggested that the $F^-(HF)_3$ species possesses the highest clustering number $n=3$.⁽⁸⁾ 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.⁽⁹⁾ On the other hand, the *ab initio* calculations indicated that limited zig-zag chains such as $FH\cdots F^- \cdots HF$ and $FH\cdots F^- \cdots HF\cdots HF$ are more stable than $(HF)_3^-$ and $(HF)_4^-$, respectively.⁽⁹⁾ With regard to the structure of the cluster $F^-(HF)_3$, Groenewold *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 *ab initio* calculations.⁽¹⁰⁾ The authors emphasized that the further addition of HF to $F^-(HF)_3$ could not be observed in the gas-phase owing to a

Scheme 1. Geometry of the cluster ions $F^-(HF)$, $F^-(HF)_2$, and $F^-(HF)_3$.Scheme 2. The zig-zag structure of $O_2^-(HF)_1$, $O_2^-(HF)_2$, $O_2^-(HF)_3$, and $O_2^-(HF)_4$.Table 2. Calculated bond length of H-F and F^--HF for the cluster ions $F^-(HF)$, $F^-(HF)_2$, and $F^-(HF)_3$.

	$F^-(HF)$	$F^-(HF)_2$	$F^-(HF)_3$
Bond length of H-F (Å)	1.148	1.013	0.980
Bond length of F^--HF (Å)	1.148	1.345	1.451

Table 3. Calculated bond length of O_2^--HF and O_2H-F for the cluster ions $O_2^-(HF)_n$ ($n=1-4$).

	$O_2^-(HF)$	$O_2^-(HF)_2$	$O_2^-(HF)_3$	$O_2^-(HF)_4$
Bond length of O_2^--HF (Å)	1.320	1.073	1.026	1.007
Bond length of O_2H-F (Å)	1.076	1.340	1.471	1.562

weak binding energy. Actually, the cluster ion $F^-(HF)_4$ as well as larger clusters could not be detected in the present study. The E_{CM} estimated here (Table 1) were well consistent to the reports of Wenthold and Squires⁶ and Groenewold *et al.*,¹⁰ although the E_{CM} just only gives maximum energy contents or rough values.

Herein, we calculated the binding energies of F^--HF , $F^-(HF)-HF$, and $F^-(HF)_2-HF$ by using an *ab initio* method, as summarized in Table 1. The E_{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 $D_{\infty h}$ and D_{3h} 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_{CM} values and the order of the energy for the loss of HF from the cluster ions $F^-(HF)_n$, *i.e.*, $F^-(HF) > F^-(HF)_2 > F^-(HF)_3$.

Stability of $O_2^-(HF)_n$ ($n=1-4$) based on *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 $F^-(HF)_4$ could not be observed owing to the weak binding energy of HF to $F^-(HF)_3$.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_2H-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^--HF decreased upon increasing of the cluster size n , while that of O_2H-F increased with increasing cluster sizes. The short bond length equal to 1.007 Å for $O_2^--HF(HF)_3$ and the long length of 1.562 Å for $O_2H-F(HF)_3$ suggested that neutral O_2H detaches from the cluster ion $O_2^-(HF)_4$, since the bond length (1.562 Å) of $O_2H-F(HF)_3$ is much longer than that of neutral H-F (0.922 Å). The absence of the peak corresponding to the cluster ion $O_2^-(HF)_4$ in Fig. 2b may be due to a less stable structure of the ion, which may be separated into O_2H 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 $F^-(HF)_n$ ($n=1-3$), $O_2^-(HF)_n$ ($n=1-3$), $HCO_2^-(HF)_n$ ($n=1, 2$), and $O_2^-[(HF)_n+HCOOH]$ ($n=1, 2$). 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 $F^-(HF)_2$ at m/z 59, depending on the collision energy and the size of the HF clusters. The E_{CM} values for the loss of HF from $F^-(HF)_3$, $F^-(HF)_2$, and $F^-(HF)$ ions were 1 eV or lower, 1 eV or higher, and 2 eV, respectively. The E_{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 $[O_2(HF)_4]^-$ possessed the structure $O_2H \cdots F \cdots (HF)_3$, 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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