Hydration Structure of the Strongly Bound Water on the Sulfonic Acid Group in a Nafion Membrane Studied by Infrared Spectroscopy and Quantum Chemical Calculation

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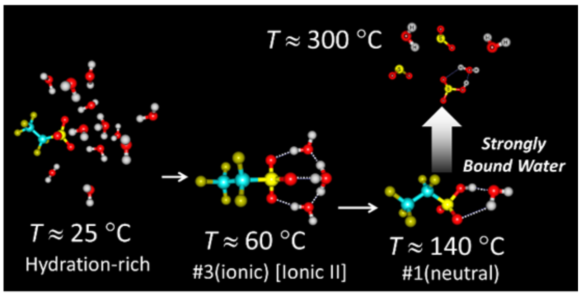

Abstract:

The hydration structure of ‘the strongly bound water’ about the sulfonic acid (SA) groups in Nafion, which has recently been revealed by ^{1}H NMR spectroscopy (*Anal. Chem.* **2013**, *85*, 7581.), is studied by using infrared spectroscopy with an aid of quantum chemical (QC) calculations. During a heated drying process, bulky water is firstly dehydrated, successively followed by the disappearance of the hydronium ion, and the appearance of some bands that have been assigned to the fully dehydrated species at 140 °C. A spectral simulation based on QC reveals, however, that the spectrum at 140 °C comes from the SA group associated with a single-water molecule via two H-bondings. This implies that a thoroughly dried membrane is unavailable even at 140 °C, and the involved water corresponds to ‘the strongly bound water.’ The QC-analytical results are experimentally confirmed by the evolved gas analysis mass spectrometry (EGA-MS). At ca. 300 °C, which is the temperature where the SA group is selectively decomposed, the molecular fragment of SO_2 is observed accompanying water molecules as expected. This confirms that the last single-water molecule can remain on the SA group until the thermal decomposition. (189 words)

Introduction: Nafion® consists of a polytetrafluoroethylene backbone and perfluoroalkyl ether side chains terminated with a sulfonic acid (SA) group (Chart 1). Since a perfluoroalkyl group strongly draws the electrons from the SA group, the SA group is ready for ionization on hydration. When the membrane is adequately hydrated, the water molecules play a role of stabilizing the dissociated proton from the SA group. In this manner, Nafion comprises both electrically neutral backbone and the ionized SA groups, which is useful as an ionomer. The dissociated proton involved in a hydrated cluster is the origin of the 'proton transportation,' which is a representative characteristic of a Nafion membrane. To improve the performance of Nafion, many researches are involved in the analysis of the ionomer structure.[1-7]

It is widely believed that the ionized groups aggregate to form a spherical cluster, and the clusters are considered to be embedded in a hydrophobic matrix made of the perfluoroalkyl chains.[1-5] The ionomer structure has been discussed by using a thermal analytical technique,[1] mechanical and dielectric relaxation,[1] small-angle X-ray (SAX),[1,2] transmission electron microscopy,[3] and NMR.[4] In particular, SAX makes a great contribution to reveal the ionomer structure: spectral simulations fitted to the SAX data provide a cluster size and a distance between the clusters. Gierke et al. proposed 'the cluster-network model'[6] to correlate the proton transportation with the ionomer structure. According to this model, the ionic clusters should be connected by thin tubes with each other, since the involved water molecules favor the hydrophilic clusters and the tubes, and the hydronium ion should move through the limited hydrophilic regions. Gebel further investigated the cluster structure in Nafion with a change of humidity using the SAX and neutron scattering techniques, and the evolution of ionomer structures from the dry states to the water swollen state was revealed.[7] Although this model is widely accepted, the molecular scheme of the proton transportation has not fully been revealed yet.

Since the performance of the proton transportation largely depends on the hydration,[8-16] the molecular scheme has to be revealed with related to the molecular structure. Infrared (IR) spectroscopic analysis is one of the most appropriate experimental approaches to reveal the hydration structure. Iwamoto et al.[8] reports that a drying process of a wet Nafion membrane can be pursued by IR spectroscopy, and the hydration waters are discriminated into 'two' species: hydrated and free-water species about the SA group. They discuss the dissociation equilibrium of the sulfonic acid group using some key IR bands. In a similar manner, conventional studies on the hydration about the SA group, the two water species have commonly been pointed out by using different analytical techniques.

In our recent study, ^{1}H NMR spectroscopy was employed to reveal the hydration process of a Nafion membrane by measuring both the chemical shift and the spin-lattice relaxation time.[17] The results revealed that the hydration process consists of "three" discriminative steps with largely different rotational dynamics. By analyzing the spin-lattice relaxation time (T_1), the second and third stages correspond to the conventionally known hydrated and free-water species, respectively. The rotation-correlation time obtained by T_1 indicates that the molecular motion of the hydrated water is about 10^3 times restricted than the free water.

The newly found water species, on the other hand, appears on the first stage of the hydration process. The molecular motion of the first-stage water has about 25 times slower rotational motion than the motion-restricted hydration water, which indicates that the first-stage water should strongly be bounded on the SA group in an extraordinary manner. In this manuscript, the first-water species is thus called “strongly bound water.” In this fashion, ^{1}H NMR has a great advantage that different water species can be distinguished in terms of molecular motion. Unfortunately, however, the binding structure of each species cannot be revealed.

In the present study, IR spectroscopy has been employed to investigate the dehydration process of Nafion, and the binding structures of the three water species are all discussed. In particular, the hydration structure of the newly found ‘strongly bound water’ in a highly dried condition is focused. To analyze the IR spectra, spectral simulations after the structural optimization based on quantum chemical (QC) calculation are employed. In addition, mass spectroscopy (MS) is employed to confirm the analytical results by QC calculation. Through the precise analysis, the assignments of the fine IR bands have also been revealed.

Experimental:

Materials: The sample membrane was a Sigma-Aldrich (St. Louis, MO, USA) Nafion NRE-212 membrane. The membrane was cut into a piece with a size of 10 mm x 10 mm. To remove contaminants such as Mg and Fe, the sample was washed by a 3% H_2O_2 aqueous solution at 100 °C for

1 h and by a 1M H_2SO_4 aqueous solution at 100 °C for 1 h, which was rinsed by pure water.[8] The sample membrane was dried in an oven at 40 °C for 12 h. A commercial reagent of 30 % H_2O_2 and a concentrated H_2SO_4 were purchased from Wako Pure Chemical Industries (Osaka, Japan). Pure water was obtained by a Millipore (Molsheim, France) Elix UV-3 pure-water generator and a Yamato (Tokyo, Japan) Autopure WT100U water purifier. The water exhibited an electric resistivity higher than 18.2 MΩ cm.

IR Measurements: IR spectra were recorded on a Jasco (Tokyo, Japan) Model FT/IR-6100 FT-IR spectrophotometer equipped with a mercury cadmium telluride (MCT) detector by coaddition of 200 interferograms at a wavenumber resolution of 4 cm^{-1}. The modulation frequency was 13 kHz. The inside of the spectrometer was air-purged by continuously flowing dry air generated by an Air-Tech (Yokohama, Japan) AT-35H dried-air generator.

The membrane was tightly pressed on a germanium plate by an O-ring for a good thermal contact, which was set on a Harrick (Pleasantville, NY, USA) TMC-M13 temperature control cell for the IR transmission measurements. The measurement temperatures were set at 25, 60, 80, 100, 120 and 140 °C. Since the membrane on the O-ring side is always exposed to the dry air, the desorbed water molecules can get away from the membrane.

QC Calculation: QC calculations were performed by using the Gaussian 09 program.エラー! 参照元が見つかりません。 Perfluoroethyl sulfonic acid (PSA) was used as the model compound. The optimal geometry, harmonic wavenumbers, and IR intensities were obtained by the density functional theory

(DFT) using the 6-31++G(d,p) basis set. For the DFT calculations, Becke's three-parameter exchange functional together with correlation functional of Lee-Yang-Parr (B3LYP) was employed.[18] Harmonic wavenumbers, $\tilde{\nu}_{\text{harm}}$, obtained by the DFT calculations were corrected to be the scaled wavenumber, $\tilde{\nu}_{\text{scaled}}$: $\tilde{\nu}_{\text{scaled}} = 0.9613 \cdot \tilde{\nu}_{\text{harm}}$.[20]

MS Measurement: The mass (MS) spectrometric analysis of the Nafion membrane was performed by using an evolved-gas analysis (EGA)-MS spectrometer. In the EGA equipment, 3 mg of Nafion was thermally decomposed (pyrolized), and the decomposed gas is led into the MS spectrometer. The EGA equipment was a Frontier Lab (Fukushima, Japan) PY-2020D temperature-programmable pyrolyzer, which was coupled with a (Agilent, Santa Clara, CA, USA) MSD5975 quadropole MS via a (Agilent) FS Deactivated fused-silica capillary tube with a size of 0.25 mm i.d. × 30 m.

The long transfer capillary tube was homogeneously heated at 250 °C by using a GC-MS interface. All the EGA parts (Py-GC interface, GC inlet and GC/MS interface) were kept at 250 °C. The Nafion membrane set in the pyrolyzer was heated at 40 °C for 15 min at the initial stage, followed by raising the temperature up to 450 °C with a rate of 10 °C min^{-1}. The carrier gas introducing the evolved gas into the capillary was high-purity helium, and the flow rate was 20 mL min^{-1}. The continuous flow of the gas was split by a splitter down to a volume of 1 mL, and each volume was analyzed by MS. The ionization in MS was carried out by the electron impact (EI) method at 70 eV, and a mass range between 10 and 800 u was chosen for the scanning.

Results and Discussion:

Dehydration about the SA group at 60 °C: Fig. 1 presents time-dependent IR transmission spectra at 60 °C during a dehydration process until reaching the thermal equilibrium. The band at ca. 1710 cm^{-1} is assigned to the asymmetric OH_3^+ deformation vibration ($\delta(OH_3^+)$) band.[8,9,21] The large bandwidth indicates that the hydronium ion accompanies additional water molecules with a variety of hydrogen bondings. Since the cationic species is formed after the water receives a proton out of the SA group, the appearance of this band strongly indicates that the SA groups should be anionized to be the 'sulfonate' group. Another support of this discussion is the appearance of the ionic marker band at 1061 cm^{-1}, which is assigned to the symmetric SO_3^- stretching vibration mode.[9,21,22]

The spectrum at the equilibrium has no component of the bulk water at 3447 cm^{-1}, which is found at 25 °C (dotted line), in the O–H stretching vibration (ν(OH)) region. Since the sulfonate group yields no ν(OH) bands, the ν(OH) band mainly comes from the hydronium ions. In the drying process with time at 60 °C, the ν(OH) band exhibits a continuous change showing an apparent isosbestic point, which indicates that the change should be an exchange of two ionic species (Ionic I → Ionic II). Note that an exchange from an ionic species to the neutral SA group is denied, since the symmetric SO_3^- stretching vibration band at 1061 cm^{-1} stays during the change.

Another notable band is the band at 2200 cm^{-1}, which develops during the dehydration. Although this band has sometimes been attributed to an overtone mode correlated with the vibration mode of a hydronium ion,[21,22] QC calculations were thus carried out for four hydronium-ion species ($H_{2n+1}O_n^+$: n =

1~4), and only $H_7O_3^+$ (n = 3) reproduces a similar band at 2295 cm^{-1}, which corresponds to the asymmetric OH_3^+ ($\nu_a(OH_3^+)$) stretching vibration mode (not an overtone).[23] This result agrees with a report in a previous study.[24] Since the rest species cannot reproduce the band, the Ionic II band can temporally be attributed to $H_7O_3^+$; whereas the Ionic I band corresponds to hydration-rich hydronium ions, which is confirmed later. In short, in the drying process at 60 °C, the hydrated ions are dehydrated down to $H_7O_3^+$.

On the other hand, the spectra at 60 °C exhibit no change in the finger print region. In the present study, the C–F stretching vibration (ν(CF)) bands are not discussed, so that only the hydration about the SA group would readily be focused on. Since the ν(CF) modes yield very strong band intensities, the bands are saturated in the IR transmission spectra as found in Fig. 1.

Dehydration of the Membrane with Increasing Temperature: After the IR measurements at 60 °C, similar measurements were carried out at 80, 100, 120 and 140 °C. Fig. 2 presents IR spectra after attaining the thermal equilibrium state at each temperature. In the ν(OH) band region, the ionic II band decreases with an increase of temperature, and the band shifts to a higher wavenumber reaching at 3036 cm^{-1}, which has the same position of the ν(OH) band of pure liquid of CF_3SO_3H.[21] Since the SA group of this molecule is considered to have the neutral form in the pure liquid, the appearance of the same band for Nafion indicates that the SA group in the membrane at 140 °C is also neutralized. This discussion is supported by the disappearance of the Ionic II band at 2200 cm^{-1}. Of another note is that the band at 2382 cm^{-1} appears at 120 °C and develops at 140 °C. This band is assigned to the ν(OH) mode of hydrogen-bonded neutral SA group[21], which also supports the neutralization of the SA group.

In contrast to the spectral changes at the fixed temperature of 60 °C, the temperature-dependent spectra exhibit a drastic change in the finger print region. The magnified spectra of the region are presented in Fig. 2b. The band at 1061 cm^{-1}, the ionic-marker band, decreases above 100 °C, and almost disappears at 140 °C. If the assignment of this band is truly correct, nearly all sulfonate groups should be neutralized to be the SA group at the temperature. At the same time, no hydronium ion should remain in the membrane. On disappearance of the band at 1061 cm^{-1}, two new bands at 1414 cm^{-1} and 907 cm^{-1} appear at 80 °C. Therefore, the two bands are regarded as the 'neutral marker.' In addition, on closer inspection, complicated spectral changes are found in this temperature region: the band at ca. 907 cm^{-1} has another component at a lower position at 140°C, and the band component at 969 cm^{-1} is lost at the temperature. These complicated spectral variations indicate that only the marker bands are insufficient to fully discuss the chemical changes in the membrane on heating. Since these minute spectral changes have not been discussed previously, spectral simulations based on QC calculation are performed.

Assignment of IR Bands of the SA group by QC Calculation: The spectrum at 140 °C presented in Fig. 2 is often considered to correspond to a thoroughly dried Nafion membrane,[21,22] in which the neutralized SA group has completely released water. If this model is correct, $CF_3CF_2SO_3H$ associated with no water[26] should reproduce the IR spectrum at 140 °C by QC calculation. Although QC calculation takes a single molecule in vacuum into account, the outstanding marker bands are expected to be reproduced at least qualitatively. The calculated IR spectrum is presented in Fig. 3b.[25a] For comparison, the experimental results at 60 °C and 140 °C are presented in Fig. 3a. The notable bands at 1414 and 982 cm^{-1} are roughly reproduced by the calculation; whereas the important key band at 906 cm^{-1} is not reproduced at all. Here, we have to recall the conclusion in the previous section that the sulfonate group is in the neutral form. Then, we have a question whether the water molecules should completely be removed from the SA group to keep it neutral. In other words, are only a few water molecules adequate to make the SA group anionized?

To answer this question, various combinations of the SA/water pairs and the sulfonate/hydronium ionic pairs were calculated by the DFT method. In Fig. 4, the representative pairs are shown. The optimal structures of the SA/water pairs are shown in Fig. 4d-f for the three complexes having one, two and three water molecules ($R\text{-}SO_3H\cdot(H_2O)_n$: n = 1~3), respectively. In a similar manner, the optimal ionic-pair complexes are shown ($R\text{-}SO_3^-\cdot H^+(H_2O)_n$: n = 1~3).

Here, the energetic stability of #3(ion) to the neutral one (#3(neutral)) is discussed. To discuss the stability, the total energies, E, of the ionic and neutral pairs are calculated. E is defined as the summation of the electronic energy of molecule and the nuclear repulsive energy. The energy difference, $E(\text{ion}) - E(\text{neutral})$, is listed in the second column of Table 1. The energy difference, -12.08 kJ mol^{-1}, indicates that the ionic pair is more stable than the neutral one. The number ratio of the ionic species to the neutral one is calculated by using the Boltzmann factor with the energy difference, which is available in the third column of Table 1. Since the ratio of #3(ion)/#3(neutral) is 1.27×10^2, the ionic pair is the winner and the neutral pair can be ignored. In a similar manner, a molecular complex having more than three water molecules was found to be an ionic complex.

On the other hand, the ionic clusters of #1(ion) and #2(ion) exhibit totally different results. The energy difference of #2, 49.31 kJ mol^{-1}, indicates that the neutral pair is more stable than the ionic one, and the ratio of the amount of #2(ion) to that of #2(neutral) is 2.60×10^{-9}. This indicates that the ionic pair of #2 can be ignored. In other words, the dehydration of a water molecule from #3 to #2 is an important step of neutralization of the sulfonate group.

On the other hand, #1(ion) exhibits an unique result that the calculation result converges to a neutral form only, even when the initial structure is set to an ionic pair before the calculation. The optimal structure is presented in Fig. 4f. Just in case, the energy of an unoptimized ionic pair (Fig. 4c), which is found at a local minimum of energy slightly before attaining the global minimum, was calculated. In the same manner as #2 and #3, the energy difference and the existence ratio are calculated (Table 1). As a conclusion, at least three water molecules are found to be necessary to make the SA group anionized, which agrees with the appearance of the $\nu_a(OH_3^+)$ band at 2200 cm^{-1} correlated with the $H_7O_3^+$ (n = 3) discussed above. The optimizations are consistent with a previous report.[26] In this fashion, the optimal molecular clusters having various numbers of water are confirmed by QC calculations.[25 b]

On the confirmed structures, IR spectra are calculated as presented in Fig. 5b, in which #4(ion) and the water-free sulfonate ion spectra are also presented for reference.[25 c] The calculated spectra are highly complicated. For example, the S–O–H out-of-ring deformation (δ^{OR}(SOH)) vibration mode of #1(neutral) denoted by (1) in Fig. 5b shifts to a higher position largely by about 150 cm^{-1} induced by addition of only one water molecule (#2(neutral)). A similar large shift is found for the ν(SO) band, which shifts by about 50 cm^{-1} from #1(neutral) to #2(neutral). We have to note that the ν(SO) band of #2 is located at nearly the same position as the δ^{OR}(SOH) band (ca. 850 cm^{-1}) in Fig. 5b. This indicates that a spectral simulation based on QC is definitely necessary to discuss the complicated spectral change.

During the drying process, the number of water molecules about the sulfonate or SA group decreases, and the molecular clusters having various numbers of water should result in the IR spectra as an average. In other words, the IR spectra at the temperatures ‘except 140 °C’ in Fig. 5 should be an average of the calculated spectra. This further means that the spectrum of the heated sample at 140 °C could be referred to the spectrum #1(neutral). In fact, the spectrum #1(neutral) readily accounts for the IR spectrum at 140 °C. In the following, the spectral changes are elucidated step by step.

In a wet state, the ionic marker band at 1061 cm^{-1} are available in the IR spectra, which is reproduced by one or two peaks about 1000 cm^{-1} of #2(neutral), #3(ion) and #4(ion) in a dashed square. When the sample is heated up to 140 °C, the IR band disappears, which is reproduced by no peak in the square of the #1(neutral) spectrum.

As for the doublet band at ca. 970 cm^{-1}, the two components are reproduced by the nearly two positions of the 'wet' spectra of #2(neutral) or above. In addition, only the lower component at 968 cm^{-1} is lost on the heating, which is readily reproduced by the #1(neutral) spectrum.

In a similar manner, the change of the broad band at about 918 cm^{-1} is also reproduced by the calculation. This band comprises two components at 918 and 907 cm^{-1}, and the higher one stays at the same position irrespective of temperature; whereas the lower one appears only at 140 °C. The calculated 'wet' spectra have only one band mainly provided by #2(neutral); whereas the #1(neutral) spectrum yields two bands in the region.

The neutral marker band at about 1414 cm^{-1} is also reproduced by the calculated spectra. This band gradually develops with temperature, which means that the band intensity depends on the water quantity about the SA group. In fact, the band is reproduced by the δ(SOH) band in the #1(neutral) and #2(neutral) spectra. Of another interest is that IR spectra at a low temperature, for example at 60 °C, another very broad band appears at 1600 cm^{-1} or higher. The broad band is attributed to the δ(H_3O^+). Although the band is sharply obtained by the QC calculation, but in a real sample, the hydronium ion is surrounded by water molecules as discussed above, which makes the band highly broad because of various hydrogen bondings. Anyway, the loss of the δ(SOH) band in place of the appearance of the δ(H_3O^+) band are beautifully reproduced by the QC calculated spectra in the series.

In this manner, the QC calculated #1(neutral) spectrum is found to elucidate the IR spectrum at 140 °C. A conclusion is thus obtained that the IR spectrum at 140 °C does not correspond to the completely dried SA group, but to the #1(neutral) SA group where “a residual single water molecule remains (Fig. 4f).” Here, the water molecule involved in #1(neutral) has the “ring-like” structure, in which two positions (O and H) of the water molecule are fixed by the SA group via the hydrogen bonding. This rigid structure readily explains the extraordinarily long rotational correlation time revealed by the T_1 measurements using ^{1}H NMR.[17]

Evidence of the Residual Water by Mass Spectrometry: The IR analysis with an aid of QC calculation suggests that many SA groups possess a single water molecule even at 140 °C. To confirm this chemical model experimentally, the EGA-MS technique was employed. With the EGA technique, an evolved gas that contains the decomposed chemical fragments on heating is led to MS.

The red curve in Fig. 6 presents a time-dependent quantity change of the decomposed species of m/z = 18 which is assigned to H_2O. The light blue line for the right axis in Fig. 6 indicates a temperature change against time. On heating from 40 °C to 450 °C, three apparent hills are obviously found, which reminds us of the three water species previously found by ^{1}H NMR measurements.

The first water species is observed in the first hill at 40 °C; whereas the other species are not obtained in this region. [27] In the previous section, the first IR spectrum at 60 °C, which is immediately measured after elevating temperature from 25 °C, indicates that the bulk water has mostly been removed (Fig. 1). This indicates that the first water can be assigned to the ‘bulky water’.

After 15 min, MS measurements were carried out with elevating temperature at a constant rate of 10 °C min^{-1}. When the temperature reaches 60 °C, the second hill appears, and it is almost lost at ca.

190 °C showing the maximum at ca. 140 °C. In the previous section, IR and QC analyses reveal that only the ‘strongly bound water’ molecule remains, when the membrane is heated for a long time at 140 °C. Although IR and EGA-MS cannot directly be compared with each other due to the different sampling techniques, the membrane state at 190 °C in the MS measurements should be similar to that at 140 °C in the thermal equilibrium involving only ‘strongly bound water’ discussed in the IR section. Therefore, the second hill can be assigned to the ‘hydrated water’, which induces the neutralization of the sulfonate group in this process. It is notable that another fragment is not observed up to ca. 200 °C.[27] Therefore, the two discriminated dehydrations occur without thermal decomposition of the membrane at a temperature lower than 200 °C.

In an additional heating process, the third water begins to be desorbed at ca. 300 °C, which is a specific temperature where the SA group is selectively decomposed. The blue curve in Fig. 6 presents a time-dependent quantity change of the species of m/z = 64, which is assigned to the SO_2 species originated from the decomposed SA group. Although the curves of water and SO_2 species cannot be compared quantitatively due to the different ionization efficiency,[27] both species exhibit a synchronous change. This indicates that the last water molecule is kept maintained at the SA group up to 300 °C, and it comes out with the SA group on the decomposition, which strongly supports the ring-like structure. It is also worth noting that the SO_2 species keeps to appear after losing the third water, which indicates that not all the SA groups possess the third water.

The rest green curve in Fig. 6 indicates the quantity change of the species of m/z = 131 that corresponds to the CF_3 species coming from the thermally decomposed perfluoroalkyl ether component. The CF_3 species appears at ca. 320 °C[29] and it drastically increases at a temperature higher than 400 °C where the perfluoroalkyl ether component is finally decomposed, while water no longer appears.

In this manner, the MS measurements reveal that: (1) three water species expected by the ^{1}H NMR measurements are qualitatively confirmed, and (2) the third water proves to be kept maintained at the SA group until the thermal decomposition of the SA group, which strongly supports the results by IR and QC.

Conclusions: The dehydration process of a Nafion membrane has been investigated by infrared spectroscopy. The dehydration process revealed in the present study is summarized as follows. After the removal of the bulk water near the room temperature, 'Ionic I' species is the major component, which involves much hydration water about the sulfonate group. When the membrane is kept at 60 °C, Ionic I species decreases and 'Ionic II' species that contains three hydration water molecules is generated exhibiting an isosbestic point. During the change, the ionic marker band at 1061 cm^{-1} is always available. When the number of hydration water molecules decreases down to two, the sulfonate group becomes the neutral SA group, but the band at 1061 cm^{-1} is still available. In this sense, it is not correct that the band at 1061 cm^{-1} is called the ionic marker band, strictly speaking. When the membrane is heated for a long time at 140 °C, the number of hydration water decreases down to one, and the last water molecule remains in the ring-like structure of the SA group. At this step, the band at 1061 cm^{-1} disappears. The neutral marker band at 1414 cm^{-1} appears when the number of water molecules about the SA group is one and two; whereas the other neutral marker band at 907 cm^{-1} appears only when the number of water is strictly one.

This indicates that a thoroughly dehydrated Nafion is not obtained by heating, and the last one water molecule is correlated with the ‘strongly bound water’ proposed by ^{1}H NMR in a previous study. EGA-MS spectroscopy has revealed that the complex of the last water remains in the SA group until the thermal decomposition.

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23. The calculated spectra are presented in Fig. S1 in the ESI.

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25. Structural parameters of the optimized molecular clusters are listed in the tables of the ESI: (a) the structural parameters of $CF_3CF_2SO_3H$ corresponding to the spectrum in Fig. 3b are listed in Table S1, (b) the structural parameters of the molecular clusters in Fig. 4 are listed in Table S2, (c) the structural parameters of the optimized molecular cluster #4(ion) and the water-free sulfonate ion, which correspond to the spectra in Fig. 5 are listed in Table S3.

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27. Averaged EGA-MS spectrum of the Nafion membrane measured up to ca. 200 °C (from 0 min to 30 min) is presented in Fig. S2 in the ESI. In the spectrum, the water species (m/z = 18) is dominantly

observed. The N_2 and O_2 peaks are due to the residual air remained in the sampling compartment. Although the air also involves water molecules, their quantity gradually decays in the first 10 min in Fig. 6, and the strongly hydrated water can be distinguished from the decay curve by the sharp peak (the first hill).

28. The ionization cross section (ICS), which governs the ionization efficiency, of H_2O^+ is 19.9×10^{-17} cm^2 at the incident electron energy of 70 eV, and ICS of SO_2^+ is 31.2×10^{-17} cm^2. The incident energy of 70 eV can generate other fragments (SO^+, S^+, O^+). These indicates that the curves of water and SO_2 species in Fig. 6 cannot be discussed quantitatively.

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Table 1 Energy difference between the ionic and neutral pairs, and the number ratios as a function of hydration number

hydration number	*E*(ion) - *E*(neutral) / kJ mol^{-1}	$\frac{n(\text{ion})}{n(\text{neutral})}$
#3	-12.08	1.27×10^{2}
#2	49.31	2.60×10^{-9}
#1	99.76	4.28×10^{-18}

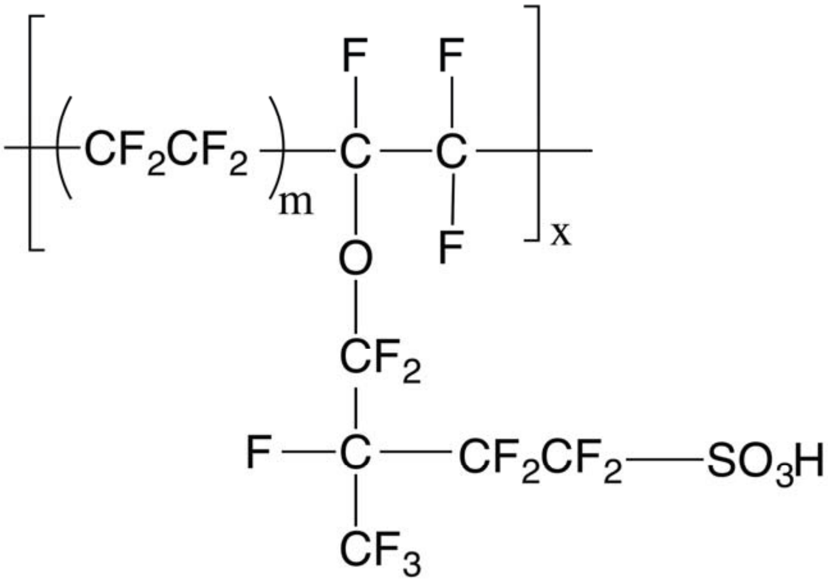

Chart 1 The primary chemical structure of Nafion.

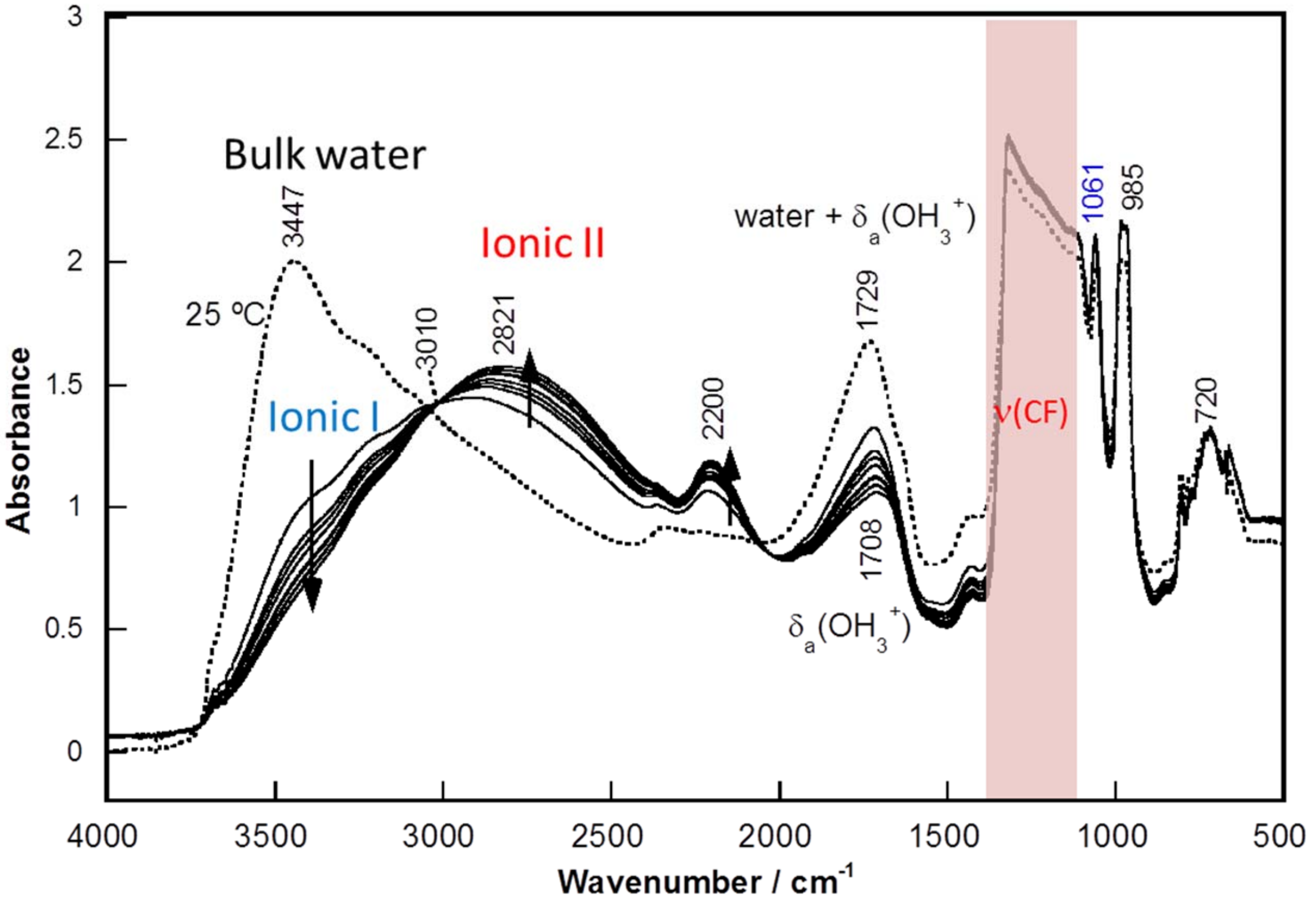

Fig. 1 IR spectra of the Nafion membrane in a dehydrating process at 60 °C. The spectrum by the dotted line is a result measured at 25 °C.

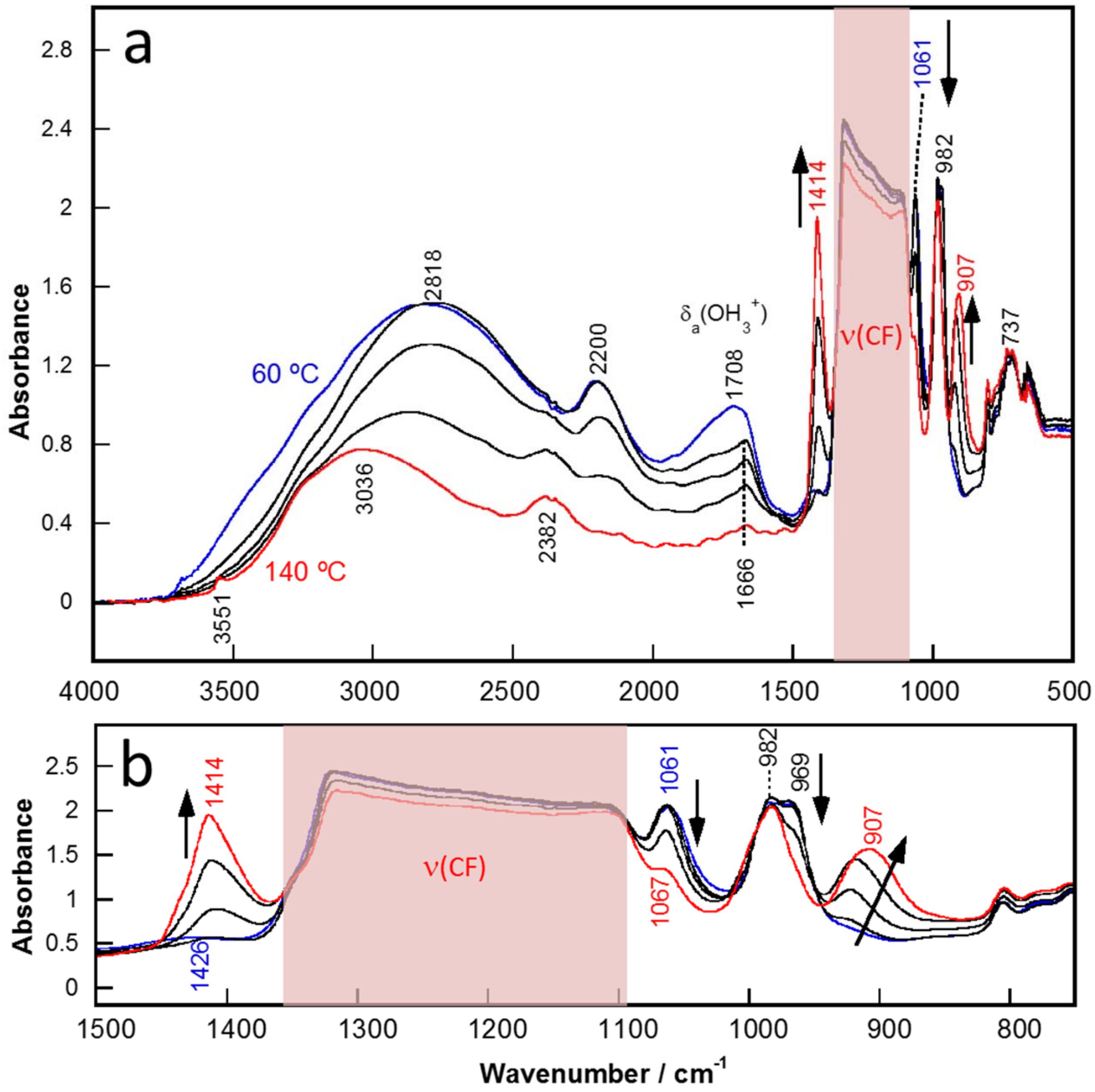

Fig. 2 (a) Temperature-dependent IR spectra of the Nafion membrane on a thermally equilibrium at 60, 80, 120 and 140 °C. (b) Magnified spectra in a fingerprint region.

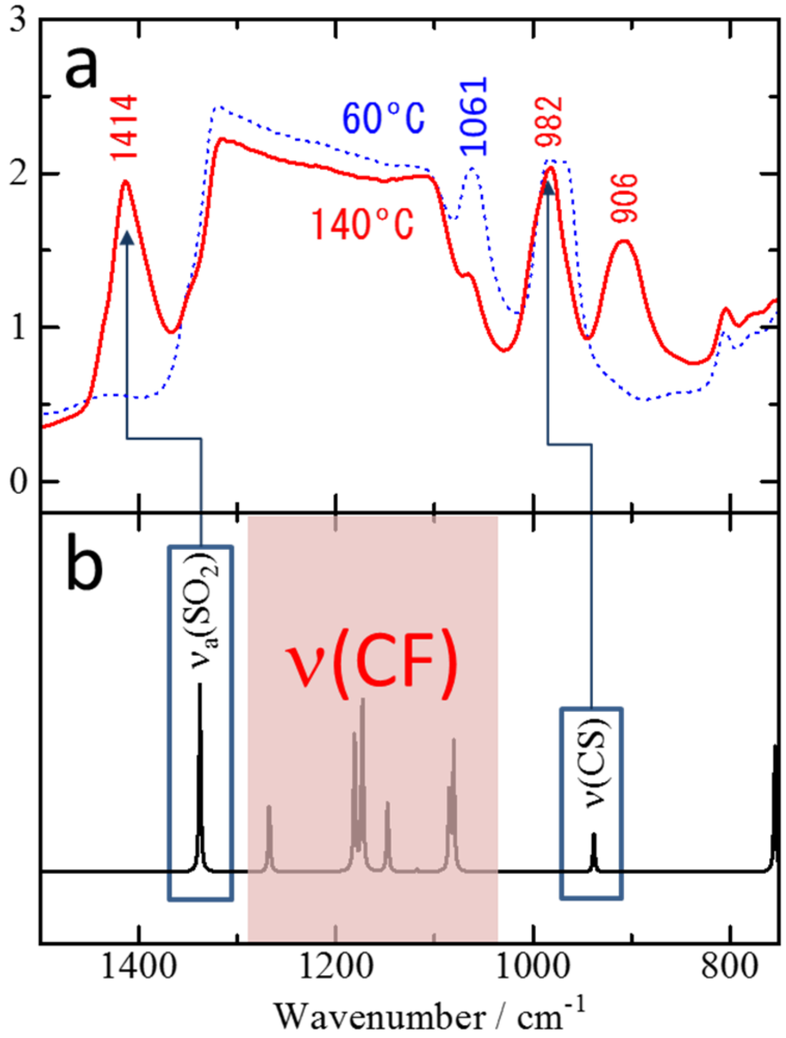

Fig. 3 (a) IR spectra of 60 °C (blue dotted line) and 140 °C (red solid line) taken from Fig. 2. (b) The calculated spectrum of the dehydrated PSA (Table S1).

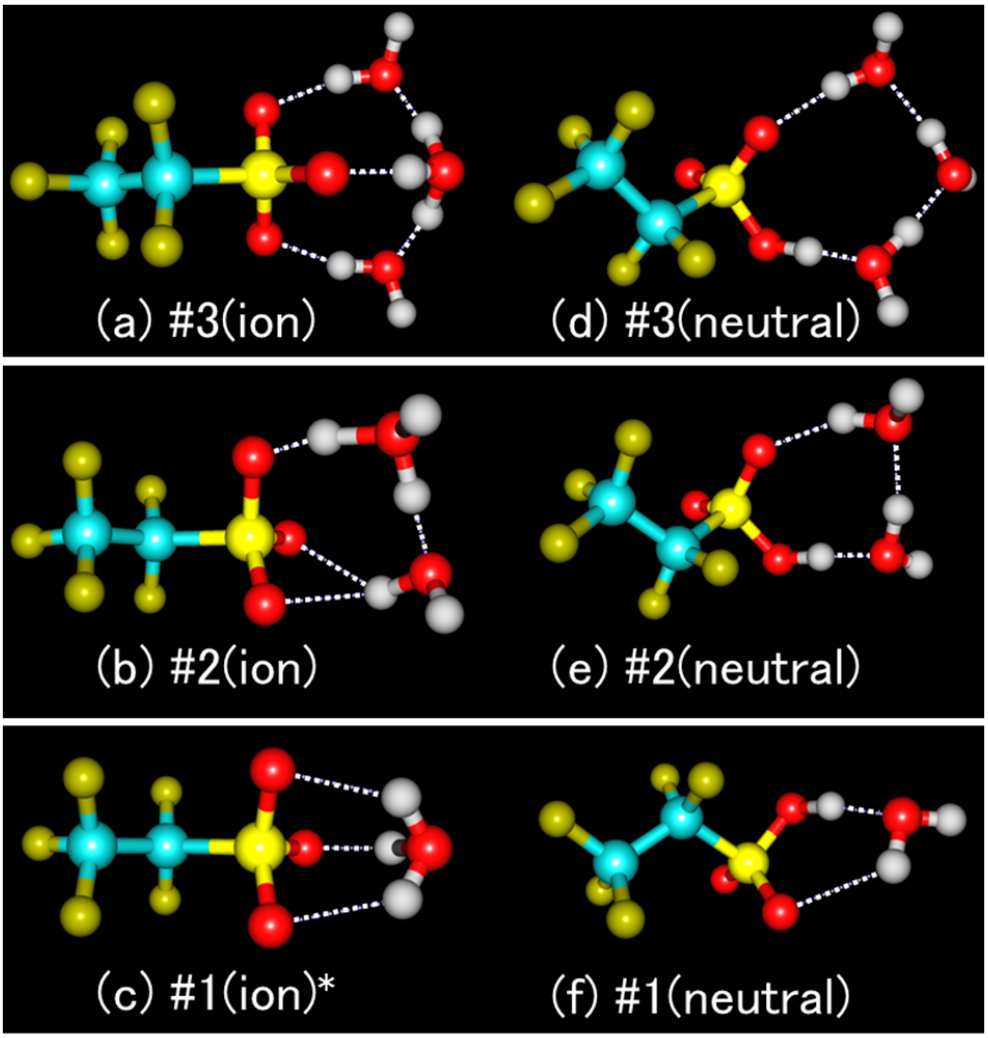

Fig. 4 The optimized structure of the ionic pairs of FE sulfonate and hydronium ion: (a) #3 ($n=3$), (b) #2 ($n=2$), and (c) #1 ($n=1$). The optimized structures of the neutral pairs of PSA and water molecules: (d) #3 ($n=3$), (e) #2 ($n=2$), and (f) #1 ($n=1$). The asterisk (*) indicates that the structure is obtained on a local minimum of energy near the global minimum.

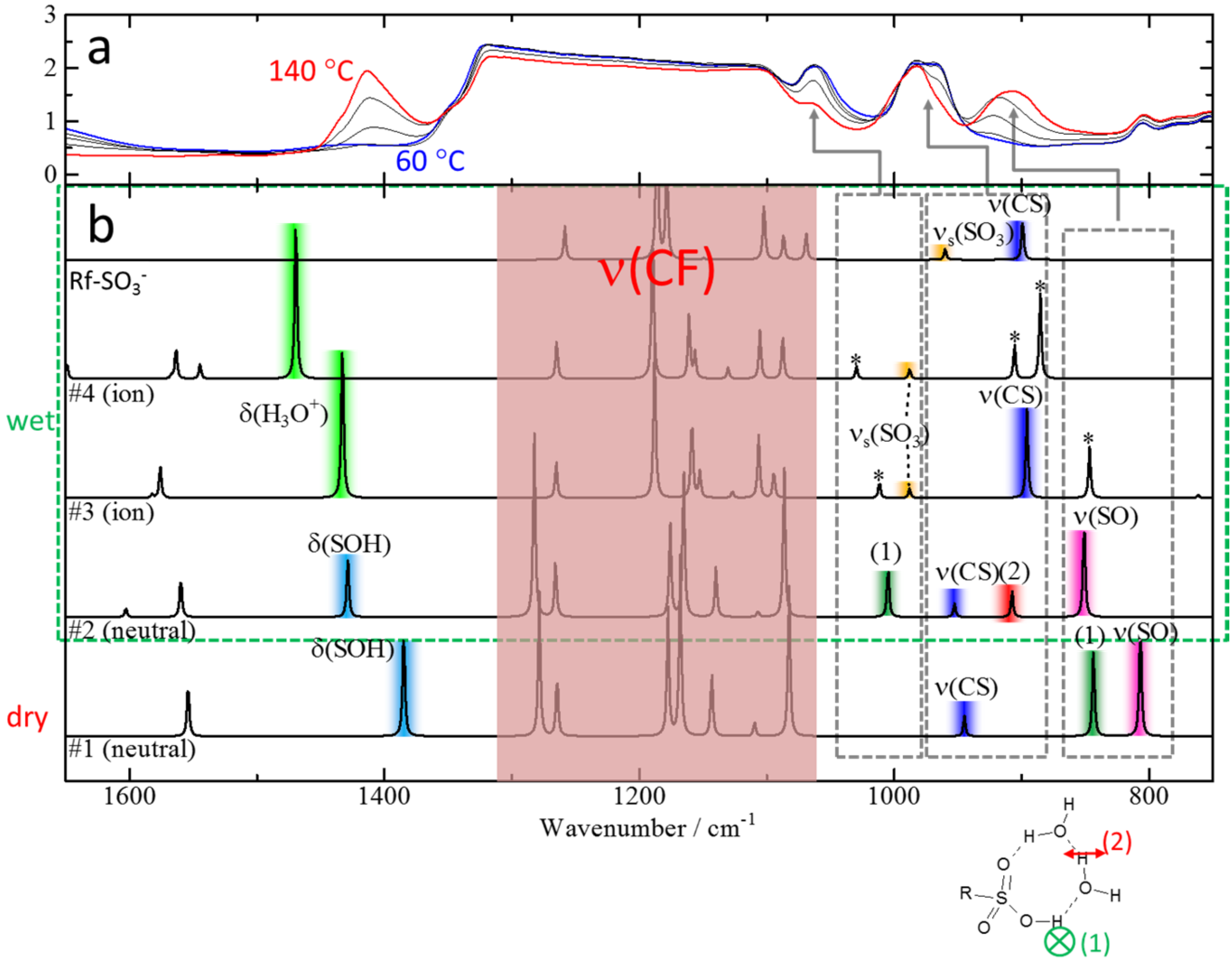

Fig. 5 (a) Temperature-dependent IR spectra in the temperature range of 60 °C and 140 °C taken from Fig. 2. (b) Calculated IR spectra of the structurally-optimized #1(neutral), #2(neutral), #3(ion pair), #4(ion pair), and perfluoroalkyl sulfonate species. The normal modes of the peaks noted as (1) and (2) are schematically drawn below the spectral frame. The peak marked by * is assigned to the H_3O^+ libration mode.

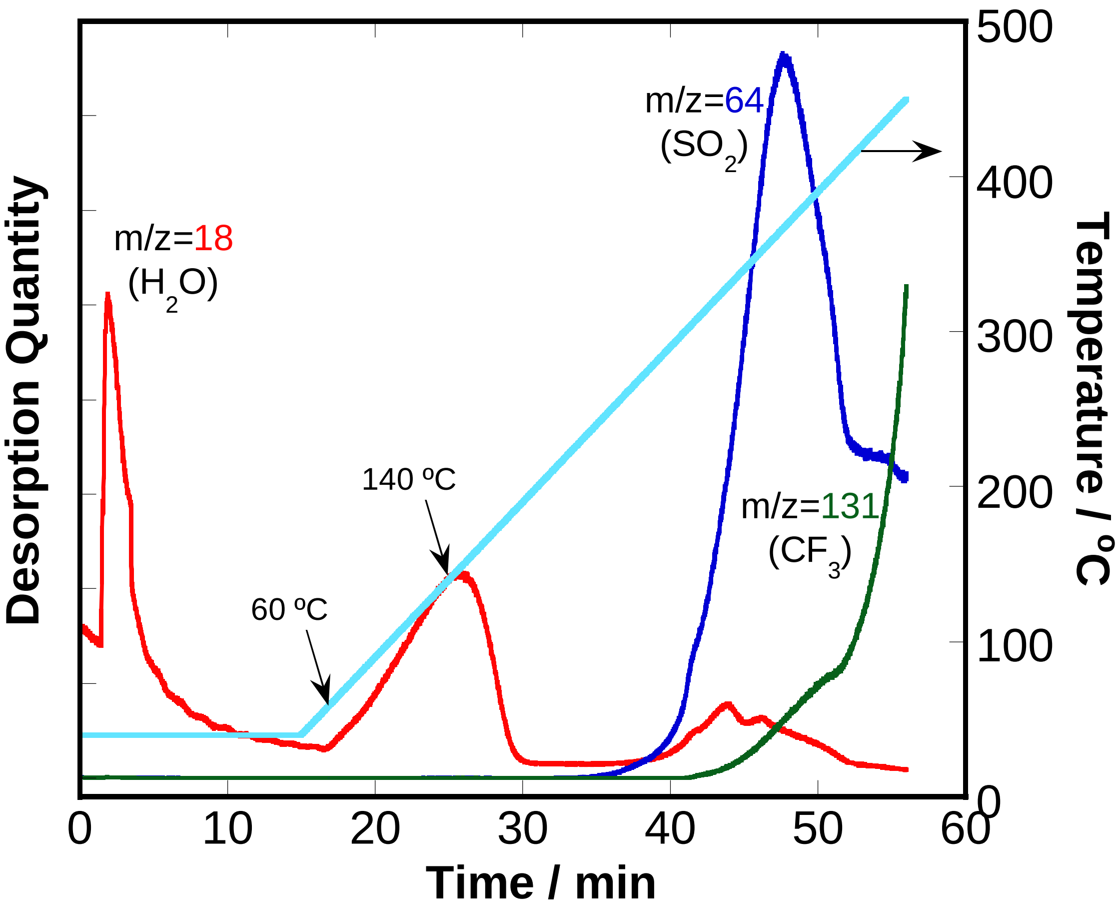

Fig. 6 Time-dependent curve of desorption quantity of a dominant fragment, H_2O (red), SO_2 (blue), and CF_3 (green), measured by EGA-MS and the correlated temperature (light blue).