Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S1 Structural parameters of $CF_3CF_2SO_3H$ (Each column is presented atomic number, coordinate x-, y-, and z-coordinates (10^{-10} m))

16	1.370445000	-0.350777000	0.027985000
8	2.388507000	0.913600000	-0.098050000
8	1.565102000	-0.916370000	1.344878000
8	1.408388000	-1.120835000	-1.206728000
1	2.556962000	1.099566000	-1.039834000
6	-0.257198000	0.620394000	0.040940000
9	-0.241775000	1.438364000	-1.035429000
9	-0.287383000	1.359532000	1.161756000
6	-1.538202000	-0.262594000	-0.021277000
9	-2.614960000	0.526194000	0.117781000
9	-1.529058000	-1.165019000	0.968605000
9	-1.616563000	-0.897414000	-1.195680000

Table S2 Structural parameters of molecular clusters presented in Fig. 4 (Each column is presented atomic number, coordinate x-, y-, and z-coordinates (10^{-10} m))

(a) #3(ion)

16	-0.407016000	0.023938000	-0.092124000
8	-0.561851000	-1.263641000	0.631583000
8	-0.606635000	1.240598000	0.735032000
8	-1.151029000	0.065551000	-1.397647000
6	1.392127000	0.077621000	-0.651030000
9	1.589378000	1.255059000	-1.282027000
9	1.580972000	-0.930364000	-1.529609000
6	2.461080000	-0.056126000	0.473018000
9	3.683392000	0.072919000	-0.077646000
9	2.388908000	-1.254527000	1.065278000
9	2.309476000	0.900345000	1.398279000
1	-3.645774000	0.808489000	-0.148360000
8	-3.636835000	-0.006399000	-0.780443000
1	-3.617601000	-0.869294000	-0.216655000
1	-2.707664000	0.025949000	-1.210457000
8	-3.189826000	-2.054800000	0.654044000
1	-3.375832000	-2.967551000	0.400810000
1	-2.211748000	-1.959790000	0.759077000
8	-3.261222000	1.935590000	0.813454000
1	-2.280490000	1.866529000	0.914108000
1	-3.477828000	2.857635000	0.626863000

(b) #2(ion)

16	1.676983000	-0.147612000	-0.141776000
8	1.731372000	-0.964736000	1.165702000
8	1.732013000	-0.985624000	-1.356924000
8	2.619791000	0.982221000	-0.129893000
6	-0.061611000	0.566825000	-0.005272000
9	-0.255904000	1.314817000	-1.114236000
9	-0.097871000	1.366178000	1.078560000
6	-1.234130000	-0.455097000	0.097605000
9	-2.395404000	0.224729000	0.089651000
9	-1.166580000	-1.161057000	1.231979000
9	-1.228771000	-1.299122000	-0.942793000
1	4.414439000	-1.899882000	-1.696451000
8	4.560326000	-1.192391000	-1.049267000
1	4.195807000	-1.632830000	0.246930000
1	3.911025000	-0.501896000	-1.319487000
8	3.927821000	-1.956631000	1.199865000
1	3.914899000	-2.923067000	1.233157000
1	2.876001000	-1.493199000	1.324361000

(c) #1(ion)*

16	1.418000000	-0.291387000	-0.014366000
8	1.492918000	-1.093829000	1.242853000
8	1.460597000	-1.132953000	-1.242668000
8	2.482202000	0.776178000	-0.042810000
6	-0.228659000	0.629409000	-0.005476000
9	-0.269832000	1.401014000	-1.109239000
9	-0.250928000	1.413435000	1.089259000
6	-1.498521000	-0.274393000	0.008778000
9	-2.584563000	0.519754000	0.036566000
9	-1.514869000	-1.060760000	1.091609000
9	-1.552957000	-1.035569000	-1.090546000
1	3.383398000	-1.639417000	0.780162000
8	3.957282000	-1.372231000	0.004565000
1	3.756621000	-0.361427000	-0.013688000
1	3.392064000	-1.668090000	-0.766240000

(d) #3(neutral)

16	-0.105930000	-0.083193000	0.938705000
8	-0.936006000	-1.411329000	0.911556000
8	0.389220000	0.157370000	2.281062000
8	-0.782085000	0.979449000	0.180132000
1	-1.634897000	-1.500251000	0.114185000
6	1.368863000	-0.595112000	-0.129556000
9	0.885424000	-1.127494000	-1.274042000
9	2.051826000	-1.542264000	0.542676000
6	2.350621000	0.554311000	-0.500151000
9	3.411272000	0.031369000	-1.139938000
9	2.780599000	1.182469000	0.602217000
9	1.762027000	1.443649000	-1.309981000
8	-2.603932000	-1.666154000	-0.903693000
1	-3.443700000	-1.125957000	-0.804845000
1	-2.831398000	-2.559149000	-1.188380000
8	-4.666535000	-0.070925000	-0.616377000
1	-5.337505000	-0.220170000	0.060869000
1	-4.269360000	0.818317000	-0.433416000
8	-3.329418000	2.189490000	-0.015609000
1	-3.285743000	2.959797000	-0.595163000
1	-2.409711000	1.890551000	0.120769000

(e) #2(neutral)

16	0.440201000	-0.887790000	-0.597989000
8	1.445750000	-1.515292000	0.433887000
8	-0.208961000	-1.944435000	-1.348211000
8	1.035160000	0.267906000	-1.283743000
1	2.218508000	-0.877843000	0.748462000
6	-0.833602000	-0.171512000	0.603291000
9	-0.170085000	0.648650000	1.451290000
9	-1.366592000	-1.191552000	1.300834000
6	-1.988553000	0.637849000	-0.054181000
9	-2.849723000	1.023110000	0.903013000
9	-2.644653000	-0.111227000	-0.948070000
9	-1.513009000	1.733142000	-0.664444000
8	3.331157000	-0.043450000	1.212586000
1	3.455943000	0.732143000	0.602356000
1	4.180252000	-0.495371000	1.298979000
8	3.304965000	1.841264000	-0.658929000
1	3.164914000	2.785008000	-0.513119000
1	2.502071000	1.495623000	-1.091847000

(f) #1(neutral)

16	-0.890667000	0.785398000	0.169683000
8	-1.994889000	0.503089000	-0.945504000
8	-1.280845000	0.126903000	1.419095000
8	-0.502164000	2.180166000	0.115623000
1	-2.614674000	-0.231175000	-0.625294000
6	0.528404000	-0.229916000	-0.563536000
9	0.818900000	0.280611000	-1.774247000
9	0.084390000	-1.497597000	-0.708200000
6	1.829174000	-0.258770000	0.290398000
9	2.755046000	-0.986247000	-0.356379000
9	1.598815000	-0.821138000	1.484320000
9	2.303355000	0.979436000	0.472943000
8	-3.452493000	-1.361669000	0.178687000
1	-4.411397000	-1.289533000	0.270924000
1	-3.070150000	-1.297046000	1.069124000

Table S2 Structural parameters of $RfSO_3^-$ and #4(ion), the spectra of which are presented in Fig. 5 (Each column is presented atomic number, coordinate x-, y-, and z-coordinates (10^{-10} m))

$RfSO_3^-$

16	1.497808000	-0.235448000	-0.000529000
8	1.487671000	-0.983923000	1.277615000
8	1.444852000	-1.065046000	-1.226855000
8	2.407024000	0.931380000	-0.053432000
6	-0.208527000	0.616941000	0.000470000
9	-0.319015000	1.420483000	-1.100230000
9	-0.315123000	1.419539000	1.102138000
6	-1.468645000	-0.286879000	0.000142000
9	-2.590964000	0.488419000	0.038799000
9	-1.514081000	-1.096348000	1.070466000
9	-1.551738000	-1.040147000	-1.108265000

#4(ion)

16	-0.058056000	-0.023759000	0.095420000
8	-0.036538000	1.358455000	0.633969000
8	0.041140000	-1.104179000	1.105685000
8	0.880655000	-0.219037000	-1.069450000
6	-1.744576000	-0.230875000	-0.721580000
9	-1.850185000	-1.516931000	-1.117436000
9	-1.781105000	0.569883000	-1.807558000
6	-2.973722000	0.110423000	0.172013000
9	-4.096165000	-0.209272000	-0.498817000
9	-3.009657000	1.417281000	0.458224000
9	-2.946732000	-0.589176000	1.314398000
1	3.172218000	-0.695277000	0.581641000
8	3.222467000	0.021790000	-0.165324000
1	3.123052000	0.953294000	0.276731000
1	2.320626000	-0.099631000	-0.674212000
8	2.574736000	2.204592000	0.932952000
1	2.822868000	3.095555000	0.656757000
1	1.591558000	2.129934000	0.906938000
8	2.693938000	-1.657170000	1.646547000
1	1.708478000	-1.651525000	1.611449000
1	2.995458000	-2.572712000	1.697855000
8	6.042604000	-0.183788000	-1.224639000
1	5.079398000	-0.141515000	-1.143013000
1	6.227621000	-0.326635000	-2.160684000

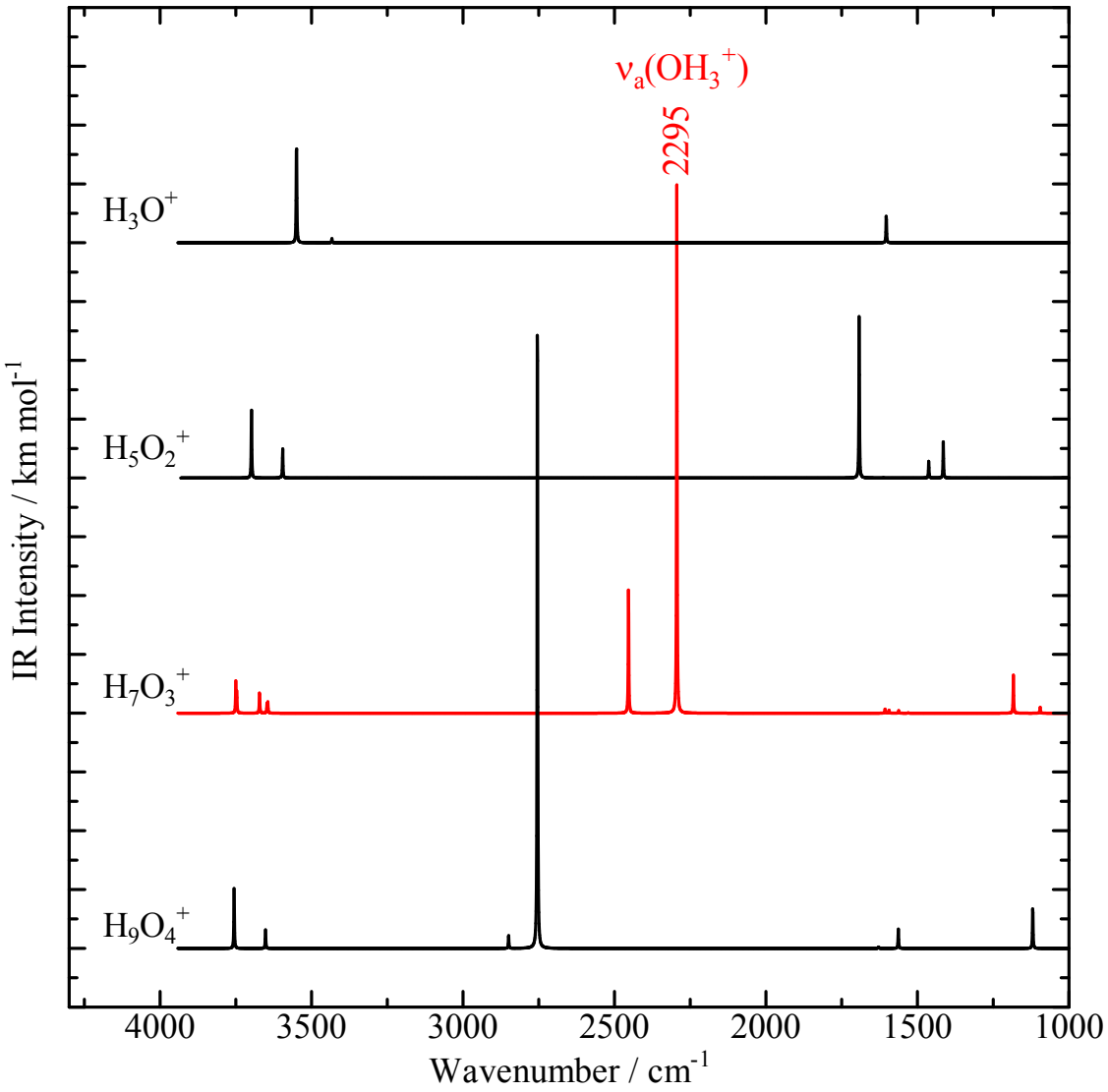

Fig. S1 Calculated IR spectra of four kinds of hydronium ions.

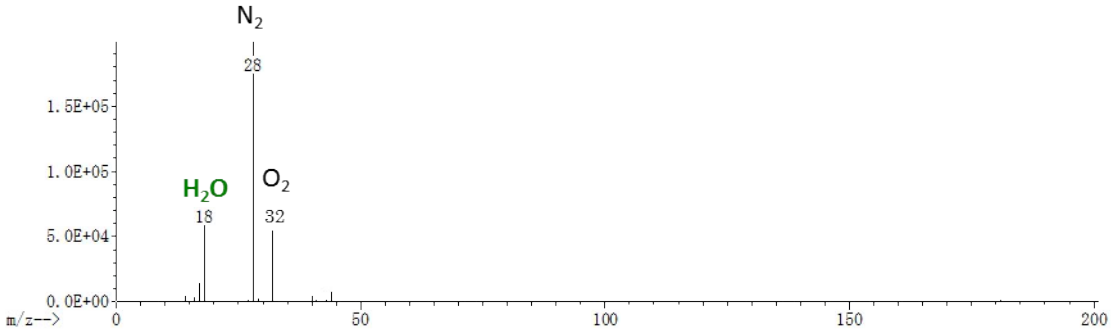

Fig. S2 Averaged EGA-MS spectrum of the Nafion membrane measured up to ca. 200 °C (from 0 min to 30 min).

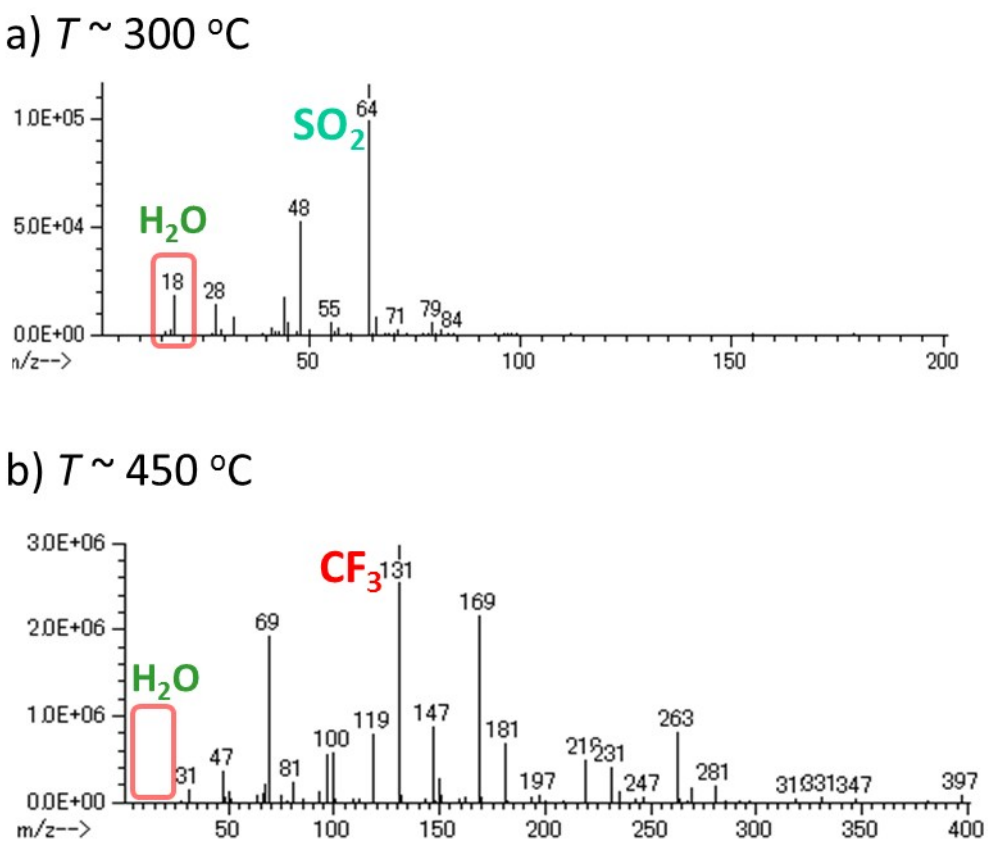

Fig. S3 EGA-MS spectra of the Nafion membrane measured at (a) 300 °C and (b) ca. 450 °C.