Structural Collapse of Fluorohydrogenate Anions in Molten Cs(FH)$_{2.3}$F Detected by High-Energy X-Ray and Neutron Diffraction Studies Combined with RMC Calculation

The authors have been working on a series of onium fluorohydrogenates, Cat$^+$(FH)$_n$F$^-$, called ionic liquids such as dialkylimidazolium and pyrrolidinium salts, the vacuum-stable composition n of which always falls to 2.3 [1,2]. Vibrational spectroscopic studies suggest the presence of (FH)$_2$F$^-$ (C_{2v}) and (FH)$_3$F$^-$ (D_{3h}) and the absence of FHF$^-$ ($D_{\infty h}$) and neutral HF monomers or oligomers in these liquid salts. This observation explains their nonvolatile nature while the other conventional fluorohydrogentates including alkali salts such as Cs(FH)$_{2.3}$F more or less have dissociation pressures in the liquid state to lose HF by evacuation. Oligofluorohydrogenate anions, (FH)$_n$F$^-$, have been structurally characterized in solid states by X-ray crystallography [3]. However, the characterization of these salts in liquid state by diffraction methods has never been reported so far. In the present study [4], we chose Cs(FH)$_{2.3}$F as a sample for structural characterization since it has an eutectic temperature of 16.9°C, lower than room temperature, at this composition [5].

The salt was prepared by the reaction of CsF and excess of anhydrous HF. The composition was adjusted to $n = 2.3$ by evacuation of the salt to yield a liquid at 16.9°C. For neutron diffraction experiments, a deuterated version of the salt was prepared in the same manner using DF instead of HF. High-energy X-ray diffraction measurement was performed on beamline **BL04B2** at SPring-8 using an incident energy of 113.8 kV. Pulsed neutron diffraction measurement was carried out at the Intense Pulsed Neutron Source, Argonne National Laboratory. Reverse Monte Carlo (RMC) simulation was performed on an ensemble of 3300 particles with a random starting configuration using the RMCA program code [6].

The calculated X-ray weighted total and partial structure factors and neutron-weighted total and partial structure factors of Cs(FH)$_{2.3}$F in liquid state from the RMC model are shown in Fig. 1. The agreement between the total RMC and experimental structure factors is excellent, indicating that the short

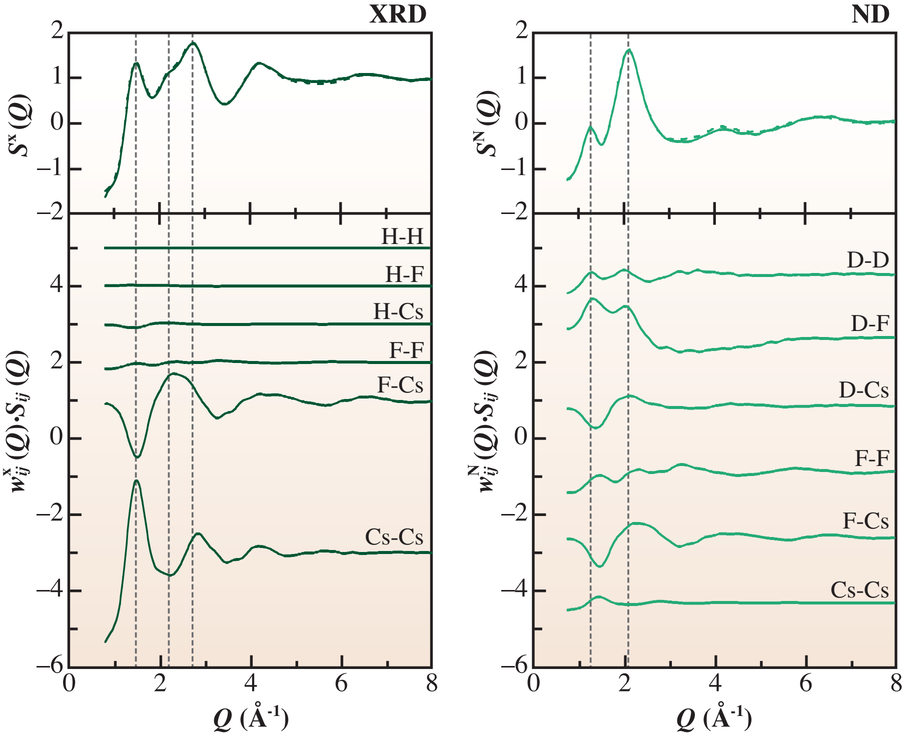

Fig. 1. Calculated X-ray-weighted and neutron-weighted total structure factors $S^{X,N}(Q)$ and associated weighted partial structure factors $w_{ij}^{X,N}\cdot S_{ij}(Q)$ obtained from the RMC model for liquid Cs(FH)$_{2.3}$F. Dotted lines: experimental data; solid lines: RMC model, where w_{ij} denotes the X-ray-weighted or neutron-weighted factor. Successive curves are displaced upward for clarity. Dashed lines are guides to the eye.

and intermediate-range orders of liquid $Cs(FH)_{2.3}F$ are well reproduced using the RMC model. Figure 2 shows a 20-Å-thick snapshot of the RMC model. Chain analysis of the RMC model revealed that the dominant chains consist of five atoms and the average number of atoms per chain is 4.4. Furthermore, a detailed analysis of the atomic configuration revealed that $(FH)_2F^-$ is the major entity in the liquid, and asymmetric FHF^- are formed in the liquid state. The chain analysis also showed that only 2.6% of the molecules form branched chains. These results suggest that branched molecules such as $(FH)_3F^-$ that existed in the solid state collapse into linear $(FH)_2F^-$ and $(HF)_n$, and a part of $(FH)_2F^-$ dissociates further to asymmetric FHF^- ($C_{\infty v}$, note that the symmetry of this anion in the solid state is $D_{\infty h}$) and neutral $(HF)_n$ oligmers in the liquid state. This model provides a reasonable explanation for the vacuum instability of the salt. Thus, in the case of vacuum-unstable fluorohydrogenates such as $Cs(FH)_{2.3}F$, the anions in the solid state are not preserved in the liquid state, releasing HF to have a dissociation pressure. This contrasts with the nonvolatile fluorohydrogenate ionic liquids, the HF dissociation pressure of which under ambient conditions is practically zero. The difference in the preservation of the anionic structures by melting should be caused by the difference in the interactions between the cationic and anionic species in the salts forming aggregates of ions in the liquid state of zero solvent system.

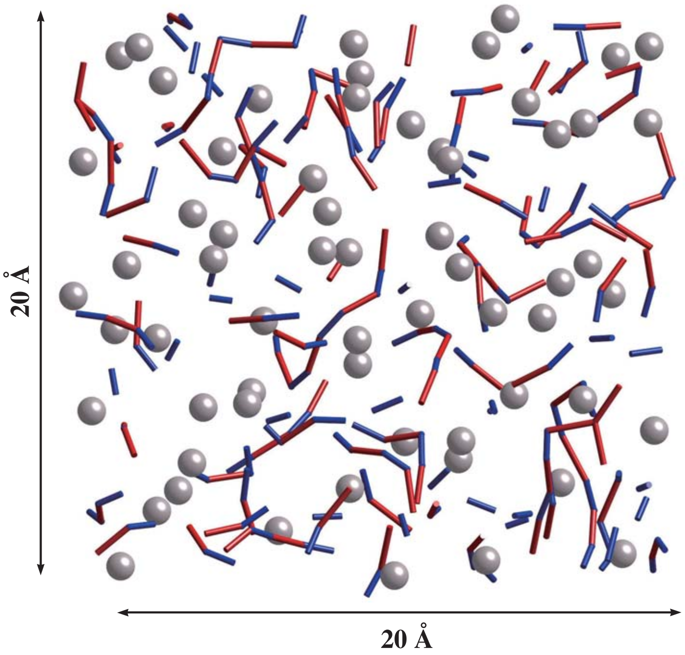

Fig. 2. A 20-Å-thick snapshot of the RMC model. Sticks represent H-F chains. Blue: H-F covalent bonds; red: H…F hydrogen bonds. Gray spheres represent the cesium ions.

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