

# Dissolution and nucleation phenomena of salts in water. Molecular dynamic approaches and supporting solution X-ray diffraction measurements

Hitoshi Ohtaki

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji-cho, Okazaki, 444 Japan.

**Abstract** - Molecular dynamics (MD) simulations have been demonstrated to elucidate the dissolution and nucleation phenomena at a molecular level for a variety of alkali halide salts in water at 25 °C. Within 12 to 20 ps anions in the LiCl, NaCl and CsF crystals have dissolved, but dissolution of cations has not been observed within the same time period. For KCl, NaF, and KF crystals which have cations and anions with similar size, no ions have dissolved within 20 ps, although the crystal lattice has significantly distorted. Thus, the rate of dissolution of ions is lower in crystals having the cations and anions with a similar size than in those with different sizes. In supersaturated aqueous solutions of NaCl and CsF ionic microclusters are formed which might be regarded as embryos of nuclei of crystals. According to solution X-ray diffraction measurements of almost saturated aqueous solutions of NaCl ( $6.18 \text{ mol (kg H}_2\text{O)}^{-1}$ ) and KCl ( $4.56 \text{ mol (kg H}_2\text{O)}^{-1}$ ), 1:1 ion pairs are formed. On the other hand, ion clusters with the average coordination numbers of the cation-anion pairs,  $n_{MX}$ , of 2.29 and 3.33 are formed in KF ( $16.15 \text{ mol (kg H}_2\text{O)}^{-1}$ ) and CsF ( $31.96 \text{ mol (kg H}_2\text{O)}^{-1}$ ) solutions, respectively, the results being in good agreement with those obtained by the MD simulations.

## INTRODUCTION

Many salt crystals are soluble in water. Thermodynamics and kinetics of crystallization from aqueous salt solutions have been widely investigated from various view-points and a huge accumulation of knowledge has been achieved in this area. Crystallization of salts from supersaturated solutions is also a well established phenomenon, and thermodynamic data such as solubilities, stability constants of complexes which exist in the solution have been thoroughly studied. It is believed that crystals form from crystal nuclei which form in supersaturated solutions. However, dynamic investigations of dissolution and nucleation processes of crystals have not been examined on the molecular level.

Recently developed molecular dynamics (MD) simulations can provide dynamic and structural information concerning dissolution and nucleation of crystals in water. In this paper we have summarized our recent studies on dissolution and nucleation processes of alkali halides studied by MD. In order to have some experimental support for the simulation studies, we have carried out solution X-ray diffraction measurements for saturated and supersaturated solutions of some alkali halides and the X-ray diffraction data have been compared with those of the MD simulations.

## MD SIMULATIONS

**Systems.** (a) Dissolution. Crystals employed for the studies on dissolution were alkali halides of rock salt type: LiCl, NaCl, KCl, NaF, KF, and CsF (Refs. 1-3). In all the cases crystals were cubic and contain 32 cations and 32 anions. The number of water molecules employed was 216. They were placed in an isolated box with the side length ( $l$ ) of about 2000 pm. The size of the box was estimated from the density of the saturated solution of the corresponding salts. Temperature was controlled at 25 °C by monitoring kinetic velocities of water molecules in the system.

In order to check the effect of the crystal faces, two corners of a cubic NaCl crystal were cut, and thus, a crystal containing 28 cations and 28 anions with (111) and (-1-1-1) faces, together with {100} faces, was dissolved in 189 water molecules (Ref. 2).

The mass effect of ions was also studied by using caesium ions with the same atomic weight as that of fluoride ion, i.e., 18.998 (Ref. 3). The *light* CsF crystal was cubic.

Water molecules were assumed to be completely elastic on the wall of the box at the center of gravity of water molecule. The electrostatic effect of ions which had moved outside the box was cut off by the introduction of a switching function  $S_W(x)$ :

$$S_W(x) = 1 \quad \text{for } -l/2 \leq x \leq l/2$$

$$S_W(x) = \exp\{-\alpha_i \{ |x| - l/2 \}^2\} \quad \text{for } |x| > l/2 \quad (1)$$

where  $x$  is any of the three Cartesian coordinates, their origin being the middle of the box. The parameter  $\alpha_i$  was defined as  $1/(0.3964r_i)^2$ , where  $r_i$  is the ionic radius of  $i$ . The side length of the box  $l$ , ionic radius  $r_i$  the  $\alpha_i$ -value of the switching function and the total time for the simulations  $t$  are tabulated in Table 1. The time step  $\Delta t$  was 1 fs for all the calculations.

(b) **Nucleation.** Nucleation of crystals from supersaturated solutions has been investigated for aqueous solutions of NaCl and CsF. The concentrations of the supersaturated solutions were: (i) 9.25 mol (kg H<sub>2</sub>O)<sup>-1</sup> NaCl, (ii) 15.42 mol (kg H<sub>2</sub>O)<sup>-1</sup> NaCl, and (iii) 36.34 mol (kg H<sub>2</sub>O)<sup>-1</sup> CsF (see Table 2) (Ref. 4). The test solutions were highly supersaturated.

All ions and water molecules were first randomly placed in the basic cell, as well as in the replicas, and then the simulation was started. In the case of (i), both water molecules and ions were allowed to freely move in the cell until the thermal equilibrium attained between the water molecules and the ions before the simulation started. In (ii) and (iii) only water molecules were pre-equilibrated, while ions were fixed at the lattice points. Although no essential difference was found for the simulations at different pre-equilibrium stages of experiments, more computer time was needed in (i) than in (ii) and (iii). Temperature was kept at 25 °C.

**Potential Functions.** Throughout the work the Born-Mayer-Huggins type Tosi-Fumi potential  $\Phi_{ij}$  (Ref. 5) was used for the ion-ion interactions.

$$\Phi_{ij}(r) = z_j z_i e^2 / r + A_{ij} b_{ij} \exp\{(\sigma_i + \sigma_j - r) / \rho\} - c_{ij} / r^6 - d_{ij} / r^8 \quad (2)$$

$A_{ij}$  denotes the Pauling factor,  $1 + (z_j / n_j) + (z_i / n_i)$ , where  $n_i$  and  $n_j$  represent the numbers of electrons in the outer-most shell of ions  $i$  and  $j$ , respectively. The parameter values in eq. (1) are summarized in Table 3.

Table 1. The side length of the box ( $l$ ), radii of ions ( $r_i$ ) and  $\alpha$ -values of the switching function for the molecular dynamics simulations of dissolution of salts in water at 25 °C.

|  | LiCl               | NaF                 | NaCl               | KF                  | KCl                | CsF                 |
|--|--------------------|---------------------|--------------------|---------------------|--------------------|---------------------|
| $l$ /pm                                | 1963               | 1938                | 1993               | 1975                | 2039               | 2019                |
| $r_i$ /pm                              | Li <sup>+</sup> 74 | Na <sup>+</sup> 102 | K <sup>+</sup> 138 | Cs <sup>+</sup> 170 | F <sup>-</sup> 133 | Cl <sup>-</sup> 181 |
| $\frac{\alpha_i}{10^4 \text{pm}^{-2}}$ | 11.68              | 6.148               | 3.359              | 2.213               | 3.616              | 1.952               |

Table 2. Experimental conditions of the molecular dynamics simulations for the nucleation of NaCl and CsF.<sup>a</sup>

|                                 | NaCl  | NaCl  | CsF   |
|---------------------------------|-------|-------|-------|
| Number of cations               | 56    | 80    | 127   |
| Number of anions                | 56    | 80    | 127   |
| Number of water molecules       | 336   | 288   | 194   |
| Concentration                   | 9.25  | 15.42 | 36.34 |
| Length of unit cell             | 2327  | 2304  | 2336  |
| Saturation concentration (25°C) | 6.15  | 6.15  | 24.13 |
| Degree of supersaturation       | 150.4 | 250.4 | 150.6 |

<sup>a</sup> Concentration/mol (kg H<sub>2</sub>O)<sup>-1</sup>, cell length/pm, degree of supersaturation/%.

Table 3. Parameter values of potential function of ion-ion interactions in the Tosi-Fumi model.<sup>a</sup>

| Salt | $\frac{\sigma_+ + \sigma_-}{\text{pm}}$ | $\frac{\rho}{\text{pm}}$ | $c_{++}$ | $c_{--}$ | $c_{+-}$ | $d_{++}$ | $d_{--}$ | $d_{+-}$ |
|------|---|--------------------------|----------|----------|----------|----------|----------|----------|
| LiCl | 240.1                                   | 34.2                     | 0.073    | 111.0    | 2.0      | 0.03     | 223.0    | 2.4      |
| NaF  | 234.0                                   | 33.0                     | 1.68     | 16.5     | 4.5      | 0.8      | 20.0     | 3.8      |
| NaCl | 275.5                                   | 31.7                     | 1.68     | 116.0    | 11.2     | 0.8      | 233.0    | 13.9     |
| KF   | 264.2                                   | 33.8                     | 24.3     | 18.6     | 19.5     | 24.0     | 22.0     | 21.0     |
| KCl  | 304.8                                   | 33.7                     | 24.3     | 124.5    | 48.0     | 24.0     | 250.0    | 73.0     |
| CsF  | 289.9                                   | 28.2                     | 152.0    | 19.1     | 52.0     | 278.0    | 23.0     | 78.0     |

<sup>a</sup>  $c/10^{-79}$  J m<sup>6</sup>,  $d/10^{-99}$  J m<sup>8</sup>.  $b = 0.338 \times 10^{-19}$  J.

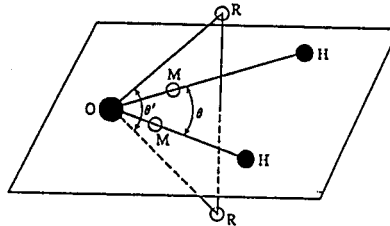
The rigid Matsuoka-Clementi-Yoshimine model for water molecule (Ref. 6) was employed for the water-water interactions:

$$\Phi_{ww}(r) = q^2\{\Sigma(1/r_{H-H}) - 2\Sigma(1/r_{H-M})\} + (4q^2/r) + Sa_{\alpha}\exp(-b_{\alpha}r) \quad (3)$$

$q$  is the charge on a proton in a water molecule.  $a_{\alpha}$  and  $b_{\alpha}$  are constants characteristic of the pair of ions. Subscripts H-H and H-M in the first term of the right hand side represent interactions between protons and between a proton and the negative center near the oxygen atom in different water molecules, respectively. The second term represents the repulsive interaction between oxygen atoms. The third term shows the short range interatomic interactions. The values of the parameters in eq. (2) are summarized in Table 4.

Table 4. Parameter values of potential function of water-water interactions in the MCY model.

| Parameter        |          | Parameter       |         | Parameter           |         |
|------------------|----------|-----------------|---------|---------------------|---------|
| $a_1/10^{-18}$ J | 8127.851 | $b_1/\text{pm}$ | 520.268 | $q/10^{-8}$ J m     | 1.30378 |
| $a_2/10^{-18}$ J | 2.8893   | $b_2/\text{pm}$ | 245.664 | $r_{H-O}/\text{pm}$ | 95.72   |
| $a_3/10^{-18}$ J | 11.7037  | $b_3/\text{pm}$ | 272.082 | $r_{O-M}/\text{pm}$ | 25.81   |
| $a_4/10^{-18}$ J | 2.9444   | $b_4/\text{pm}$ | 215.714 |                     |         |



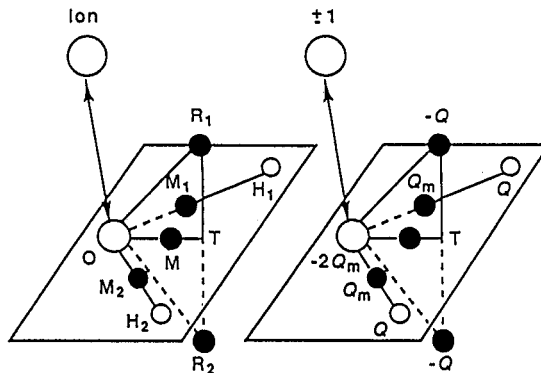
For ion-water interactions the Kistenmacher-Popkie-Clementi (KPC) model was employed (Ref. 7):

$$\begin{aligned} \Phi_{iw}(r) = & z_j Q (1/r_{j-H1} + 1/r_{j-H2} - 1/r_{j-R1} - 1/r_{j-R2}) \\ & + z_j Q_m (1/r_{j-M1} + 1/r_{j-M2} - 2/r_{j-O}) \\ & + a_1 \{ \exp(-b_1 r_{j-H1}) + \exp(-b_1 r_{j-H2}) \} + a_2 \exp(b_2 r_{j-M}) \end{aligned} \quad (4)$$

$Q$  denotes the charge on the protons, and thus  $2Q$  the charge at  $R_1$  and  $R_2$ ,  $Q_m$  the charge on  $M_1$  and  $M_2$ , and thus,  $-2Q_m$  on the oxygen atom in the KPC water molecule.  $z_j$  is either +1 or -1. The parameter values used for the KPC model are listed in Table 5.

Table 5. Parameter values of potential function of ion-water interactions in the KPC model.

| Parameter            | Li <sup>+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Cs <sup>+</sup> | F <sup>-</sup> | Cl <sup>-</sup> |
|----------------------|-----------------|-----------------|----------------|-----------------|----------------|-----------------|
| $Q/10^{-8}$ J m      | 1.475145        | 1.366318        | 1.374209       | 1.8540          | 1.505345       | 1.418066        |
| $Q_m/10^{-8}$ J m    | 0.1428564       | 0.151531        | 0.1175474      | 0.3543          | 0.06667557     | 0.292957        |
| $a_1/10^{-18}$ J     | 32.9275         | 817.884         | 19.4217        | 3413.5          | 18.63855       | 26.44733        |
| $a_2/10^{-18}$ J     | 291.1605        | 854.891         | 1629.645       | 2618.7          | 915.7706       | 303.504         |
| $b_1/\text{pm}^{-1}$ | 6.712196        | 7.45962         | 4.992545       | 5.660           | 3.762637       | 3.097243        |
| $b_2/\text{pm}^{-1}$ | 4.496114        | 4.46437         | 4.088386       | 3.70            | 4.388116       | 3.305397        |
| OM/pm                | 2.08337         | 1.791264        | 4.220187       | 4.19            | 8.169964       | 14.91644        |
| OT/pm                | 13.7882         | 13.99303        | 18.65296       | 25.370          | 22.38101       | 24.73109        |
| TR/pm                | 0.29528         | 9.56011         | 0.7131189      | 4.030           | 15.09266       | 11.29475        |
| OR/pm                | 13.7914         | 14.1072         | 18.6666        | 25.6881         | 26.9944        | 27.1883         |



**Pair Correlation Function and Running Coordination Number.** The correlation function  $g_{ij}(r)$  for the  $i$ - $j$  atom pair is defined as follows:

$$g_{ij}(r) = N_{ij}(r) / (4\pi\rho_j r^2 \Delta r N_i) \quad (5)$$

where  $N_{ij}(r)$  denotes the number of particles  $j$  in the range from  $r$  to  $r + \Delta r$  around the central ion  $i$ .  $N_i$  is the total number of particles  $i$  in a given volume  $V$ .  $\rho_j$  is the number density.

The number of  $j$  particles around a particle  $i$  is given as a function of the distance  $r$  of the particles from  $i$  and is defined as the running coordination number  $n_{ij}(r)$  as follows:

$$n_{ij}(r) = 4\pi\rho_j \int_0^r r^2 g_{ij}(r) dr \quad (6)$$

### SOLUTION X-RAY DIFFRACTION EXPERIMENTS FOR SATURATED AND SUPERSATURATED ALKALI HALIDE AQUEOUS SOLUTIONS

A  $\theta$ - $\theta$  type solution X-ray diffractometer made by JEOL, Tokyo, was employed for the experiments.  $\text{MoK}\alpha$  radiation ( $\lambda = 71.07$  nm) was used. Times to obtain 40,000 counts were measured at each angle point and the measurements were repeated twice over the range  $\theta = 1^\circ - 72^\circ$ , where  $\theta$  is a half of the scattering angle. The variable  $s$  is defined as  $s = (4\pi/\lambda) \sin \theta$ .

**Methods of Calculations.** Intensities of scattered X-rays  $I(s)$ , corrected for polarization, absorption, and multiple scattering, were normalized and converted to the absolute scale.  $K$  is the normalizing factor. The reduced intensities  $i(s)$  were calculated with respect to a given stoichiometric volume of the solution according to eq. (7):

$$i(s) = KI(s) - \sum n_j f_j(s) \quad (7)$$

where  $n_j$  is the number of particles  $j$  in the stoichiometric volume, and  $f_j(s)$  is the scattering factor, corrected for the anomalous dispersion, of atom  $j$  at  $s$ .

The radial distribution function  $D(r)$  or  $G(r) = D(r)/4\pi r^2 \rho_0$  is given as follows:

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{s_{\max}} s \cdot I(s) \cdot M(s) \cdot \sin(rs) ds \quad (8)$$

where  $M(s)$  denotes the modification function in the form:

$$M(s) = \{ \sum [n_j f_j(0)]^2 / \sum [n_j f_j(s)]^2 \} \cdot \exp(-ks^2) \quad (9)$$

where  $k$  is the damping factor and  $k = 0.001 \text{ pm}^2$  was used throughout the calculations.

The structure function  $s \cdot i(s)$  can be separated into intramolecular and intermolecular terms as follows:

$$s \cdot i(s) = s \sum n_{pq} c_{pq}(s) j_0(sr_{pq}) \exp(-b_{pq}s^2) - 4\pi\rho_0 \sum n_p n_q c_{pq}(s) R_{pq}^2 j_1(sR_{pq}) \exp(-B_{pq}s^2) \quad (10)$$

where  $c_{pq} = f_p(s)f_q(s)M(s)$ ,  $r_{pq}$ ,  $b_{pq}$ , and  $n_{pq}$  denote the distance, temperature factor, and frequency factor of the  $p$ - $q$  atom pair, respectively.  $R_{pq}$  is the distance beyond which a continuous distribution of atoms  $q$  around  $p$  was assumed.  $B_{pq}$  is the parameter describing the sharpness of the boundary at  $R_{pq}$ .  $j_m(x)$  is the spherical Bessel function of the  $m$ -th order.

The structure parameters  $r_{pq}$ ,  $b_{pq}$ , and  $n_{pq}$  were finally obtained by the application of the least squares method to the reduced intensities so as to minimize the error square sum  $U$ :

$$U = \sum_{s_{\min}}^{s_{\max}} s^2 \{ i_{\text{calc}}(s) - i(s) \}^2 \quad (11)$$

$i_{\text{calc}}(s)$  is the calculated reduced intensities by using eq. (10) on the basis of the model proposed.

**Systems.** X-Ray diffraction experiments were carried out for saturated or supersaturated aqueous solutions of NaCl, KCl, KF and CsF (Ref. 8). The concentrations of the solutions are listed in Table 6. The solutions were so stable that no precipitate was formed during the X-ray diffraction measurements.

Table 6. Concentrations of alkali halide solutions used for X-ray diffraction measurements.

| Salt   | NaCl  | KCl   | KF    | CsF   |
|--|-------|-------|-------|-------|
| Concentration (mol/kg H <sub>2</sub> O)            | 6.18  | 4.56  | 16.15 | 31.96 |
| Molar ratio H <sub>2</sub> O/MX                    | 8.98  | 12.18 | 3.44  | 1.74  |
| Saturation concentration (mol/kg H <sub>2</sub> O) | 6.16  | 4.81  | 17.50 | 24.13 |
| Degree of supersaturation (%)                      | 100.3 | 94.8  | 92.3  | 132.4 |

## RESULTS

**Dissolution Process.** The evolution of the distance  $R$  of ions from the center of the box in the dissolution process of various alkali halide crystals is shown in Figs. 1 and 2. The typical result for dissolution of a cubic sodium chloride crystal within 7 ps is graphically represented in Fig. 3.

(a) **Fluoride System** (Fig. 1). No dissolution of ions was found for NaF and KF. Distortion of the crystal was more pronounced in the former than the latter. In the CsF crystal with atoms of the normal atomic weights, three fluoride ions dissolved within 12 ps. Fluctuation of the positions of fluoride ions in the crystal were more rapid for F<sup>-</sup> than for Cs<sup>+</sup>, as expected from the difference in mass. In the CsF crystal with the *light* Cs<sup>+</sup>, dissolution of fluoride ions was retarded for a few picoseconds, and fluctuation of the positions of Cs<sup>+</sup> and F<sup>-</sup> ions were similar; i.e., the fluctuation of the position of the former ion was enhanced in the *light* crystal over the normal one. Thus, the mass of the ions affected the dissolution mechanism of the CsF crystals.

(b) **Chloride System** (Fig. 2). Dissolution of cations was observed for the LiCl and NaCl systems, while no ion was dissolved from the KF crystal within 20 ps. In the LiCl system eight chloride ions dissolved within 12 ps, and thus the remaining crystal had the composition of [Li<sub>3</sub>Cl<sub>24</sub>]<sup>8+</sup>. First four Cl<sup>-</sup> ions dissolved immediately, and then the next four Cl<sup>-</sup> ions successively dissolved after about 3 ps from the beginning of the dissolution of the crystal. A similar trend in the dissolution process was seen in the NaCl system, although totally five chloride ion dissolved within about 5 ps, and then the dissolution of ions ceased for several picoseconds, and thus the microcluster [Na<sub>3</sub>Cl<sub>127</sub>]<sup>5+</sup> formed in the solution seemed to be rather stable. In the case of KCl no dissolution of ions was observed within 20 ps. The distortion of the crystal structure of KCl was greater than that of KF due to the smaller lattice energy of the former crystal.

**Nucleation Process.** The coagulation process of ions from supersaturated solutions of NaCl and CsF was expressed in terms of the change in the coordination numbers of ions with time. Formation of metastable microclusters was confirmed by the solution X-ray diffraction method.

(a) **Molecular Dynamics Simulations.** The running coordination numbers defined by eq. (6) were calculated in the regions of the first and second coordination spheres of the ions in the microclusters. The first coordination sphere ( $r_1$ ) of an ion was defined as  $L/2$ , where  $L$  denotes the lattice constant of the crystals (564.5 pm for NaCl and 602.5 pm for CsF), for different ions and as  $L/\sqrt{2}$  for ions with the same charge. The second coordination sphere ( $r_2$ ) was defined to be  $r_2 = (\sqrt{3}/2)L$  for ions with different charges and to be  $L$  for ions with the same charges. The results are summarized in Table 7.

It is seen from Table 7 that the degree of coagulation of ions depends on the concentration rather than the degree of supersaturation. The growth of the microclusters seems to be practically stopped after about 10 ps in all the cases. The number of cations and anions in the clusters may not necessarily be the same, because the running coordination numbers for the cation-cation and anion-anion pairs are not equal. Thus, the microclusters may be charged, although the sign of the charge of the microclusters should be dependent of the composition.

(b) **Solution X-Ray Diffraction for Supersaturated Solutions.** A typical result is given in Fig. 4 for the structure function,  $f(s)$ , and the radial distribution curve,  $G(r)$ , of a supersaturated aqueous solution of CsF. It is seen from the figure that the Cs<sup>+</sup>-Cs<sup>+</sup> atom pairs are formed in the solution, although the F<sup>-</sup>-F<sup>-</sup> pairs are not clearly seen because of their small scattering power. The distances, temperature

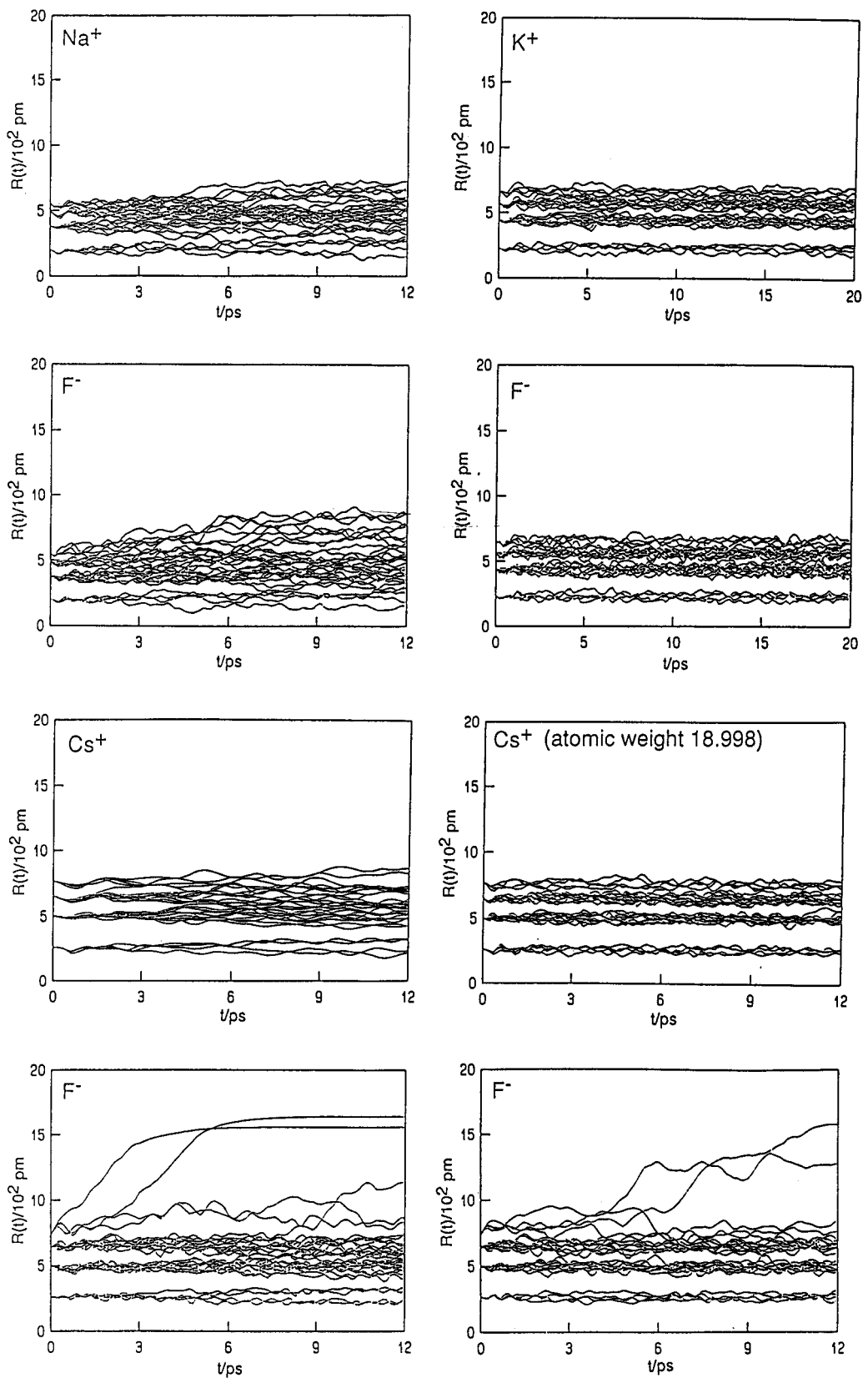


Fig. 1. Evolution of the distance  $R$  from the center of the box of the ions of NaF, KF, CsF and CsF with the *light* Cs.

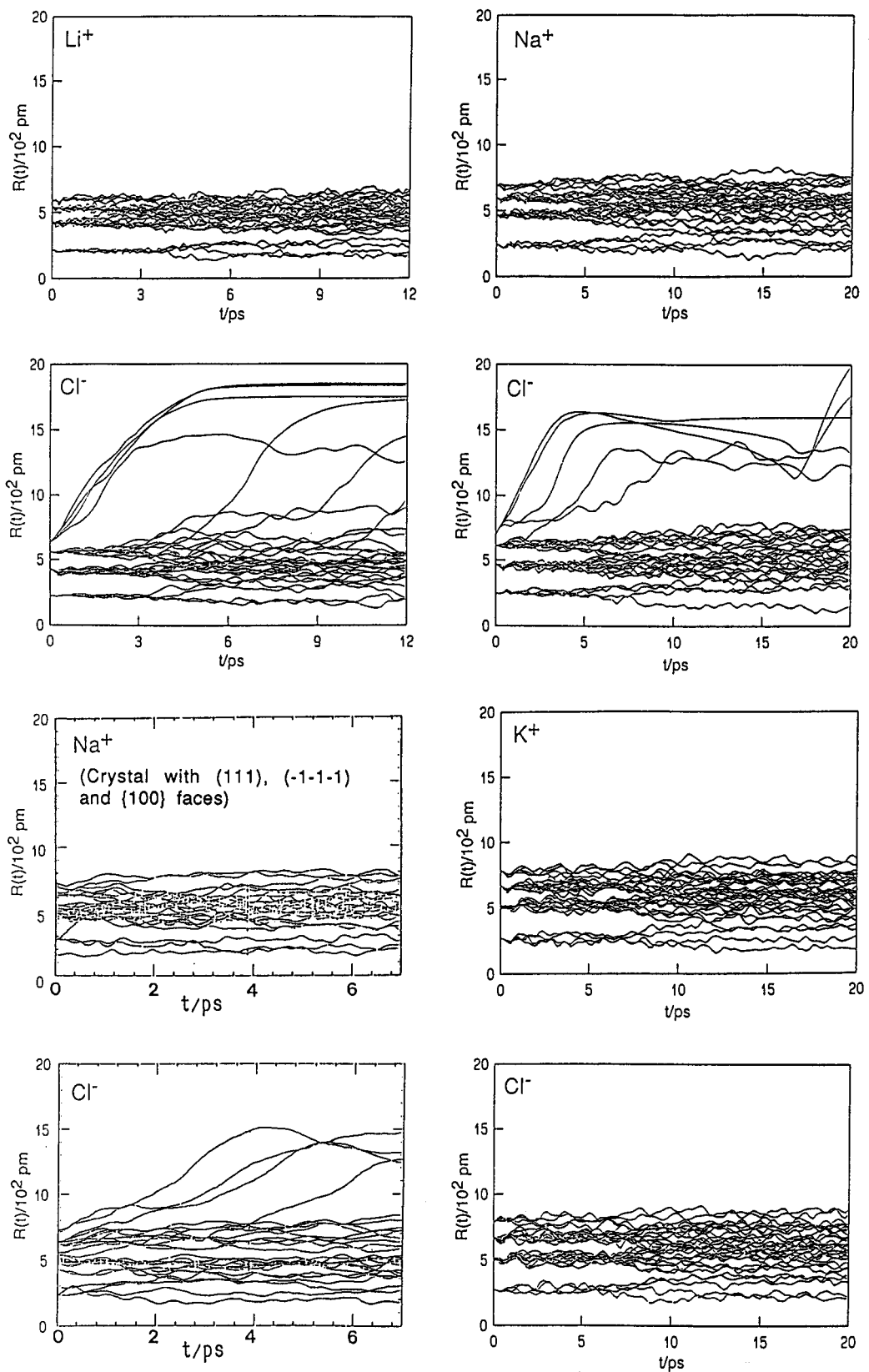


Fig. 2. Evolution of the distance  $R$  from the center of the box of the ions of LiCl, NaCl with the {100} faces, NaCl with the (111) and (-1-1-1) faces together with the {100} faces, and KCl.



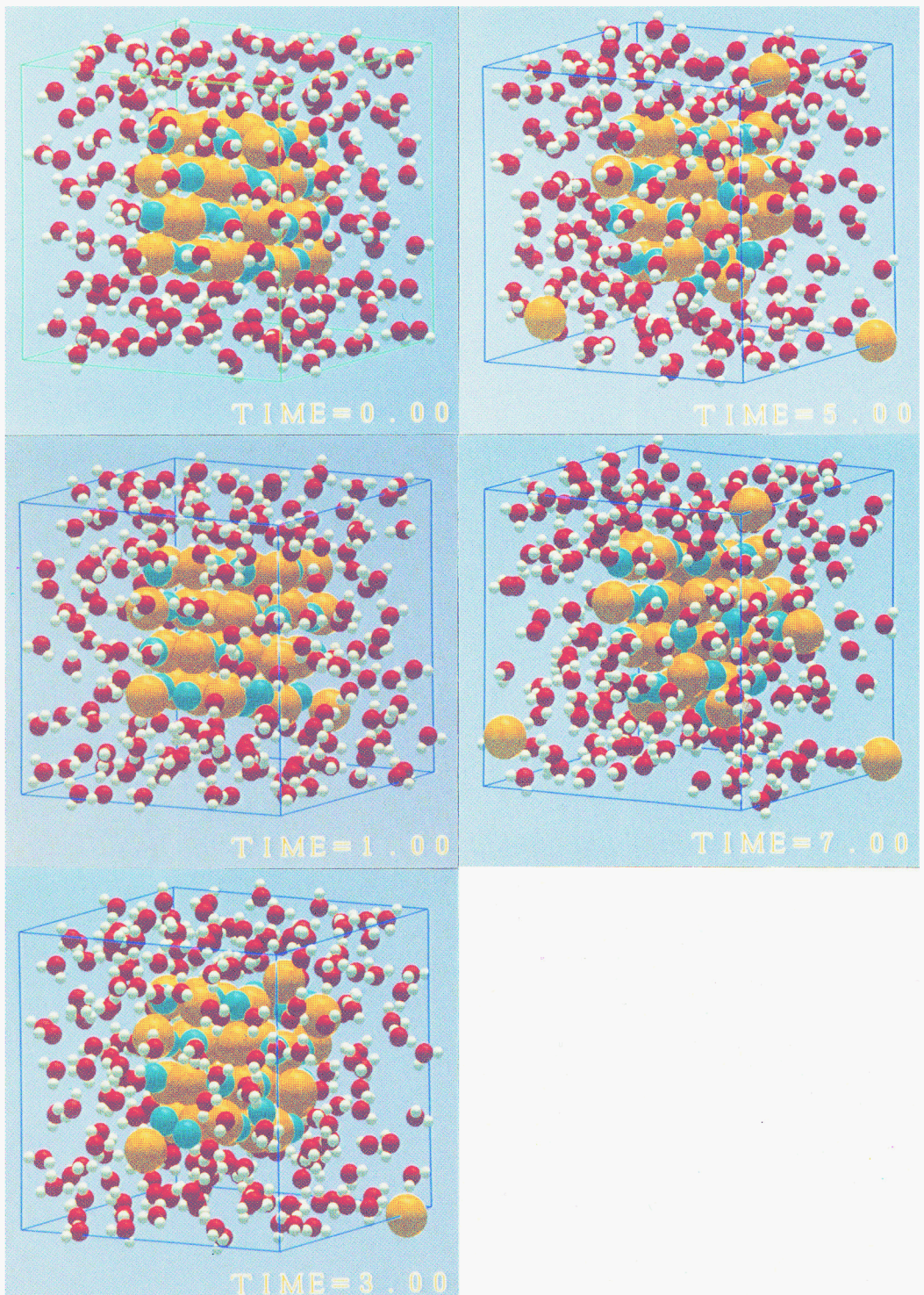


Fig. 3. Snapshots of the dissolution process of an NaCl crystal with the {100} faces.  
The unit of time is ps.



Table 7. The time dependence of the coordination number of ions in the first and second spheres.

| System | Concentration<br>mol<br>kg H <sub>2</sub> O | Degree of super-<br>saturation<br>% | Coordination<br>number<br>$n_{ij}$ | Coordination<br>sphere<br>$r/\text{pm}$ | Time/ps |      |      |      |
|--------|---|-------------------------------------|------------------------------------|---|---------|------|------|------|
|        |   |                                     |                                    |   | 0       | 6    | 12   | 18   |
| NaCl   | 9.25  | 150.4                               | $n_{\text{NaCl}}$                  | 282.5                                   | 0.13    | 0.64 | 0.55 | 0.55 |
|        |   |                                     |                                    | 489.3                                   | 1.98    | 2.36 | 2.38 | 2.43 |
|        |   |                                     | $n_{\text{NaNa}}$                  | 399.5                                   | 0.95    | 0.69 | 0.69 | 0.58 |
|        |   |                                     |                                    | 564.5                                   | 3.75    | 3.02 | 3.02 | 2.84 |
| NaCl   | 15.42                                       | 250.4                               | $n_{\text{ClCl}}$                  | 399.5                                   | 0.15    | 0.18 | 0.18 | 0.18 |
|        |   |                                     |                                    | 564.5                                   | 2.51    | 2.15 | 2.15 | 2.25 |
|        |   |                                     | $n_{\text{NaCl}}$                  | 282.5                                   | 0.00    | 1.25 | 1.25 | 1.24 |
|        |   |                                     |                                    | 489.3                                   | 3.53    | 3.55 | 3.65 | 3.76 |
| NaCl   | 15.42                                       | 250.4                               | $n_{\text{NaNa}}$                  | 399.5                                   | 0.94    | 0.96 | 0.94 | 0.99 |
|        |   |                                     |                                    | 564.5                                   | 4.43    | 4.41 | 4.43 | 4.66 |
|        |   |                                     | $n_{\text{ClCl}}$                  | 399.5                                   | 0.00    | 0.71 | 0.81 | 0.78 |
|        |   |                                     |                                    | 564.5                                   | 4.20    | 4.15 | 4.18 | 4.25 |
| CsF    | 36.34                                       | 150.6                               | $n_{\text{CsF}}$                   | 301.5                                   | 1.66    | 1.79 | 2.10 | 1.90 |
|        |   |                                     |                                    | 522.1                                   | 5.15    | 6.06 | 6.01 | 5.85 |
|        |   |                                     | $n_{\text{CsCs}}$                  | 426.3                                   | 1.65    | 2.24 | 2.29 | 2.27 |
|        |   |                                     |                                    | 602.5                                   | 8.17    | 8.78 | 9.00 | 9.30 |
|        |   |                                     | $n_{\text{FF}}$                    | 426.3                                   | 3.00    | 2.37 | 2.37 | 2.38 |
|        |   |                                     |                                    | 602.5                                   | 8.54    | 8.33 | 8.54 | 8.76 |

factors and the frequency factors for the M<sup>+</sup>-O, X<sup>-</sup>-O, M<sup>+</sup>-X<sup>-</sup>, M<sup>+</sup>-M<sup>+</sup>, and X<sup>-</sup>-X<sup>-</sup> pairs in the solutions of NaCl, KCl, KF and CsF are summarized in Table 8.

## DISCUSSION

*The Mechanism of Dissolution of Ions.* It is obviously wrong to consider that the larger the hydration energy of an ion, the more rapidly the ion dissolves. Water molecules coordinating with an ion do not pull the ion away from the crystal surface. The driving force for dissolution is the repulsion between the larger ion and the charged site of the water molecules which hydrate the adjacent smaller ions. This force pushes ions way from the crystal surface by overcoming the electrostatic interactions in the crystal. In the case of LiCl and NaCl, the repulsive force acts between the anions and the oxygen atoms in the water molecules hydrating the lithium and sodium ions, respectively. On the other hand, the repulsive interaction should occur between caesium ions and a proton of a water molecule which hydrates a fluoride ion at a corner or at a corner-like edge produced by the deformation of the CsF crystal.

After some period of time from the beginning of dissolution of ions, rather stable, charged microclusters form and the shape of the microclusters is very distorted. Due to the repulsive forces among ions which exist in excess in the microclusters, some of the excess ions in the deformed microcluster probably start to dissolve after some time elapsed. The microclusters may also be explosively decomposed to smaller clusters.

*Nucleation of Crystals.* Clusters formed in the supersaturated solutions have an irregular shape. We do not know either the irregular nuclei will be rearranged to a regular form during the crystal growth or the irregular atomic arrangement still remains at a very center of a large crystal. The question still remains unsolved. Much longer calculations with a much larger system should be examined to elucidate this problem.

In supersaturated solutions ionic aggregates higher than 1:1 ion pairs sometimes exist as metastable species which are detectable by the solution X-ray diffraction method and other techniques. The degree of coagulation of ions depends on the concentration of the ions rather than the degree of supersaturation.

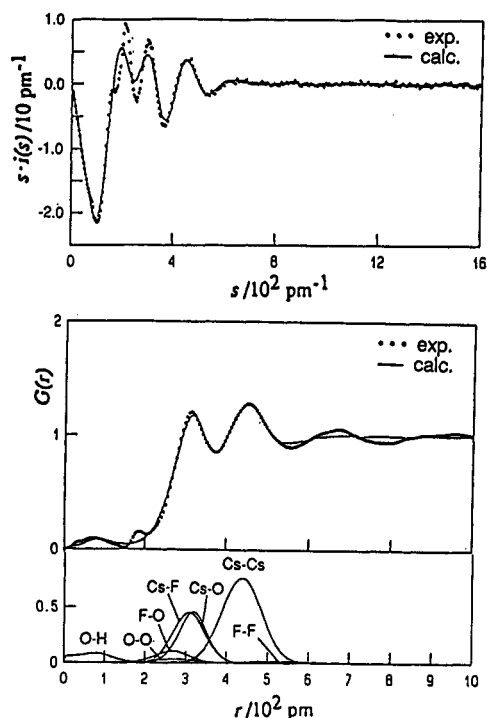


Fig. 4. The structure function,  $i(s)$ , and the radial distribution function,  $G(r)$ , of 31.96 mol (kg H<sub>2</sub>O)<sup>-1</sup> CsF aqueous solution.

Table 8. Structure parameters of saturated and supersaturated alkali halide aqueous solutions determined by means of solution X-ray diffraction at 25 °C.

| System | Concentration<br>mol<br>kg H <sub>2</sub> O | Degree of super-<br>saturation<br>% | Atom Pair | $\frac{r}{10 \text{ pm}}$ | $\frac{b}{10 \text{ pm}^2}$ | $n$              | Atom               | $\frac{R}{10 \text{ pm}}$              | $\frac{B}{10 \text{ pm}^2}$                             |
|--------|---|-------------------------------------|-----------|---------------------------|-----------------------------|------------------|--------------------|--|---|
| NaCl   | 6.18  | 100.3                               | O - H     | 95.7 <sup>a</sup>         | 10 <sup>a</sup>             | 2.0 <sup>a</sup> | H<br>O<br>Na<br>Cl | 279(5)<br>275(1)<br>361(6)<br>399(4)   | 70(42)<br>100(11)<br>72(46)<br>110(32)                  |
|        |   |                                     | H - H     | 151 <sup>a</sup>          | 28 <sup>a</sup>             | 1.0 <sup>a</sup> |                    |  |   |
|        |   |                                     | O - O     | 285(1)                    | 85(7)                       | 1.8(1)           |                    |  |   |
|        |   |                                     | Na - O    | 241(1)                    | 27(7)                       | 4.6(1)           |                    |  |   |
|        |   |                                     | Cl - O    | 318(2)                    | 20(5)                       | 5.3(1)           |                    |  |   |
|        |   |                                     | Na - Cl   | 282(17)                   | 45(71)                      | 0.3(1)           |                    |  |   |
| KCl    | 4.56  | 94.8                                | O - H     | 95.7 <sup>a</sup>         | 10 <sup>a</sup>             | 2.0 <sup>a</sup> | H<br>O<br>K<br>Cl  | 310(4)<br>310(1)<br>340(5)<br>385(6)   | 70(33)<br>100(8)<br>250(56)<br>1100<br>(125)            |
|        |   |                                     | H - H     | 151 <sup>a</sup>          | 28 <sup>a</sup>             | 1.0 <sup>a</sup> |                    |  |   |
|        |   |                                     | O - O     | 285(1)                    | 81(6)                       | 1.8(1)           |                    |  |   |
|        |   |                                     | K - O     | 281(1)                    | 8(3)                        | 5.8(1)           |                    |  |   |
|        |   |                                     | Cl - O    | 322(1)                    | 11(4)                       | 5.8(1)           |                    |  |   |
|        |   |                                     | K - Cl    | 315(5)                    | 11(2)                       | 0.6(1)           |                    |  |   |
| KF     | 16.15                                       | 92.3                                | O - H     | 95.7 <sup>a</sup>         | 10 <sup>a</sup>             | 2.0 <sup>a</sup> | H<br>O<br>K<br>F   | 314(7)<br>301(2)<br>416(2)<br>389(6)   | 60(58)<br>59(13)<br>407(32)<br>587(86)                  |
|        |   |                                     | H - H     | 151 <sup>a</sup>          | 28 <sup>a</sup>             | 1.0 <sup>a</sup> |                    |  |   |
|        |   |                                     | O - O     | 289(3)                    | 27(10)                      | 1.4(1)           |                    |  |   |
|        |   |                                     | K - O     | 282(1)                    | 14(4)                       | 3.3(1)           |                    |  |   |
|        |   |                                     | F - O     | 268(2)                    | 18(8)                       | 4.0(1)           |                    |  |   |
|        |   |                                     | K - F     | 269(2)                    | 33(7)                       | 2.3(1)           |                    |  |   |
|        |   |                                     | K - K     | 388(2)                    | 120(12)                     | 1.9(1)           |                    |  |   |
|        |   |                                     | F - F     | 432(9)                    | 48(39)                      | 1.6(2)           |                    |  |   |
| CsF    | 31.96                                       | 132.4                               | O - H     | 95.7 <sup>a</sup>         | 10 <sup>a</sup>             | 2.0 <sup>a</sup> | H<br>O<br>Cs<br>F  | 309(28)<br>330(7)<br>490(1)<br>393(12) | 170 <sup>a</sup><br>318(86)<br>254(13)<br>1143<br>(235) |
|        |   |                                     | H - H     | 151 <sup>a</sup>          | 28 <sup>a</sup>             | 1.0 <sup>a</sup> |                    |  |   |
|        |   |                                     | O - O     | 280(25)                   | 104(136)                    | 1.2(3)           |                    |  |   |
|        |   |                                     | Cs - O    | 321(2)                    | 32(6)                       | 3.6(1)           |                    |  |   |
|        |   |                                     | F - O     | 271(8)                    | 45(34)                      | 4.1(5)           |                    |  |   |
|        |   |                                     | Cs - F    | 312(2)                    | 53(7)                       | 3.3(1)           |                    |  |   |
|        |   |                                     | Cs - Cs   | 442(7)                    | 105(3)                      | 2.3(1)           |                    |  |   |
|        |   |                                     | F - F     | 548(30)                   | 450(268)                    | 5.3(11)          |                    |  |   |

<sup>a</sup> Fixed value.

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