Dissolution of Alkali Fluoride and Chloride Crystals in Water Studied by Molecular Dynamics Simulations

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

The dissolution of cubic crystals of NaF, KF, CsF, LiCl, NaCl, and KCl consisting of 32 cations and 32 anions in an isolated box containing 216 water molecules was studied at 298 K by molecular dynamics simulations. The ion-ion, ion-water and water-water interactions were described in terms of the Tosi-Fumi, Kistenmacher-Popkie-Clementi, and Matsuoka-Clementi-Yoshimine potentials, respectively. During the simulation periods of 12 ps for NaF, CsF and LiCl and 20 ps for KF, NaCl and KCl cations did not dissolve, while anions *dissolved* from the CsF, LiCl and NaCl crystals but not from the NaF, KF and KCl crystals. The mass effect in the dissolution of CsF was examined by giving the ceasium ions the atomic weight of the fluoride ion (18.998). In case of the "light" caesium ions in the crystal fluctuated less far and again fluoride ions but no caesium ions were dissolved.

I. Introduction

In molecular dynamics simulations of the dissolution of sodium chloride crystals in water [1, 2] it has been found that within 7 ps some chloride ions but no sodium ions were liberated from the crystal. In the present work the dissolution of NaCl and some other alkali halide crystals in water was simulated for time spans up to 20 ps.

II. The Simulation

a) *The systems* were crystals of the rock-salt type alkali halides NaF, KF, CsF, LiCl, NaCl, and KCl in water. The simulations were started after equilibration of the water. In the case of CsF we examined two systems, the normal one and one in which Cs had the atomic weight of F, i.e. 18.998. 32 cations and 32 anions, first assembled to a cubic crystal in the middle of the box, and 216 water molecules were placed in a nonperiodic box. For details see Table 1.

b) *Potentials:* For the ion-ion interactions the Born-Mayer-Huggins type Tosi-Fumi potential [3] was employed:

$$\Phi_{ij}=z_i z_j e^2/r+A_{ij} b_{ij}\exp\{(\sigma_i+\sigma_j-r)/\varrho\}-c_{ij}/r^6-d_{ij}/r^8. \tag{1}$$

A_{ij} denotes the Pauling factor, $1+(z_i/n_i)+(z_j/n_j)$, where n_i and n_j denote the numbers of electrons in the outer-most shell of ions i and j, respectively. Values of the parameters in (1) are listed in Table 2.

The Matsuoka-Clementi-Yoshimine (MCY) model [4] was used for the water-water interactions. Ion-water interactions were expressed by the Kistenmacher-Popkie-Clementi (KPC) potential [5]

$$\begin{aligned}\Phi_{iw} = {} & z_i Q(1/r_{i\text{-H1}}+1/r_{i\text{-H2}}-1/r_{i\text{-R1}}-1/r_{i\text{-R2}})\\ & +z_i Q_m(1/r_{i\text{-M1}}+1/r_{i\text{-M2}}-2/r_{i\text{-O}})\\ & +a_1\{\exp(-b_1 r_{i\text{-H1}})+\exp(-b_1 r_{i\text{-H2}})\}\\ & +a_2\exp(b_2 r_{i\text{-M}}).\end{aligned} \tag{2}$$

Values of the parameters and illustration are given in Table 3.

Table 1. The side-lengths of the box (l), total time (t) for the simulations, and the number of steps (N). Time step: 10^{-15} s.

	LiCl	NaF	NaCl	KF	KCl	CsF
l/pm	1963	1938	1993	1975	2039	2019
t/ps	12.0	12.0	20.0	20.0	20.0	12.0
N	12 000	12 000	20 000	20 000	20 000	12 000

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Table 2. Parameter values for the Tosi-Fumi potential of ion-ion interactions. c is given in 10^{-79} J m^6 and d is given in 10^{-99} J m^8. The value of b is 0.338×10^{-19} J for all the salts.

Salt	$(\sigma_+ + \sigma_-)$/pm	ϱ/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

Table 3. Parameter values of potential function of ion-water interactions in the KPC model.

Parameter	Li^+	Na^+	K^+	Cs^+	F^-	Cl^-
$Q/10^{-8}$ 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/pm^{-1}	6.712196	7.45962	4.992545	5.660	3.762637	3.097243
b_2/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

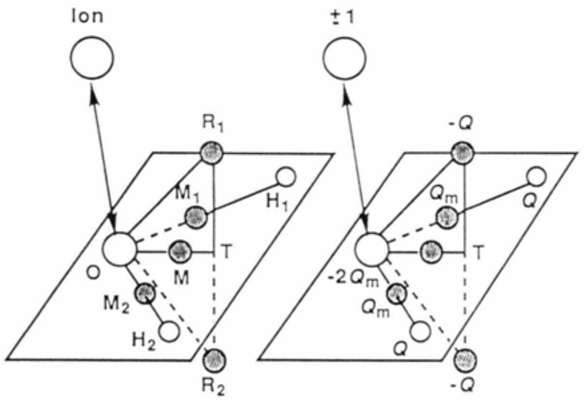


Table 4. Radii of ions and α-values of the switching function.

	Li^+	Na^+	K^+	Cs^+	F^-	Cl^-
r_i/pm	74	102	138	170	133	181
$\alpha_i/10^{-4}\,\mathrm{pm}^{-2}$	11.68	6.148	3.359	2.213	3.616	1.952

For the Cs^+–H_2O interaction, where no parameter values of the KPC potential are reported, we assumed that the potential of the ST2 model for water and the charged Lennard-Jones sphere model for the ion [6] can be expressed in the form of the KPC potential. We thus obtained the parameter values from a least squares fit of the KPC potential to the potential curves obtained from the above two models.

c) *The temperature* was kept at 298 K by scaling the thermal velocities.

d) *Switching function:* Water molecules were assumed to be completely elastic with respect to their center of gravity on collisions with the rigid wall. Ions could pass the wall. Therefore we introduced a switching function $S_w(x)$ to cut off electrostatic effects arising from ions which went beyond the wall. The function used was

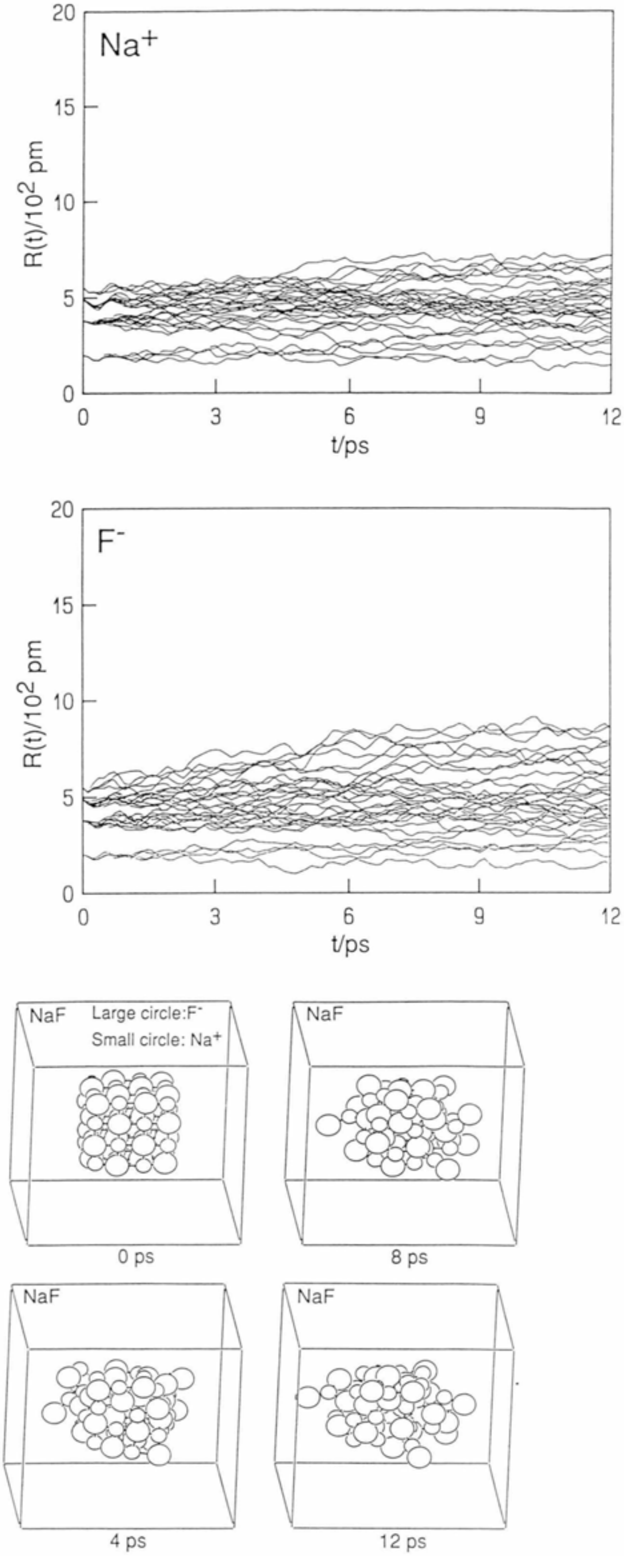
$$S_w(x) = 1 \qquad \text{for} \quad -l/2 \le x \le l/2,$$

$$S_w(x) = \exp\{-\alpha_i(|x| - l/2)^2\} \quad \text{for} \quad |x| > l/2, \qquad (3)$$

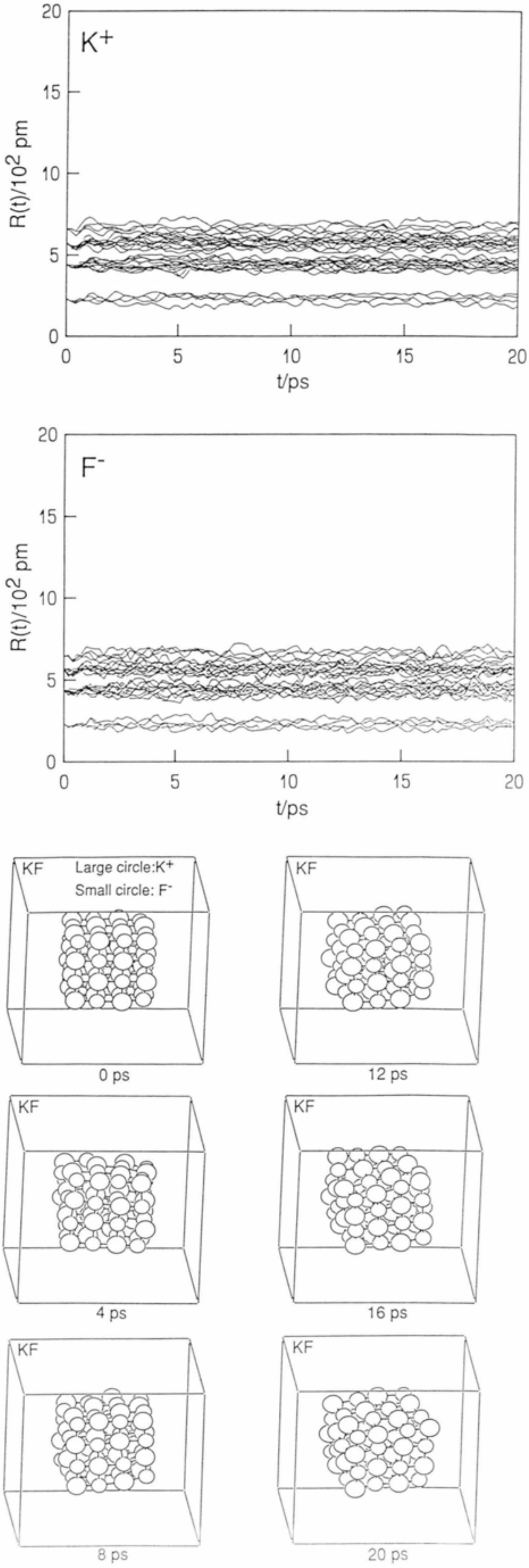
where x is any of the three Cartesian coordinates, their origin being the middle of the box. The parameter α_i was defined as $1/(0.3954\,r_i)^2$, where r_i is the ionic radius of i (cf. Table 4).

III. Results

Figure 1 shows the evolution of the distances R of ions from the center of the box and corresponding snapshots of the dissolution process. Water molecules are not shown in the pictures. The dissolution of NaCl and CsF crystals has been visualized on video types

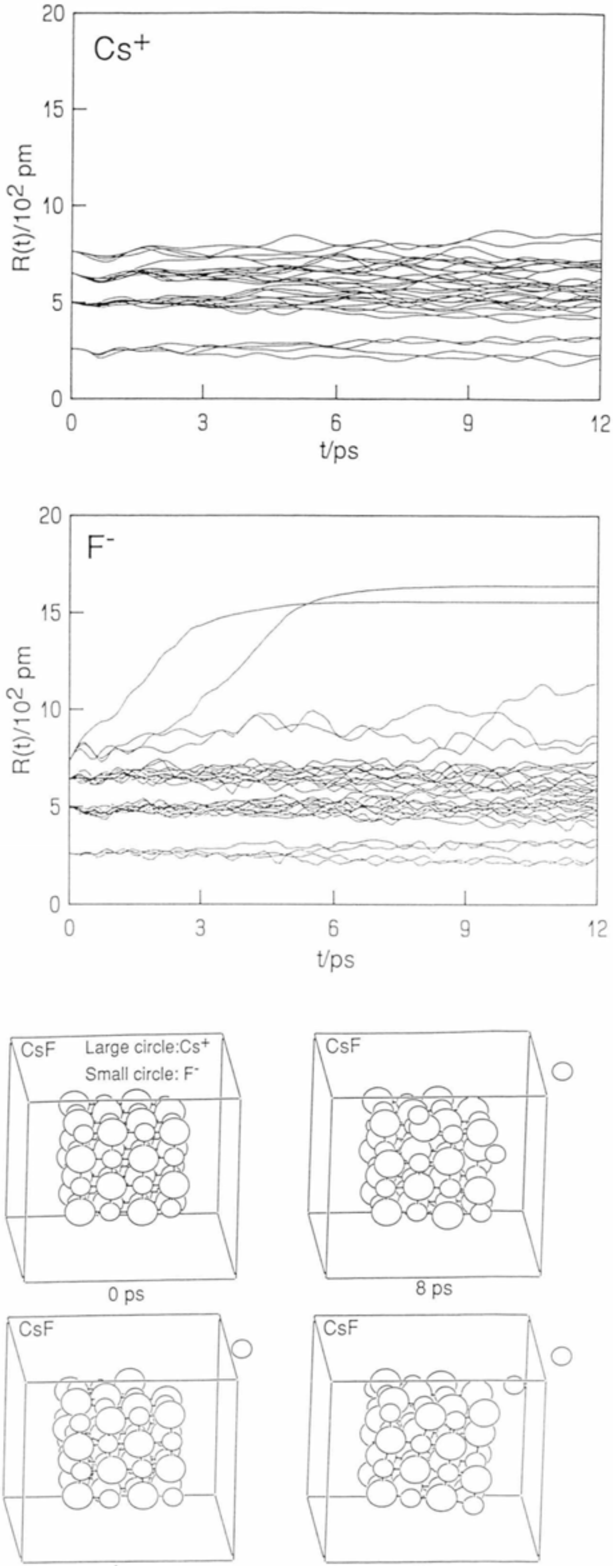


(a)

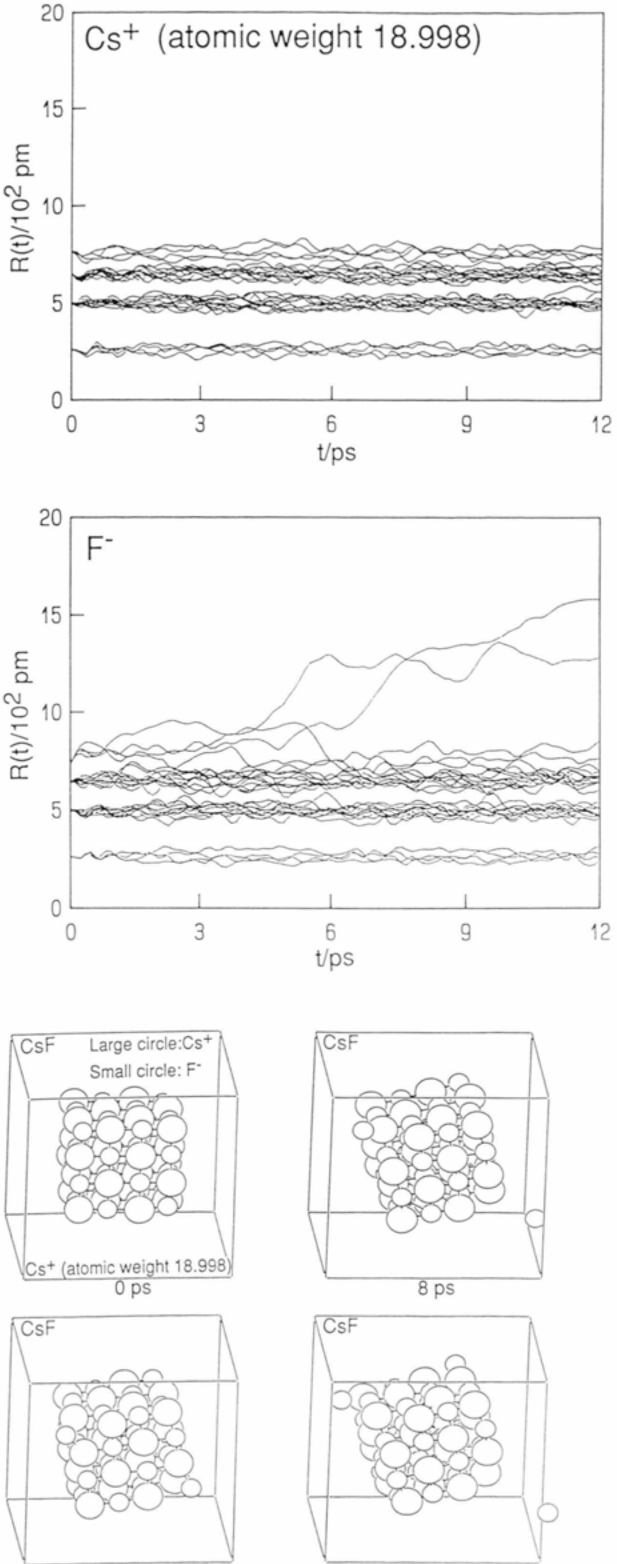


(b) →

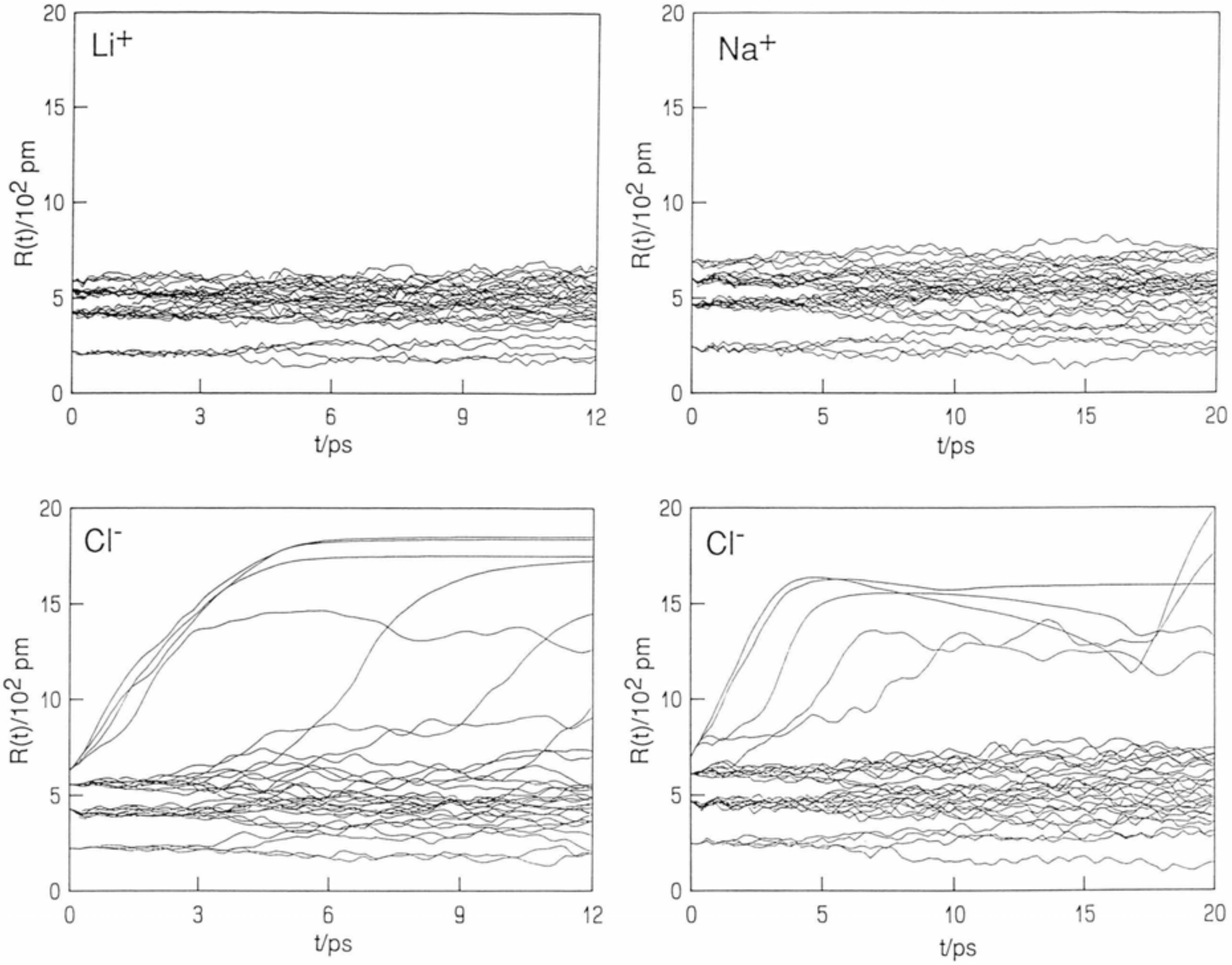
Fig. 1. Evolution of the distances *R* from the center of the box of the ions of seven alkali halide crystals in water, and corresponding snapshots. Cation-anion pairs with distances equal to or smaller than the sum of the ionic radii are connected with solid lines: (a) NaF, (b) KF, (c) CsF, (d) light CsF, (e) LiCl, (f) NaCl, (g) KCl.


Cs+
R(t)/10² pm
t/ps
0
5
10
15
20
0
3
6
9
12
F-
CsF
Large circle:Cs+
Small circle: F-
0 ps
8 ps
4 ps
12 ps

(c)


Cs+ (atomic weight 18.998)
R(t)/10² pm
t/ps
0
5
10
15
20
0
3
6
9
12
F-
CsF
Large circle:Cs+
Small circle: F-
Cs+ (atomic weight 18.998)
0 ps
8 ps
4 ps
12 ps

(d)


Li+
R(t)/10² pm
t/ps
0
3
6
9
12
5
10
15
20
Na+
R(t)/10² pm
t/ps
0
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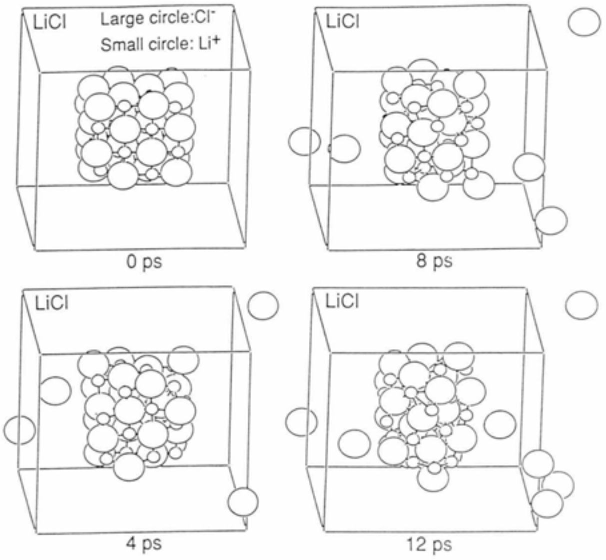
20
Cl-
R(t)/10² pm
t/ps
Cl-
R(t)/10² pm
t/ps


LiCl
Large circle: Cl-
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0 ps
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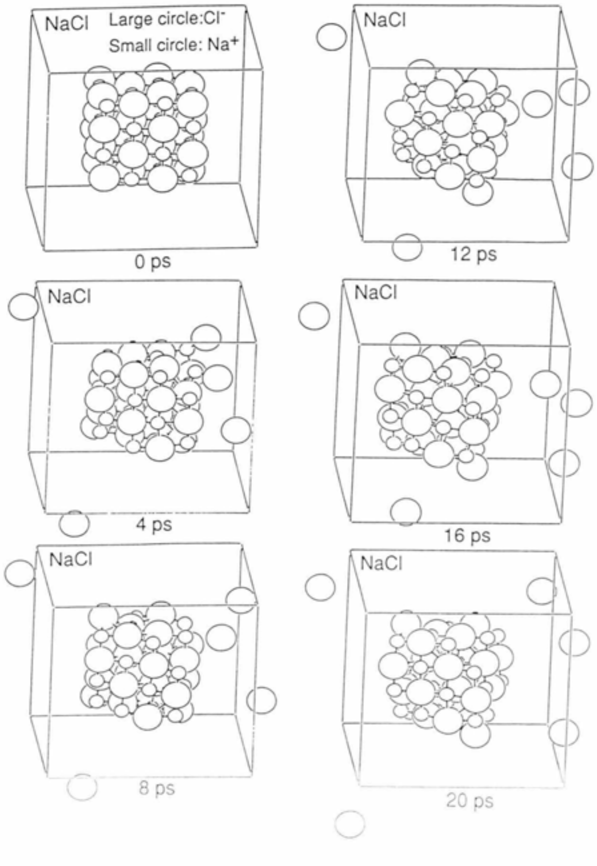
LiCl
4 ps
LiCl
12 ps

(e)


NaCl
Large circle: Cl-
Small circle: Na+
0 ps
NaCl
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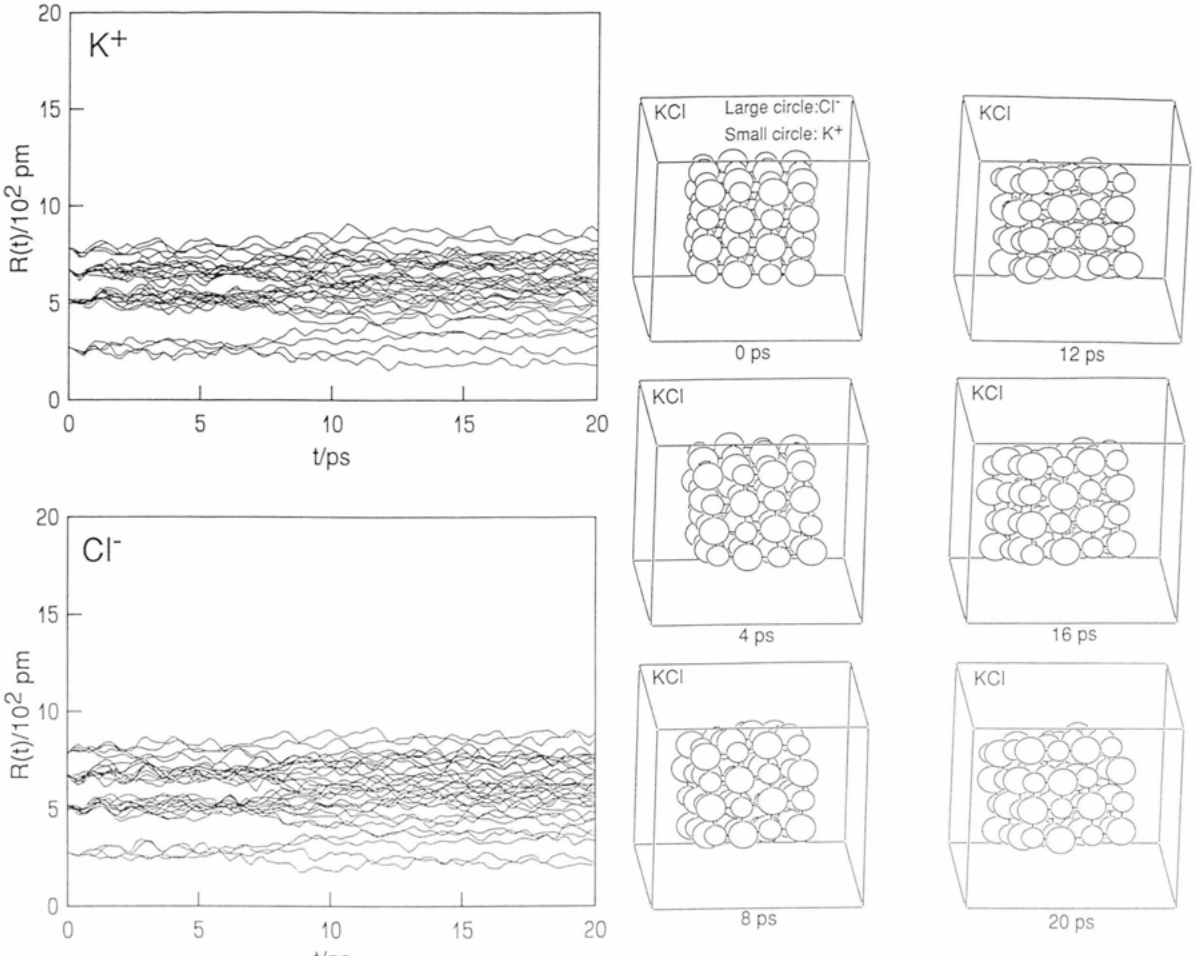
NaCl
4 ps
NaCl
16 ps
NaCl
8 ps
NaCl
20 ps

(f) →



(g)

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NaF (Fig. 1 a): No dissolution of ions was observed within 12 ps, although the structure of the crystal was distorted very much due to thermal vibrations of the lattice. Fluctuations of the positions of ions are more pronounced for F^- than for Na^+.

KF (Fig. 1 b): No dissolution was observed within 20 ps. Distortion of the lattice of the crystal is less pronounced than for NaF.

CsF (Fig. 1 c): Three fluoride ions dissolved within 12 ps. Some fluoride ions moved around the surface of the crystal but were not separated from it. Fluctuations of the positions of ions in the crystals are more rapid for F^- than for Cs^+, as expected due to the difference in mass.

"Light" CsF (Fig. 1 d): The frequencies of the thermal vibrations of Cs^+ and F^- are almost equal, but still no dissolution of Cs^+ is observed, while again two fluoride ions dissolved.

LiCl (Fig. 1 e): Eight chloride ions dissolved within 12 ps. Thus 12 ps after the start of dissolution the rest of the crystal had the composition of $[Li_{32}Cl_{24}]^{8+}$. The four chloride ions at the corners of the crystal went out at the very beginning of the process, then the dissolution of ions stopped for a few pico seconds, then some chloride ions dissolved from corner-like positions in the distorted crystal, and then a further dissolution of chloride ions could be observed after 10 ps. Fluctuations of the ions are further for Cl^- than for Li^+. The result was essentially the same as that of NaCl, but more chloride ions were liberated from the LiCl crystal than from NaCl within the same period.

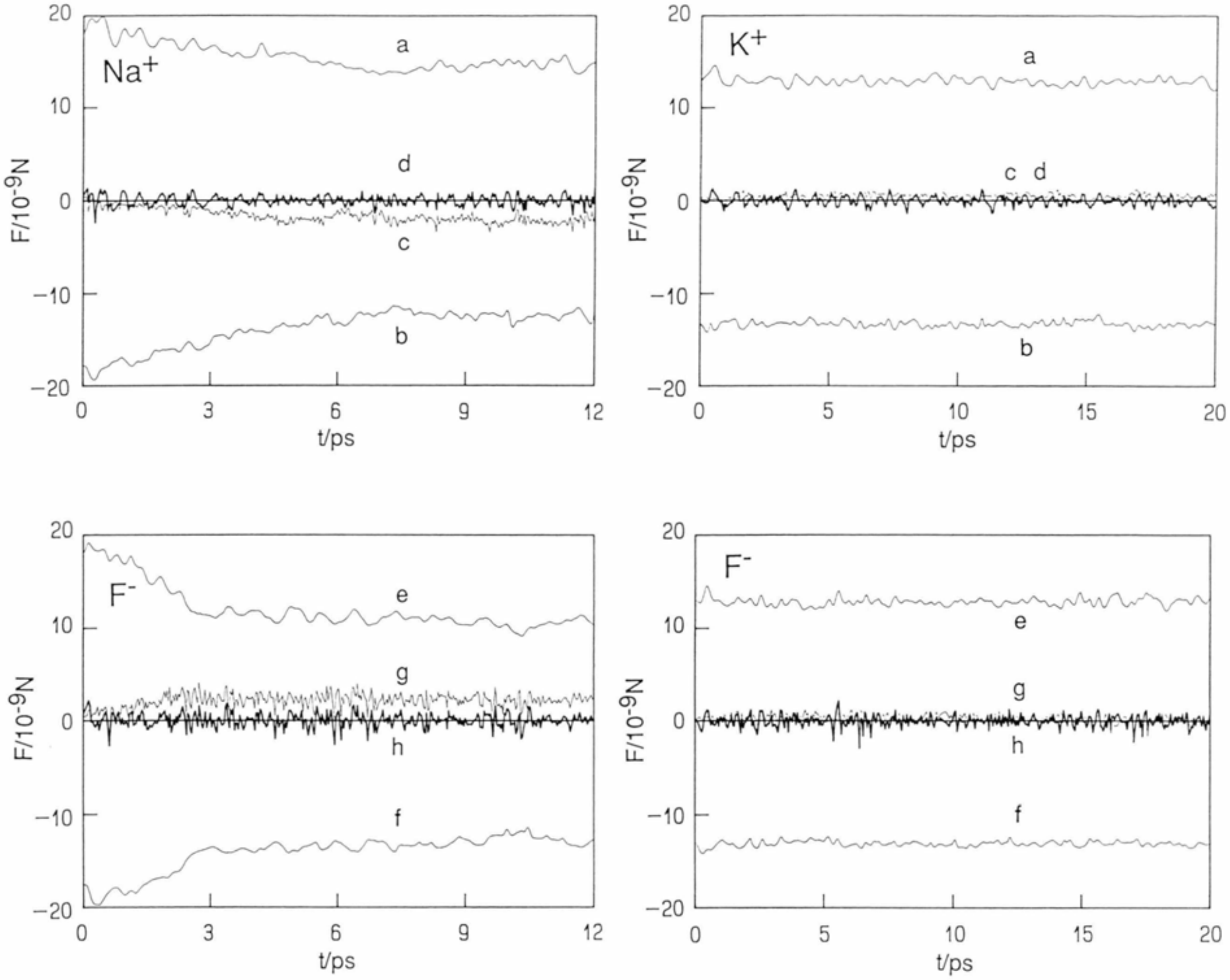


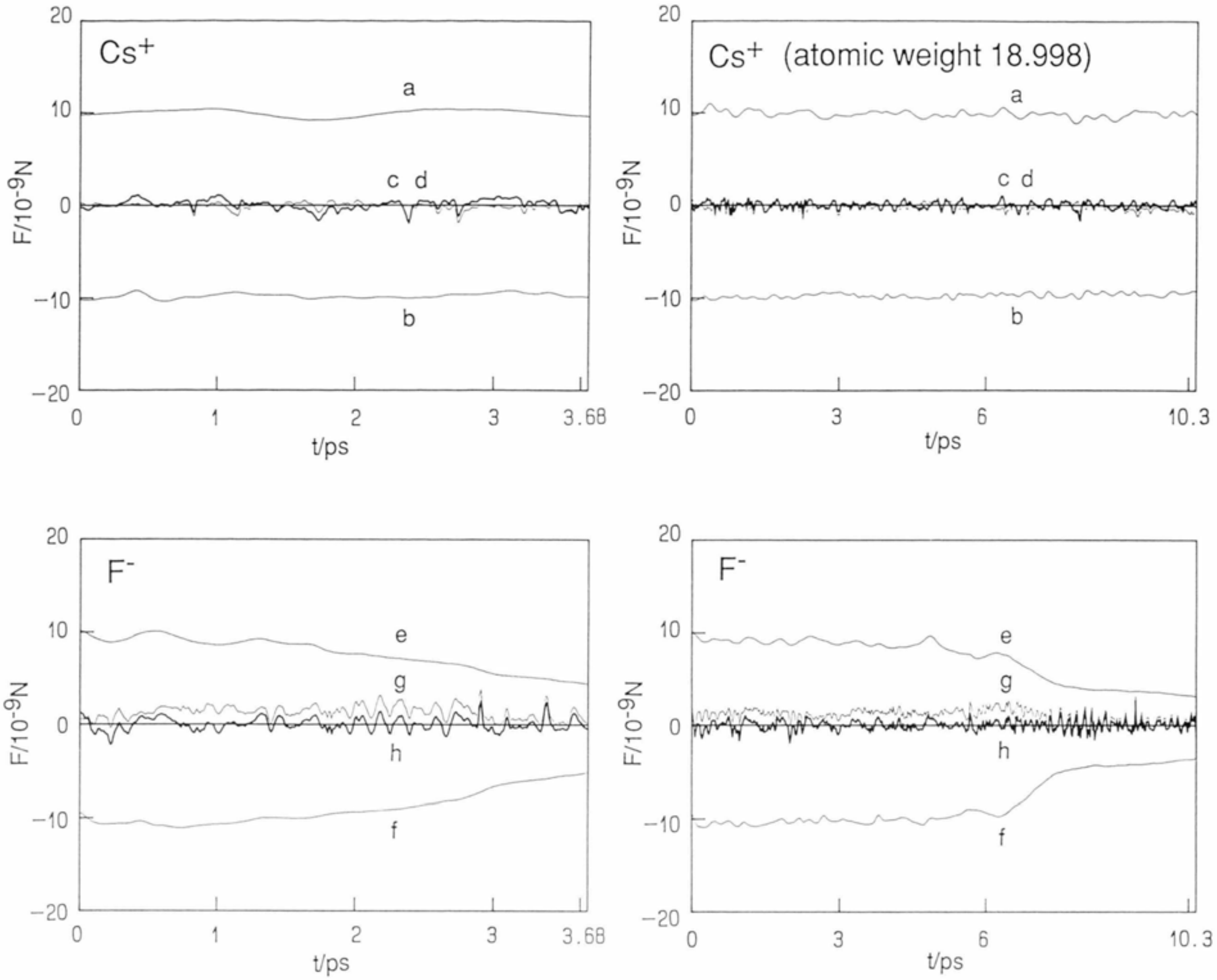
Fig. 2. Evolution of the averaged forces acting on a cation at a corner and the anion at the opposite corner of the crystals. (a) and (e): Force resulting from all coions, (b) and (f): Force resulting from all counterions, (c) and (g): Force resulting from all water molecules, (d) and (h): The sum of the forces, (a)+(b)+(c) and (e)+(f)+(g), respectively. For LiCl, NaCl, and CsF the evolution is shown up to the time when the first ion left the box. Forces are positive when pointing away from the center of the box.

NaCl (Fig. 1f): As in the previous paper [1], five chloride ions were readily dissolved. No further ions were dissolved, and thus the microcluster $[Na_{32}Cl_{27}]^{5+}$ remained in the water for more than 15 ps. Some chloride ions collided in the solution phase at about 17 ps.

KCl (Fig. 1g): No dissolution of ions was observed within 20 ps. Distortion of the crystal structure of KCl was greater than that of KF due to the smaller lattice energy of the former crystal.

IV. Discussion

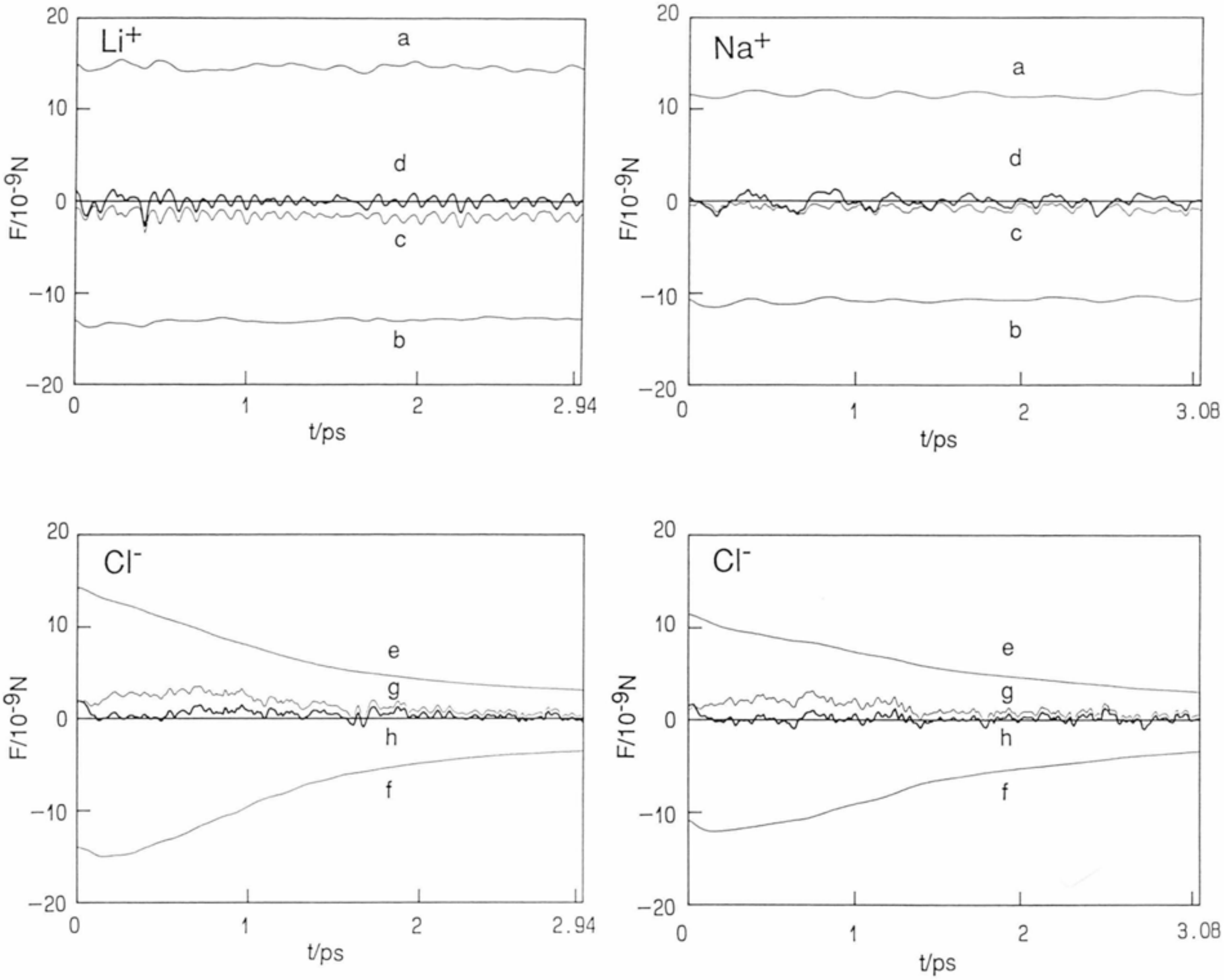
We discuss the forces acting on an ion at a corner of a crystal. These forces can be divided into three contributions; (i) forces from the rest of the coions, (ii) forces from all counterions, and (iii) forces from all water molecules. The sign of the forces was defined to be positive when directed away from the center of the box. Figure 2 shows the evolution of these forces on a cation at a corner and the anion at the opposite corner. Curves a and e show the forces (i), curves b and f the



forces (ii), and curves c and g the forces (iii). Curves d and h, given by the thick solid lines, represent the sum of the forces (i), (ii), and (iii) acting on the corner cations and anions, respectively, as indicated.

The sum of the three forces fluctuated around zero, indicating that the ions remained close to equilibrium positions. As expected, the interionic forces decreased if the crystal became deformed or if ions left it.

As to the ion-water interactions, one observes the following: On the cations the water molecules exert a force towards the liquid (KF), no force (CsF, KCl), or a force towards the crystal (NaF, LiCl, NaCl). In all cases the cations did not dissolve. On the anions the water molecules exert a force towards the liquid in all cases. If this force is large (CsF, LiCl, NaCl), anions dissolved; if it is small (KF, KCl), anions did not dissolve. An exception is NaF, where the force is large but no fluoride ions dissolved. In this case, however, the whole crystal reached a "semidissolved" state (Figure 1 a). These findings can be interpreted as follows: A corner ion is neighboured by three counterions, and water molecules tend to bridge such ion-counterion pairs. This may result in an attraction or a repulsion between ion and counterion. Evidently, if the corner



ion is an anion, a repulsion results, while if it is a cation, the effect is ambiguous with a tendency to the attractive. This difference for corner anions and corner cations results from the different orientation of the bridging water molecules, the oxygen of the water molecules being oriented towards one of the three cations if the corner ion is an anion, and vice versa. One of the protons in the hydrated water molecules tends to form a hydrogen bond with the anion so as to make the anion−H−O bond to be linear, and thus repulsion arises between the proton and the neighbour cation, which reduces the anion-cation bond strength.

Interestingly, the video shows that the water molecules liberating the corner chloride ions (LiCl, NaCl) did not accompany them while leaving the crystal, whereas they did so in case of the corner fluoride ions (CsF).

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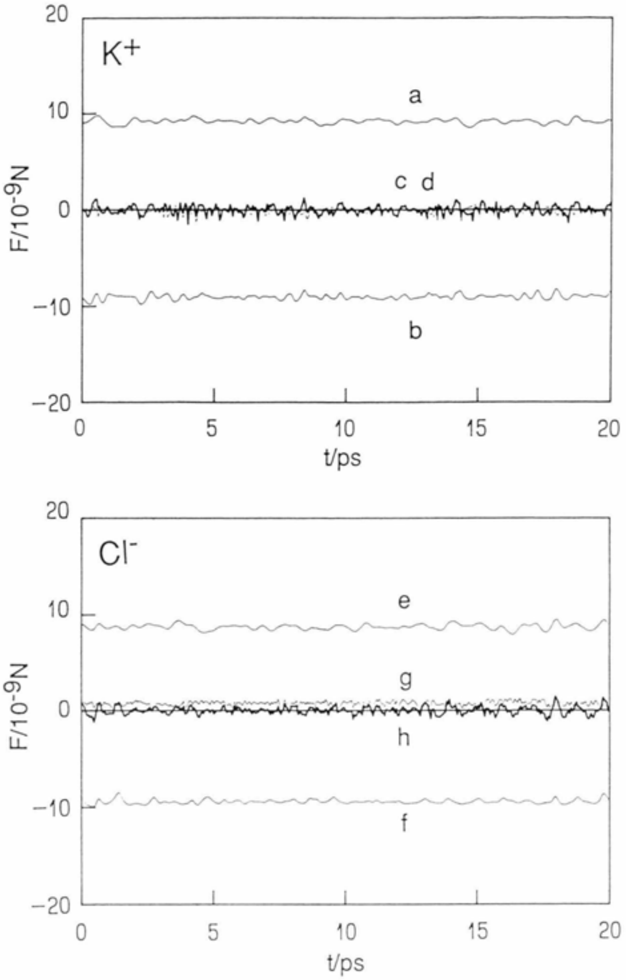

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