Molecular Dynamics Study of Aqueous Solutions
IX. Dynamical Properties of an NH_4Cl Solution

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Z. Naturforsch. **34a**, 1083–1092 (1979); received July 9, 1979

The dynamical properties of an aqueous ammonium chloride solution have been calculated from a molecular dynamics simulation over 3.5 picoseconds at a temperature of 301 K where the basic periodic cube contained 200 water molecules, 8 ammonium ions and 8 chloride ions. The effective pair potentials are based on the ST 2 water model, a rigid tetrahedral four point charge model for NH_4^+, and a single point charge model for Cl^-. The coefficients of self-diffusion and of rotational diffusion, the spectral densities of hindered translations and of librations, the correlation times of the dipole moment vector and the vector connecting the two protons in a water molecule are reported separately for the various subsystems — NH_4^+, Cl^-, bulk water, hydration water of NH_4^+ and Cl^- — and are compared with the available experimental data. Implications with respect to the structure breaking ability of the ions are discussed.

I. Introduction

In the preceding paper of this series [1] improvements of the molecular dynamics (MD) simulation of aqueous solutions are reported and the structural properties of an NH_4Cl solution are discussed. The results are based on a simulation over 16000 time steps equivalent to a total elapsed time of 3.5 picoseconds. The basic cube contains 200 water molecules, 8 ammonium ions and 8 chloride ions corresponding to a 2.2 molal solution. The ST2 water model is employed. The NH_4^+ is modelled as a regular tetrahedron with a N–H distance of 1.05 Å, a Lennard-Jones (LJ) sphere with the same parameters as in the ST2 model is centered at the nitrogen atom and 0.25 elementary charges are located at each of the four hydrogen atom positions. The chloride ion is described as a LJ sphere with a point charge in the center. For the evaluation of the Coulombic part of the ion-ion interaction the Ewald summation is used while for all the other interactions the shifted force potential is employed. The fluctuation of the energy $\Delta E/E$ was less than $3 \cdot 10^{-5}$. The average temperature of the simulation was 301 K and showed no trend, so that an adjustment of the temperature was at no time necessary.

In this paper the dynamical properties of the NH_4Cl solution resulting from the same MD simulation are discussed. They are evaluated for the various subsystems — total water, NH_4^+, Cl^- bulk water, hydration water of NH_4^+ and Cl^- — on the basis of time dependent autocorrelation functions.

In Sect. II the self-diffusion coefficients and the spectral densities of the hindered translations for the subsystems are calculated from the velocity autocorrelation functions. They are compared with the few available experimental data. The angular velocity autocorrelation functions and the spectral densities of the librations are discussed in Section III. In Sect. IV the correlation functions for the molecular reorientation of the water molecules are evaluated. The resulting reorientation times for the electric dipole moment and for the proton-proton vector are accessible by dielectric and proton relaxation measurements.

II. Self-Diffusion

The normalized velocity autocorrelation functions for the various subsystems in a 2.2 molal NH_4Cl solution — total water, ammonium ions, chloride ions, bulk water, hydration water of NH_4^+ and of Cl^- — have been calculated and are shown in Fig. 1 for the total water, for the ammonium ions and the chloride ions. (The curves for bulk water and the two kinds of hydration water are similar to the one for total water.) The particle average extends over 200 water molecules but only over 8 ions of each kind. The oscillatory behavior for NH_4^+ will be discussed below in connection with the spectral density of the velocity autocorrelation function.

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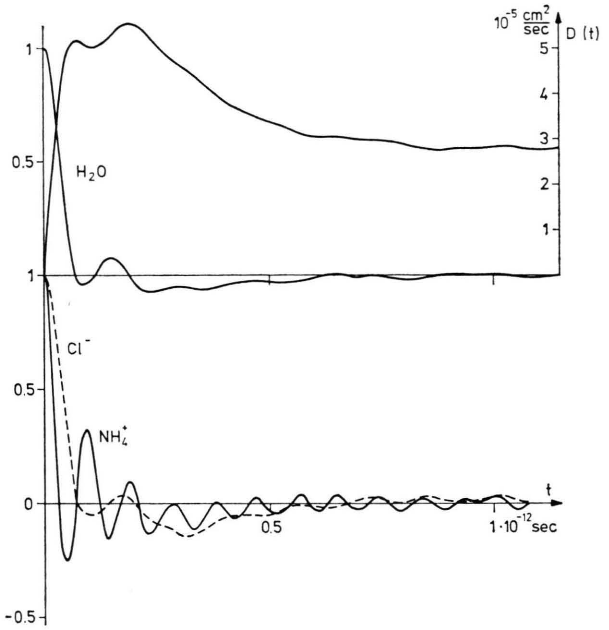

Fig. 1. Normalized velocity autocorrelation functions for the water molecules (upper part), the ammonium ions and the chloride ions (dashed), and the self-diffusion coefficient of water as a function of the upper limit of the integral (1) in a 2.2 molal NH_4Cl solution.

The coefficients of self-diffusion are evaluated from the velocity autocorrelation functions with the help of the Green-Kubo relation:

$$D = \lim_{t\to\infty} \tfrac{1}{3} \int_0^t \langle \boldsymbol{v}(0)\, \boldsymbol{v}(t') \rangle \, \mathrm{d}t' \,. \tag{1}$$

In order to minimize the error in D the upper limit of the integration t has to be chosen appropriately, because an increase in t reduces the number of reference vectors $\boldsymbol{v}(0)$ resulting in a larger statistical uncertainty. With a total simulation time of 3.5 psec a proper choice of 1 psec for t was found by trial and error, and it can be seen from Fig. 1, where D is shown as a function of the upper limit of the integral (1), that this time is long enough for D to reach its limiting value. But it is on the other side short enough for the hydration water to remain essentially within the hydration spheres during this time, which allows to attribute three different diffusion coefficients as defined by (1) to the three kinds of water. The residence times of the water molecules in the hydration shells of NH_4^+ and Cl^- were estimated from the simulation to be 10 and 7 psec, respectively. These values are in reasonable agreement with experimental results of 5 psec for Cl^- and 10 psec for Na^+ [4]. A value for NH_4^+ could not be found in the literature. From the radial pair distribution functions $g_{\mathrm{NO}}(r)$ and $g_{\mathrm{ClO}}(r)$ a hydration number of eight was deduced for both ions. For the calculation of the velocity autocorrelation functions the eight nearest neighbors of each ion were therefore considered as hydration water. Each time a new reference vector $\boldsymbol{v}(0)$ was chosen, the eight water molecules were newly determined and were considered hydration water for the whole integration time of 1 psec.

The self-diffusion coefficients for the various subsystems as calculated according to (1) are given in Table 1 together with the available experimental data. The errors for the MD values in units of 10^{-5} cm²/sec are estimated to be 0.1 for total water, 0.15 for bulk and hydration water, and 0.2 for the ions from the fluctuation of the correlation functions in the range between 0.8 and 1 psec. The different errors result from the different numbers of particles over which the average extends.

Experimentally determined self-diffusion coefficients for the subsystems in a 2.2 molal NH_4Cl solution at 301 K are not directly available. The value for total water is derived by interpolation with respect to temperature and concentration from the investigation of the concentration dependence of D in a NH_4Cl solution at 295 K [2] and from the temperature dependence of D in pure water [3]. The value for Cl^- is taken from a measurement of the concentration dependence of D in a NaCl solution at 298 K, cited in [2]. The value of D for the hydration water of the chloride ion is

Table 1. Self-diffusion coefficients for the various subsystems in a 2.2 molal NH_4Cl solution in units of 10^{-5} cm²/sec from the molecular dynamics simulation (MD) and from experiment.

Subsystem	MD	exp.
H_2O (total)	2.80	2.66[a]
NH_4^+	1.0	—
Cl^-	1.3	1.58[b]
H_2O (bulk)	2.72	—
H_2O (NH_4^+)	2.90	—
H_2O (Cl^-)	2.98	2.78[c]

[a] Interpolated from the results given in [2, 3].

[b] This value has been measured in a NaCl solution cited in [2].

[c] Calculated on the basis of Table V of [4] with a value of $D_0 = 2.48 \cdot 10^{-5}$ cm²/sec for pure water at 301 K [3].

calculated from the one for pure water at 301 K and the ratio of the self-diffusion coefficients of hydration water and pure water as well as its concentration dependence as given in Table V of Ref. [4].

Considering the uncertainties of the D values for the chloride ion in Table 1 together with an unknown change in replacing Na^+ by NH_4^+ as counter ion the difference between MD simulation and experiment is within the limits of error. The same is true for the ammonium ion if one accepts the structural arguments of the preceding paper [1] that for NH_4^+ a similar D value is to be expected as for Na^+, which has been measured to be $1.1 \cdot 10^{-5}$ cm^2/sec [2, 5]. The agreement between simulation and experiment as far as the self-diffusion coefficients of the various kinds of water are concerned can be called fair if the errors in both methods are taken into account. The MD values seem to be higher generally by about 5–10%. There are indications from the simulation that an increase in the integration time t might lead to slightly smaller values and therefore still better agreement. (The low upper limit of the integration employed in the evaluation of D values from the simulation of pure water at different temperatures [6] might be responsible for the discrepancy between MD and experimental values.) It should be stressed that the ratios of the self-diffusion coefficients of the hydration water of Cl^- and total water from simulation and experiment are in very good agreement.

On the basis of structural arguments the eight water molecules in the hydration shell of NH_4^+ have been subdivided in the preceding paper [1] into two groups: four water molecules which are positioned opposite of point charges (kind I) and the remaining four (less strongly bound) opposite of the tetrahedral planes (kind II). The self-diffusion coefficients for kind I and kind II have been calculated to be 2.6 and $3.1 \cdot 10^{-5}$ cm^2/sec, respectively, in agreement with what has been expected from structural information.

The structure breaking ability of the chloride ion, known from measurements (see e.g. [7]), and of the ammonium ion expected from experimental investigations (see e.g. [8]), follows also from the simulation because of the larger D values of the hydration water of both ions when compared with bulk water. The different D values for the two kinds of water in the hydration shell of NH_4^+ indicate that the structure breaking effect of the ammonium ion results solely from the water molecules opposite of the tetrahedral planes. The agreement of all self-diffusion coefficients with experimental results — as far as they are available — in the limits of error and especially the correct relations between the D values for the various subsystems allows the conclusion that the models employed in the simulation describe the NH_4Cl solution correctly at least as far as the self-diffusion coefficients are concerned.

The spectral densities have been calculated from the velocity autocorrelation functions through the Fourier transformation

$$f(\omega) = \int_0^\infty \frac{\langle \boldsymbol{v}(0)\, \boldsymbol{v}(t)\rangle}{\langle \boldsymbol{v}(0)^2\rangle} \cos(\omega\, t)\, \mathrm{d}t\,. \tag{2}$$

They are given in Fig. 2 for the three kinds of water separately and in Fig. 3 for the two ions.

The differences between bulk water and the hydration water of NH_4^+ and Cl^- are rather small. The curves which show three peaks at approximately 40, 145 and 215 cm^{-1} seem to indicate a decrease of the high frequency peak in the Cl case, which would be expected from the structure breaking effect of the chloride ion. A comparison with the spectral densities from the simulation of pure water at various temperatures [6] shows that the relative height of the peaks for the solution corresponds to the one for pure water at elevated temperatures. The bands for the hindered translations of water determined from IR, Raman, and inelastic neutron

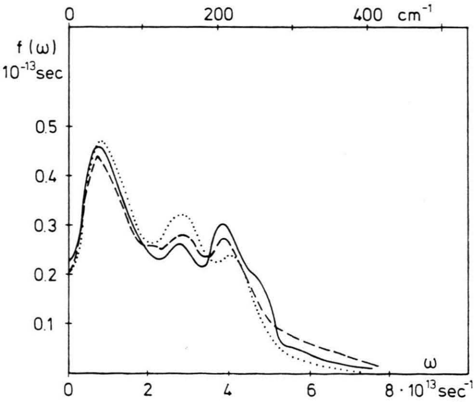

Fig. 2. Spectral densities of hindered translations for bulk water (full), hydration water of NH_4^+ (dashed), and hydration water of Cl^- (dotted).

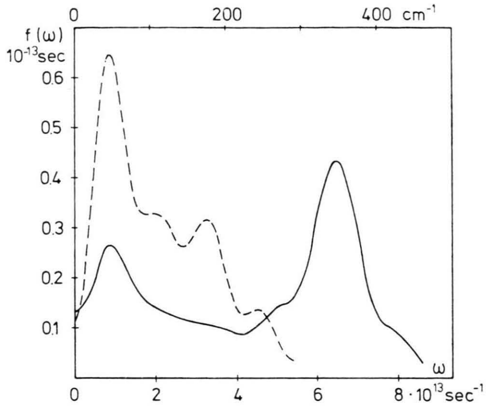

Fig. 3. Spectral densities of hindered translations for the chloride ion (dashed) and the ammonium ion.

scattering investigations (see e.g. Ref. [9]) as well as from model calculations [10] agree at least qualitatively with the spectral densities calculated from the simulations.

While the spectral density for the chloride ion (Fig. 3) consists of a peak at about 50 cm^{-1} with a shoulder towards higher frequencies (qualitatively similar to the spectrum of the hindered translations of water), the main peak for the ammonium ion appears outside this range at about 350 cm^{-1} and might be a consequence of the bonds to the neighbouring water molecules through the point charges of the NH_4^+. Additionally the spectral densities for the relative motion of ions and neighbouring water molecules have been calculated. They are not shown in Fig. 3 as they are almost identical with the ones for the motion of the ions themselves. This agreement indicates that both ions move without attached water molecules as it is expected for structure breaking ions.

III. Rotational Diffusion

The normalized angular velocity autocorrelation function and the rotational diffusion coefficient $D_r(t)$ for all water molecules in the NH_4Cl solution are shown in Fig. 4 for the resulting angular velocity and in Fig. 5 for its three components in respect to a molecule fixed coordinate system. The definition of the three axes is shown as insertion in Figure 5. The corresponding curves for the subsystems — bulk water, hydration water of NH_4^+ and of Cl^- — have been calculated too but are not drawn because they are very similar to those in Figure 5. The

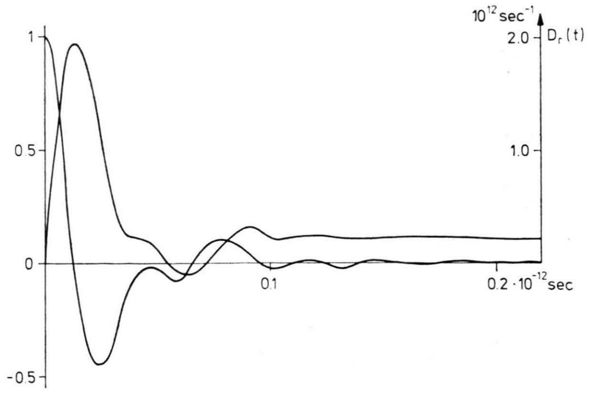

Fig. 4. Normalized angular velocity autocorrelation function and the rotational diffusion coefficient as a function of the upper limit of the integral (4) for the water molecules in a 2.2 molal NH_4Cl solution.

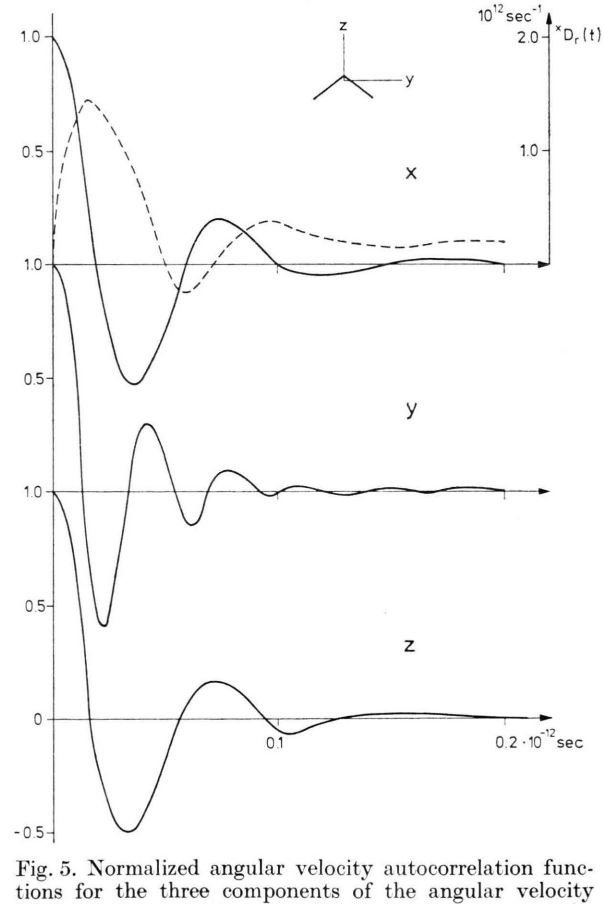

Fig. 5. Normalized angular velocity autocorrelation functions for the three components of the angular velocity with respect to a molecule fixed coordinate system for the water molecules in a 2.2 molal NH_4Cl solution. The dashed curve gives as example the rotational diffusion coefficient for the x-component as a function of the upper limit of the integral (4). The insertion shows the axes of the molecule fixed coordinate system.

angular velocity autocorrelation function for the ammonium ion is shown in Figure 6. Some characteristic values of the autocorrelation functions are given in Table 2 together with the moments of inertia. τ_0 is the time when $\langle \boldsymbol{\omega}(0)\, \boldsymbol{\omega}(t)\rangle / \langle \boldsymbol{\omega}(0)^2\rangle$ is zero for the first time. The effective correlation time τ_{eff} is given by

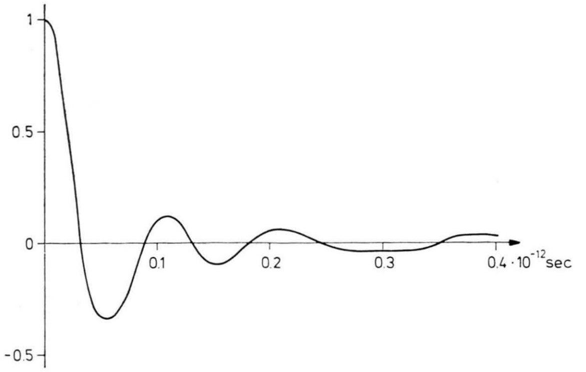

Fig. 6. Angular velocity autocorrelation function for the ammonium ions in a 2.2 molal NH_4Cl solution.

$$\tau_{\text{eff}} = D_{\text{r}} / \langle \boldsymbol{\omega}(0)^2 \rangle \tag{3}$$

and the rotational diffusion coefficient is defined in the usual way:

$$D_{\text{r}} = \lim_{t \to \infty} \tfrac{1}{3} \int_0^t \langle \boldsymbol{\omega}(0)\, \boldsymbol{\omega}(t') \rangle \, \mathrm{d}t' \,. \tag{4}$$

The much faster decay of the angular velocity autocorrelation function when compared with the translational one allows to reduce the integration time to 0.4 psec for water and 0.6 psec for the ammonium ion. The errors in D_{r} are estimated from the fluctuation of the integral to be $\pm 0.03 \cdot 10^{12}$ sec^{-1}.

Table 2. Moments of inertia, correlation times and rotational diffusion coefficients as defined in the text for the three components of the angular velocity of water and the ammonium ions. The D_{r} are calculated separately for bulk water, hydration water of NH_4^+ and of Cl^-.

	H_2O			NH_4^+
	ω_x	ω_y	ω_z	
I $[10^{-40}\ \text{g cm}^2]$	3.2	1.0	2.2	4.9
τ_0 $[10^{-13}\ \text{sec}]$	0.20	0.12	0.19	0.33
τ_{eff} $[10^{-14}\ \text{sec}]$	0.13	0.03	0.12	1.1
D_{r} $[10^{12}\ \text{sec}^{-1}]$	0.16	0.07	0.20	0.93
D_{r}^{B}	0.18	0.08	0.25	—
D_{r}^{+}	0.18	0.07	0.18	—
D_{r}^{-}	0.13	0.05	0.16	—

It can be seen from Table 2 and Fig. 5 that the librational motions of the different components are qualitatively in accordance with what is expected from the moments of inertia. The effective correlation times for water are by one order of magnitude smaller than τ_0 because of the librations. τ_{eff} and D_{r} for the ammonium are unproportionally high indicating a smaller hindrance of the rotational motion compared with water in spite of the fact that the point charges are similar in size and distance from the center of mass. The rotational diffusion coefficients for the water subsystems show smaller values for the hydration water than for bulk water, contrary to what has been found for the self-diffusion coefficients. This is unexpected for structure breaking ions under the assumption that bulk water and pure water have the same structure. This assumption can not be checked as the rotational diffusion coefficients from the simulation of pure ST2 water have not been given by Stillinger and Rahman [6]. (The results for bulk water agree qualitatively with results from the simulation of pure BNS water [13].) Therefore it remains open how far bulk water in a 2.2 molal NH_4Cl solution represents pure water as far as the librational motions are concerned. A further discussion of this question follows in the next section in connection with the calculation of the reorientation times for the dipole moments and the proton-proton vector, quantities which can be derived from experiments.

The spectral densities calculated by Fourier transformation from the normalized angular velocity

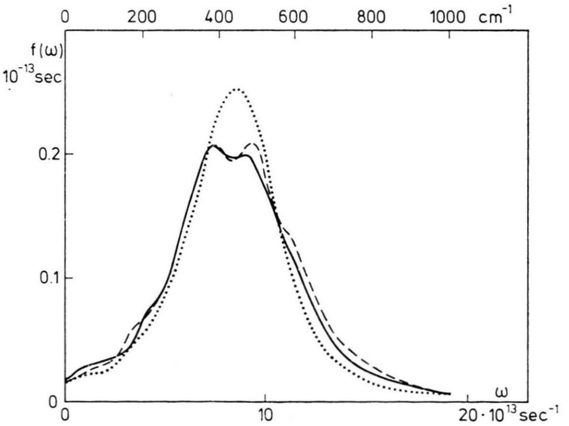

Fig. 7. Spectral density of the x-component of the angular velocity for the water molecules in a 2.2 molal NH_4Cl solution, calculated separately for bulk water (full), hydration water of NH_4^+ (dashed) and of Cl^- (dotted).

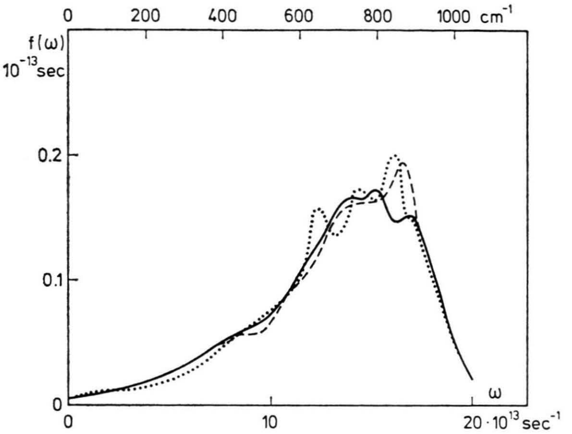

Fig. 8. Spectral density of the y-component of the angular velocity for the water molecules in a 2.2 molal NH_4Cl solution, calculated separately for bulk water (full), hydration water of NH_4^+ (dashed), and of Cl^- (dotted).

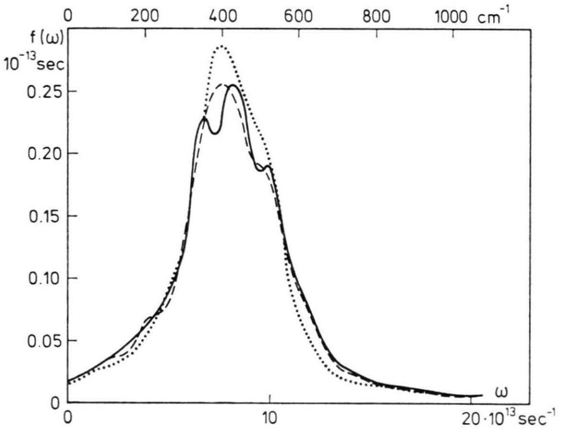

Fig. 9. Spectral density of the z-component of the angular velocity for the water molecules in a 2.2 molal NH_4Cl solution, calculated separately for bulk water (full), hydration water of NH_4^+ (dashed), and of Cl^- (dotted).

autocorrelation functions for water are shown in Figs. 7—9 for the three components and are given separately for the three kinds of water in the NH_4Cl solution. The bands cover the range of librational frequencies measured by far infrared and Rahman spectroscopy (see e.g. Refs. [11, 12]) and deduced from model calculations [10]. The differences between bulk water and hydration water of NH_4^+ are rather small for all three components. Therefore an interpretation appears to be premature especially because the structure of the hydration shell of the ammonium ion is complicated by the existence of the two kinds of hydration water different by their orientation and self-diffusion coefficients as discussed above. The differences of the spectral densities between bulk water and hydration water of Cl^- seem to be significant for the x and z components. The bands become narrower and the intensity of the central frequency increases for the water molecules in the hydration shell of the chloride ion. If a coplanar arrangement of H_2O and Cl^- is assumed this difference means that the librations leading to a deviation from the linear hydrogen bond become predominant as soon as a water molecule approaches the chloride ion.

In Fig. 10 the librational band for the total water in the NH_4Cl solution is shown for comparison with the one for the ammonium ion, drawn in Fig. 11. While in the case of water the band extends over the frequency range 200—1000 cm^{-1}, the one for the ammonium ion is restricted to

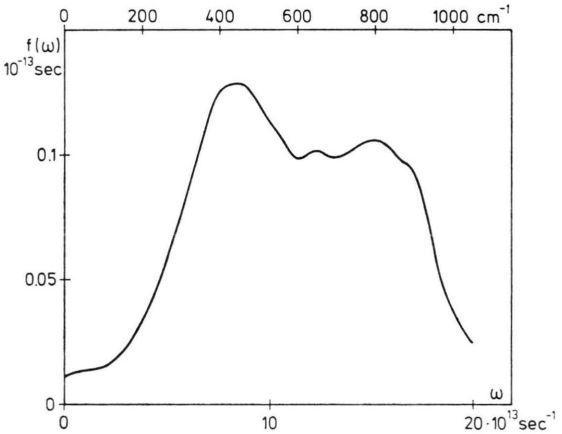

Fig. 10. Spectral density of the angular velocity for the water molecules in a 2.2 molal NH_4Cl solution.

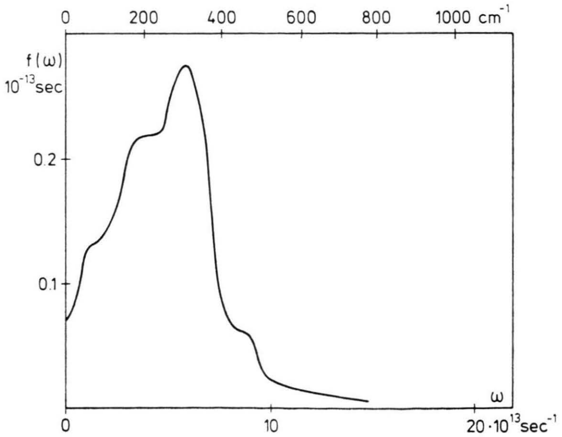

Fig. 11. Spectral density of the angular velocity for the ammonium ions in a 2.2 molal NH_4Cl solution.

wavenumbers below 500 cm^{-1}, with a main peak at about 320 cm^{-1} and a shoulder at 200 cm^{-1}. The lower librational frequency range for NH_4^+ results partly from the larger moment of inertia compared with water. Additionally the same sign of the point charges seems to result in smaller hindrance of rotational motion already indicated by the larger rotational diffusion coefficients as discussed above. It is interesting to note that the main peak for the hindered translation at about 350 cm^{-1} occurs at a frequency slightly higher than the one for the librational band. This indicates that the point charges of NH_4^+ lead to stronger hindrance of the translational motion but a less strong one for the rotational motion when compared with water. The overlap of the translational and librational band of NH_4^+ at relative to water high translational and low librational frequencies together with the slow decay of the normalized velocity and angular velocity autocorrelation functions points to a coupling of rotational and translational motion of the ammonium ion.

IV. Dielectric and Proton Magnetic Relaxation

The molecular reorientation times τ_{lD} and τ_{lP} of the electric dipole moment unit vector $\boldsymbol{\mu}(t)$ and of the unit vector $\boldsymbol{\pi}(t)$ connecting the two protons in a water molecule, respectively, can be calculated from the simulation through

$$ {}^{MD}\tau_l = \int_0^\infty \Gamma_l(t)\,\mathrm{d}t \tag{5}$$

with

$$ \Gamma_l(t) = \langle P_l[\cos\vartheta(t)]\rangle\,, \tag{6}$$

where P_l is the lth Legendre polynomial and

$$ \begin{aligned} \cos\vartheta_D(t) &= \boldsymbol{\mu}(0)\,\boldsymbol{\mu}(t)\,,\\ \cos\vartheta_P(t) &= \boldsymbol{\pi}(0)\,\boldsymbol{\pi}(t)\,. \end{aligned} \tag{7}$$

As the simulation time of 3.5 picoseconds is shorter than most of the correlation times τ_l and as Γ_l decays for large t exponentially, the following extrapolation is employed in order to calculate the integral (5):

$$ \Gamma_l(t) = \Gamma_{0l}\exp(-t/\tau_l')\,. \tag{8}$$

In order to have a reasonable statistical average through a sufficient number of starting vectors, $\boldsymbol{\mu}(0)$ and $\boldsymbol{\pi}(0)$, actually the Γ_l were calculated directly up to 1.6 psec and the exponential functions fitted in the range 1.0—1.6 psec. The $\Gamma_l(t)$ have been calculated for the three subsystems — bulk water, hydration water of NH_4^+ and of Cl^- — separately. Γ_{1D} and Γ_{2P} are shown in Figs. 12 and 13, respectively. The fit parameters Γ_{0l} and τ_l' and the resulting reorientation times ${}^{MD}\tau_l$ are given in Table 3.

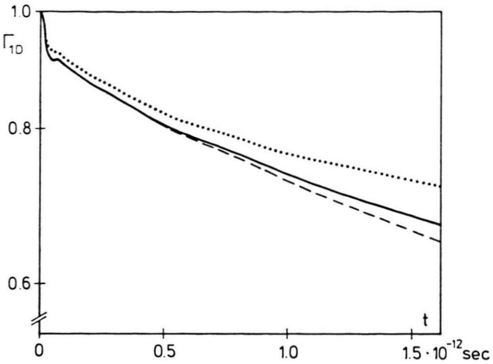

Fig. 12. Autocorrelation function for the water dipoles in a 2.2 molal NH_4Cl solution, calculated separately for bulk water (full), hydration water of NH_4^+ (dashed), and of Cl^- (dotted).

The short time behavior of the correlation functions Γ_{1D} and Γ_{2P} ($t < 0.1$ psec) is determined by the moments of inertia as discussed e.g. by Gordon [14] while for $t > 1$ psec the decay is approximately exponential. As the accuracy of the calculations is not yet sufficient for a detailed analysis of the intermediate part of the correlation functions the following discussion is restricted to the reorientation times τ_l for the three kinds of water in the NH_4Cl solution.

Table 3. Fit parameters Γ_{0l} and τ_l' for the exponential extrapolation of the correlation function Γ_l according to (8) and correlation times ${}^{MD}\tau_l$ as defined by (5). All τ's are given in psec.

	Bulk water	Hydration water	
		NH_4^+	Cl^-
$\Gamma_{01}{}^{D}$	0.86	0.89	0.86
τ_{1D}'	6.8	5.1	9.2
$\Gamma_{02}{}^{D}$	0.65	0.60	0.66
τ_{2D}'	2.4	2.7	3.4
$\Gamma_{02}{}^{P}$	0.64	0.52	0.67
τ_{2P}'	2.2	4.0	3.0
${}^{MD}\tau_{1D}$	5.8	4.6	7.9
${}^{MD}\tau_{2D}$	1.6	1.7	2.4
${}^{MD}\tau_{2P}$	1.4	2.1	2.0

The calculated microscopic ${}^{\mathrm{MD}}\tau_{1\mathrm{D}}$ can not be compared directly with measured macroscopic dielectric relaxation times ${}^{\exp}\tau_{\mathrm{D}}$. In the relation ${}^{\exp}\tau_{\mathrm{D}} = c\,{}^{\mathrm{MD}}\tau_{1\mathrm{D}}$ the value of c depends on the model employed in the interpretation of the experimental data and falls in the range $1 \leqq c \leqq 2$ (see e.g. Ref. [15]). Measurements for a 1 molal NH_4Cl solution at 298 K have been reported by Kaatze [16]. If the temperature dependence of τ_{D} for pure water is employed [15] and a linear concentration dependence assumed the resulting experimental value for the 2.2 molal NH_4Cl solution at 301 K is ${}^{\exp}\tau_{\mathrm{D}}{}^{\mathrm{S}} = 6.8 \cdot 10^{-12}$ sec. With a value for pure water at this temperature ${}^{\exp}\tau_{\mathrm{D}}{}^{\mathrm{W}} = 7.7 \cdot 10^{-12}$ [15] one finds ${}^{\exp}\tau_{\mathrm{D}}{}^{\mathrm{S}}/{}^{\exp}\tau_{\mathrm{D}}{}^{\mathrm{W}} = 0.88$. From the weighted average of the ${}^{\mathrm{MD}}\tau_{1\mathrm{D}}$ values in Table 3 results ${}^{\mathrm{MD}}\tau_{1\mathrm{D}}{}^{\mathrm{S}} = 5.9 \cdot 10^{-12}$ sec. If instead of the MD value of pure water, which is not available, the one for bulk water ${}^{\mathrm{MD}}\tau_{1\mathrm{D}}{}^{\mathrm{B}}$ is employed one finds ${}^{\mathrm{MD}}\tau_{1\mathrm{D}}{}^{\mathrm{S}}/{}^{\mathrm{MD}}\tau_{1\mathrm{D}}{}^{\mathrm{B}} = 1.02$. The experimental and the MD ratios can be compared if it is assumed that c has the same value for pure water and for the solution. The discrepancy in the ratios of the dielectric relaxation times between experiment and simulation indicates that bulk water is different from pure water. This is no surprise for a 2.2 molal solution. An expected larger MD value for pure water than for bulk water could reduce the discrepancy significantly. It might even be concluded that the structure breaking effect of the ions occurs outside the first hydration shell at least as far as rotational motions are concerned. This conclusion is supported by the larger rotational diffusion coefficients for bulk water than for hydration water as can be seen from Table 2 and is discussed in Section III.

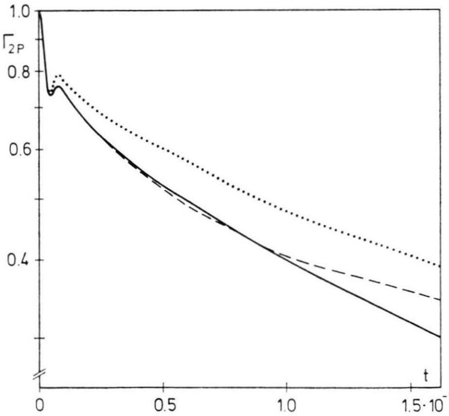

Fig. 13. Autocorrelation function for the proton-proton vector of the water molecules in a 2.2 molal NH_4Cl solution, calculated separately for bulk water (full), hydration water of NH_4^+ (dashed), and of Cl^- (dotted).

The comparison of the correlation time of the proton-proton vector $\boldsymbol{\pi}(t)$ from experiment and the MD simulation leads to a similar conclusion with an even larger discrepancy. An NMR investigation of an NH_4Cl solution has not been analyzed with respect to the correlation time for $\boldsymbol{\pi}(t)$ because of problems connected with the separation of the ammonium protons from water protons [17]. But from the invesitgation of an NaCl solution the correlation time of the hydration water of Cl^- is known: ${}^{\exp}\tau_{2\mathrm{P}^-} = 2.3 \cdot 10^{-12}$ sec at 25 °C. The value for pure water at 301 K is ${}^{\exp}\tau_{2\mathrm{P}}{}^{\mathrm{W}} = 2.3 \cdot 10^{-12}$ sec [4]. Under the assumption that the temperature dependence of $\tau_{2\mathrm{P}^-}$ is negligible the discrepancy in the ratios ${}^{\exp}\tau_{2\mathrm{P}^-}/{}^{\exp}\tau_{2\mathrm{P}}{}^{\mathrm{W}} = 1$ and ${}^{\mathrm{MD}}\tau_{2\mathrm{P}^-}/{}^{\mathrm{MD}}\tau_{2\mathrm{P}}{}^{\mathrm{B}} = 1.43$ is even larger than in the case of the dielectric relaxation. Again an increase in the value for bulk water would reduce the discrepancy. While this is true for the hydration water of both ions in the case of ${}^{\mathrm{MD}}\tau_{2\mathrm{P}}$, the dielectric relaxation time is smaller for the hydration water of NH_4^+ and larger for Cl^- compared with bulk water.

These differences can be specified under the assumption of a linear concentration dependence for the dielectric relaxation [15], if in spite of the doubts discussed above, bulk water is employed instead of pure water.

$$\frac{1}{\tau_{\mathrm{D}}{}^{\mathrm{W}}} \left(\frac{\mathrm{d}\tau_{\mathrm{D}}{}^{\mathrm{S}}}{\mathrm{d}c} \right)_{c \to 0} = B_{\mathrm{D}^+} + B_{\mathrm{D}^-} \tag{9}$$

$$B_{\mathrm{D}^\pm} = \frac{{}^{\mathrm{MD}}\tau_{1\mathrm{D}^\pm} - {}^{\mathrm{MD}}\tau_{1\mathrm{D}}{}^{\mathrm{B}}}{{}^{\mathrm{MD}}\tau_{1\mathrm{D}}{}^{\mathrm{B}}\, c}\,. \tag{10}$$

The resulting values $B_{\mathrm{D}^\pm}$ are compared in Table 4 with values derived from the measurements of Kaatze [16]. The results from the simulation imply significantly larger effects of the ions than the experiments. While the B^+ from simulation and experiment have the same sign, it is opposite for B^-.

	B_{D^+}	B_{D^-}
exp.	− 4	− 1
MD	− 9	+ 16

Table 4. B coefficients in 10^{-2} kg H_2O/mole as definedin (9) for hydration water of NH_4^+ and of Cl^- from experiment and MD simulation.

Table 5. Check of the Debye diffusion model (11) for the three kinds of water in a 2.2 molal NH_4Cl solution. The correlation times are taken from Table 3 and the rotational diffusion coefficients from Table 2, where ${}^{ij}D_r = (1/2) \cdot ({}^{i}D_r + {}^{j}D_r)$. From the uncertainties in τ and D_r the overall error is estimated to be ± 0.25.

	Bulk water	Hydration water	
		NH_4^+	Cl^-
$2\,{}^{MD}\tau_{1D}\,{}^{xy}D_r$	1.5	1.2	1.4
$6\,{}^{MD}\tau_{2D}\,{}^{xy}D_r$	1.2	1.3	1.3
$6\,{}^{MD}\tau_{2P}\,{}^{xz}D_r$	1.8	2.3	1.7

Thus, even if pure water shows a larger correlation time than bulk water the discrepancy is only reduced in the case of Cl^- but it will be enlarged in the case of NH_4^+.

The Debye diffusion model relates the correlation times and the rotational diffusion coefficients through

$$\tau_l D_r l(l+1) = 1 . \tag{11}$$

Table 5 shows the result of a check of this relation. The values for τ_l are taken from Table 3 and the rotational diffusion coefficients for the three kinds of water molecules from Table 2, where ${}^{ij}D_r = (1/2)({}^{i}D_r + {}^{j}D_r)$ and i and j refer to the components of the angular velocity in a molecule fixed coordinate system. Although the error, resulting from the uncertainties in τ_l and D_r, is estimated to be as large as ±0.25, most of the numbers in Table 5 indicate that the Debye diffusion model does not apply to the motion of the water molecules in the 2.2 molal NH_4Cl solution. It should be noted that the reorientational motion of the proton-proton vector deviates significantly more from the Debye model than the dipole moment vector.

V. Summary and Conclusions

From the molecular dynamics simulation of a 2.2 molal NH_4Cl solution which extended over 3.5 picoseconds the self-diffusion coefficients, the rotational diffusion coefficients, the corresponding spectral densities and the reorientation times of the dipole moment vector and the vector connecting the two protons in the water molecule have been calculated separately for bulk water, hydration water of NH_4^+ and Cl^- from the autocorrelation functions and are compared with experimental data in the few cases were information is available.

The self-diffusion coefficients of the hydration water of both ions have been found to be about 10% higher than of bulk water. This difference agrees with experimental results for Cl^-. The increase of the self-diffusion coefficients is expected as both ions are considered structure breakers. The eight water molecules found for the first hydration shell of NH_4^+ from the radial distribution function have been separated into two groups: four water molecules located opposite to the tetrahedrally arranged point charges (kind I) and the remaining four located opposite to the tetrahedral planes (kind II). The self-diffusion coefficients for the water molecules of kind I are smaller and for kind II are larger than for bulk water. This result seems to indicate that the less strongly bound water molecules opposite to the tetrahedral planes are solely responsible for the structure breaking effect of NH_4^+.

The calculated rotational diffusion coefficients are smaller and the correlation times of the proton-proton vector and the dipole moment vector are larger for the hydration water of the ions than for bulk water. Reverse effects are expected for structure breaking ions if the dynamical properties of bulk water correspond to the ones of pure water. Therefore, the simulation allows the conclusion that in a 2.2 molal NH_4Cl solution the water outside of the first hydration shells of the ions differs significantly in its structure from pure water. This means that at least part of the structure breaking effect of the ions occurs — as far as the rotational motions are concerned — outside of the first hydration shell.

The velocity and angular velocity autocorrelation functions indicate that the translational and the rotational motions of NH_4^+ are coupled and the movements of ions and surrounding water molecules are not correlated.

The reorientational motion of the proton-proton vector deviates significantly more from the Debye diffusion model than the motion of the dipole moment vector.

Acknowledgement

Helpful discussions with Dr. W. Dietz and Dr. L. Schäfer and financial support by Deutsche Forsungsgemeinschaft are gratefully acknowledged.

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