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Dynamical structure of water in aqueous solutions of LiCl, NaCl, and KCl by low-frequency Raman scattering: Comparison between the multiple random telegraph model and Cole-Cole relaxation

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Depolarized low-frequency Raman spectra of aqueous solutions of LiCl, NaCl, and KCl have been investigated over a wide concentration range. The spectra were analyzed with one relaxation mode and two damped harmonic oscillators. We applied two types of relaxation model: the multiple random telegraph (MRT) model and the Cole-Cole-type relaxation. Each relaxation time becomes longer than that of liquid water in both relaxation models. Structure making (Li, Na) and structure breaking (K) effects were concluded from a fitting parameter corresponding to the modulation speed in the MRT model. [S1063-651X(98)04512-7]

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I. INTRODUCTION

Intermolecular motion of water and aqueous solutions have been investigated by many workers for a long time. However, the basic property of water has not yet been fully clarified. Low-frequency Raman scattering has been employed to investigate the dynamical structure of water and aqueous solutions [1–13]. There are three spectral bands in the Raman spectra below 300 cm^{-1}. Two spectral bands, around 190 and 60 cm^{-1}, were attributed to stretchinglike and bendinglike vibration of hydrogen bonds among water molecules, respectively [7,14,15]. The stretchinglike mode needs five water molecules. The origin of the bendinglike mode is not confirmed yet. The lowest component is well fitted by a relaxational mode. The relaxation time is considered to be the duration time of the hydrogen bond network of water molecules.

Low-frequency Raman scattering of aqueous electrolyte solutions has been carried out in our laboratory [10]. The Cole-Cole-type function was used to analyze the spectra, and the relation between the relaxation time and viscosity were discussed. The empirical Cole-Cole function, which is an extended version of the Debye function, contains the parameter β for relaxation time distribution. The Debye relaxation is obtained from the Langevin equation of rotational Brownian motion under the overdamped and narrowing limits. These approximations are valid only below GHz region, and they should be broken down above about 1 THz [16]. Therefore the overdamped limit could not be applicable to the relaxation observed in low-frequency Raman-scattering spectra.

In the present work, we have measured low-frequency Raman scattering of LiCl, NaCl, and KCl aqueous solutions. Two types of relaxation models, the multiple random telegraph (MRT) model [17] taking account into inertia and memory effects and the Cole-Cole relaxation, were used to analyze the obtained spectra [18]. We investigate the difference between the two relaxation models and show that the interpretation of low-frequency Raman spectra depends on the models adapted.

II. EXPERIMENT

Solutes of LiCl, NaCl, and KCl were purchased from Wako Pure Chemical Industries, Co. Ltd. Aqueous solutions were prepared by dissolving solute into deionized distilled water and further purified by milli-Q Jr. (Millipore Co. Ltd). The concentration range of solutions are from 0.00 (water) to 0.15 molar ratio, 0.00 to 0.10, and 0.00 to 0.07 for LiCl, NaCl, and KCl, respectively. Molar ratio means the ratio of mole number of solute against mole number of water. A silica flow cell (T-45FL_UV_10, Nippon Silica Glass Inc.) was used for measurements. To change solution in the cell, more than 50 ml of solution was passed through the cell. Depolarized Raman spectra were obtained by using a double grating spectrometer (Ramanor U1000, Jovin-Yvon). The exciting light source was an argon-ion laser operating at 488 nm with power of 400 mW. The right-angle scattering geometry was adopted with (VH) configuration. The depolarized Raman spectrum was recorded in the frequency range from −50 to 250 cm^{-1}. The spectral resolution was 0.2 cm^{-1}. All spectra were recorded at room temperature (298 K).

III. RESULTS AND ANALYSIS

The dynamical susceptibility $\chi''(\nu)$ is given by

$$\chi''(\nu)=K(\nu_i-\nu)^{-4}[n(\nu)+1]^{-1}I(\nu), \tag{1}$$

where $I(\nu)$ is the Raman spectral intensity, $n(\nu)=[\exp(hc\nu/kT)-1]^{-1}$ is a Bose-Einstein factor, $\nu(=f/c)$ and $\nu_i(=f_i/c)$ are the Raman frequency shift and the incident laser light frequency, respectively. The frequencies ν and ν_i are represented by cm^{-1}, f and f_i are represented by Hz, and c is light velocity. The K is the instrumental constant.

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The imaginary part of the susceptibility of the Cole-Cole-type relaxation function is given by

$$\chi''_r(t,\beta;\omega)=\frac{\sin(\beta\pi/2)}{\cosh(\beta x)+\cosh(\beta\pi/2)}, \tag{2}$$

where $x=\ln(\omega\tau)$.

The imaginary part of the susceptibility of the damped harmonic oscillator is represented by

$$\chi''_\nu(\omega_j,\gamma;\omega)=\frac{\omega_j^2\gamma_j\omega}{(\omega_j^2-\omega^2)^2+(\omega\gamma_j)^2}, \tag{3}$$

where $\omega_j=2\pi c\nu_j(j=1,2)$ and $\gamma_j=2\pi c g_j(j=1,2)$ are characteristic angular frequencies and damping constants, respectively. The ν_j and g_j are characteristic frequencies and damping constants represented by cm^{-1}. In the case of the Cole-Cole relaxation model, the fitting function has the form

$$\chi''(\nu)=A_r\chi''_r(g_r,\beta;\nu)+A_1\chi''_\nu(\nu_1,g_1;\nu)+A_2\chi''_\nu(\nu_2,g_2;\nu), \tag{4}$$

where A_r, A_1, and A_2 are the strength of each model.

In the MRT model [17], the complex susceptibility is written in the form

$$\chi^*(\omega)=1-i\omega v[s], \tag{5}$$

where $s=i\omega$. In the asymmetric case, $v[s]$ is given by continued fraction,

$$v[s]=\cfrac{1}{s+\cfrac{N\tilde{\Delta}_0^2}{s+\tilde{\gamma}+\cfrac{2(N-1)\tilde{\Delta}_0^2}{s+2\tilde{\gamma}+\cfrac{3(N-2)\tilde{\Delta}_0^2}{s+3\tilde{\gamma}+\dots}}}}, \tag{6}$$

$$\frac{\qquad\qquad}{s+(N-1)\tilde{\gamma}+\cfrac{N\tilde{\Delta}_0^2}{s+N\tilde{\gamma}}}$$

where $\tilde{\Delta}_0^2=\Delta_0^2(1-\sigma^2)$ and $\tilde{\gamma}=\gamma-2i\sigma$. The multiple random telegraph process is composed of N-independent random telegraph processes each of which takes the value $\pm\Delta_0$. The γ is the inverse of the characteristic time of the random telegraph processes. A nonzero value of σ means that each probability of the random telegraph processes was asymmetric. This model contains two specific case: Gaussian-Markovian limit ($N\rightarrow\infty$) and narrowing limit ($\alpha_0\ll 1$). The narrowing limit corresponds to a Debye-type relaxation. We use Δ_0, $\alpha_0(=\Delta_0/\gamma)$, σ, N, and relaxation strength A_{MRT} as fitting parameters. In this model, N must be a positive integer. We suppose the simplest case in the present analysis, $N=1$. In the case of the MRT model, the fitting function is given by

$$\chi''(\nu)=A_{\mathrm{MRT}}\chi''_{\mathrm{MRT}}(\Delta_0,\alpha_0,\sigma,N;\nu)+A_1\chi''_\nu(\nu_1,g_1;\nu)$$
$$+A_2\chi''_\nu(\nu_2,g_2;\nu). \tag{7}$$

In Eq. (7), the relaxation time is not a fitting parameter. To calculate the relaxation time, we define $v(t)$ in the time domain as the inverse Laplace transform of $v[s]$ given by

$$v(t)=\{\cosh(\tilde{\gamma}t/2\tilde{a})+\tilde{a}\sinh(\tilde{\gamma}t/2\tilde{a})\}^N e^{-N\tilde{\gamma}t/2}, \tag{8}$$

where

$$\tilde{a}=[1-4(\tilde{\Delta}_0/\tilde{\gamma})^2]^{-1/2} \tag{9}$$

and $v(0)=1$. Then we obtain the relaxation time from the following equation:

$$|v(t)|-\frac{1}{2}=0. \tag{10}$$

Figures 1(a) and 1(b) show the reduced low-frequency Raman spectra of NaCl aqueous solution at the concentration of 0.07 molar ratio. Both fitting functions fit well with the experimental spectra. The Cole-Cole relaxation has the long tail that acts as the background of the damped oscillators in the low-frequency region. The MRT model, which takes into account the inertia effect, does not produce the background. The MRT component and the damped oscillator component share the intensity around the 60 cm^{-1} mode.

Figures 2(a), 2(b), 2(c) show the concentration dependence of spectral shape of LiCl, NaCl, and KCl solutions, respectively. The central mode changed with increasing concentration. The broad peak around 50 cm^{-1} is larger than the central peak in LiCl and NaCl solutions.

Figures 3(a)–3(d) show the concentration dependence of fitting parameters in the MRT model. Figures 4(a)–4(c) show the concentration dependence of fitting parameters in the Cole-Cole relaxation. The intensity of the relaxation

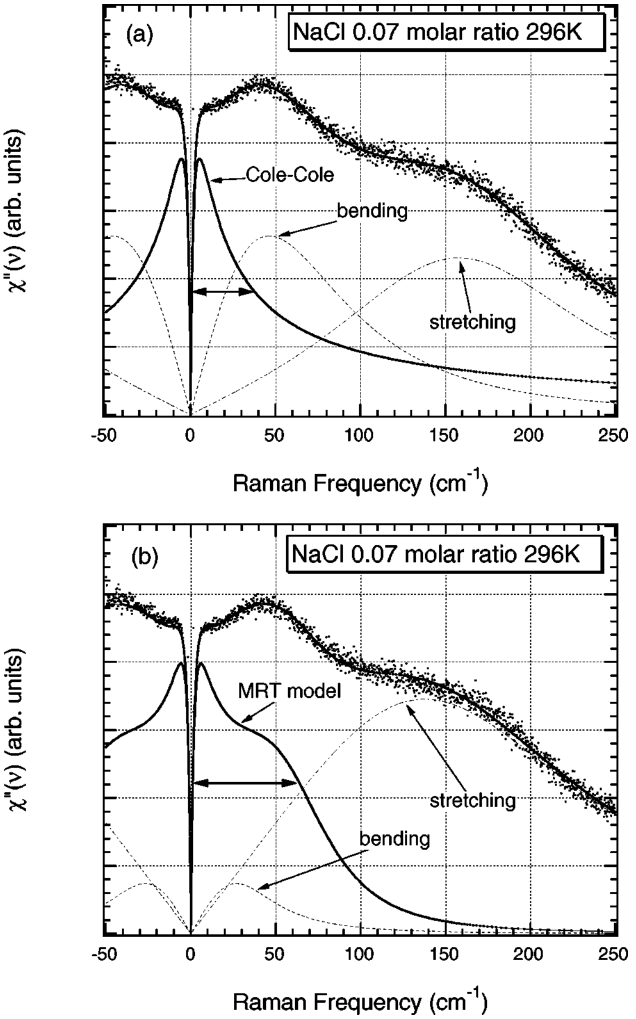

FIG. 1. The best fit result of NaCl aqueous solution at 0.07 molar ratio. (a) The fitting function contains a Cole-Cole relaxation mode and two damped harmonic oscillations. (b) The best-fit result for the same spectrum. The MRT model is used for the relaxation mode.

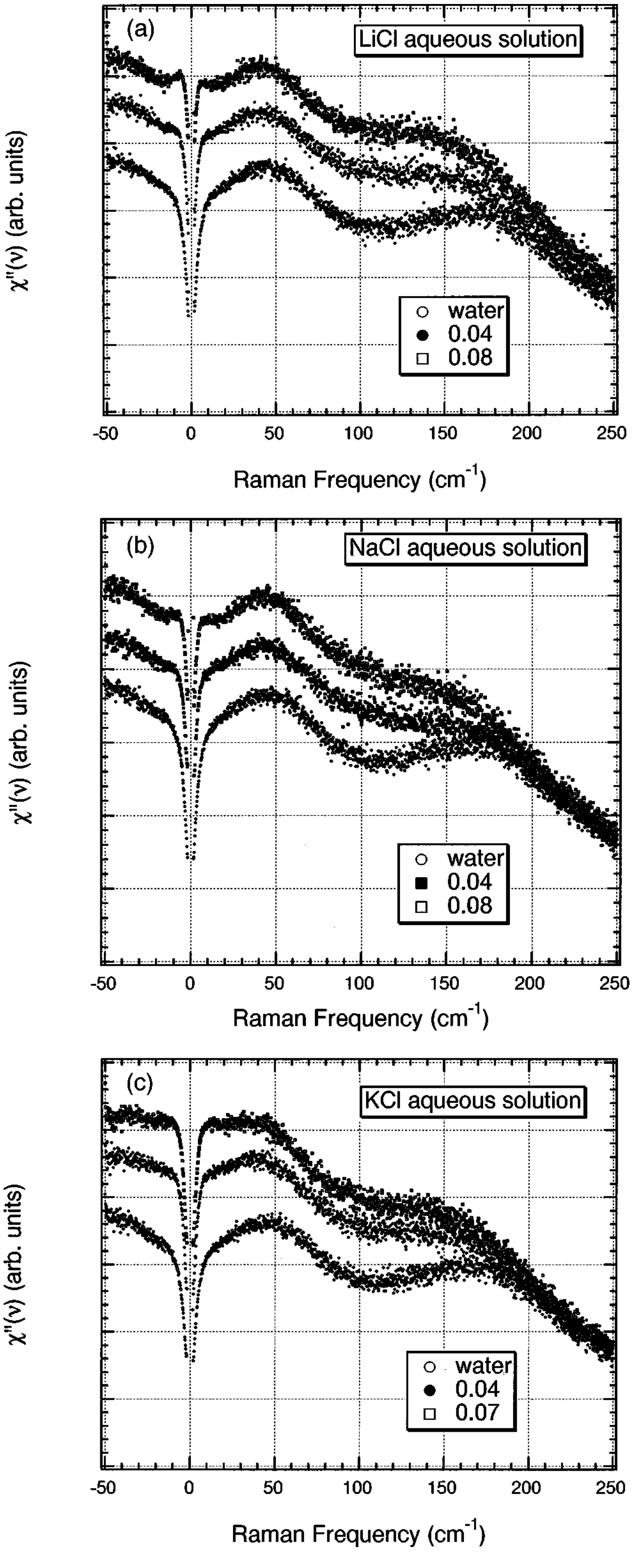

FIG. 2. The concentration dependence of the reduced low-frequency Raman spectra. (a) LiCl aqueous solution. (b) NaCl aqueous solution. (c) KCl aqueous solution.

mode increases with increasing concentration. The relaxation time also increases with increasing concentration. The order of the relaxation time is $\mathrm{Li}^{+} > \mathrm{Na}^{+} > \mathrm{K}^{+}$.

The relaxation time of the MRT model is longer than that of the Cole-Cole-type relaxation mode. The Cole-Cole β, which represents the distribution of relaxation times, slightly decreases with increasing concentration. The α_0, which is a measure of the modulation speed of angular frequency of the MRT model, increases in LiCl and NaCl solution with increasing concentration, while it decreases in KCl solution.

Figures 5(a)–5(d) and 6(a)–6(d) show the concentration dependence of the parameters of the two damped harmonic oscillators coupled with the MRT model and the Cole-Cole-type relaxation, respectively. A_{60}, ν_{60}, g_{60} are the parameters of 60 cm^{-1} band, A_{190}, ν_{190}, g_{190} are the parameters of 190 cm^{-1} band. Subscripts MRT and CC specify the relaxation types, that is, MRT model or Cole-Cole type relaxation. The intensities of the 60 and 190 cm^{-1} modes increase with increasing concentration. The characteristic frequency of the 190 cm^{-1} mode slightly decreases with increasing concentration. As for 60 cm^{-1} mode, the characteristic frequency in the case of the MRT model slightly decreases but in the case of the Cole-Cole-type relaxation it is almost constant. The damping constants of the 190 cm^{-1} mode increase at lower concentration, and then become almost constant at higher concentration in both relaxation models. The damping constant of the 60 cm^{-1} mode in the MRT model is almost

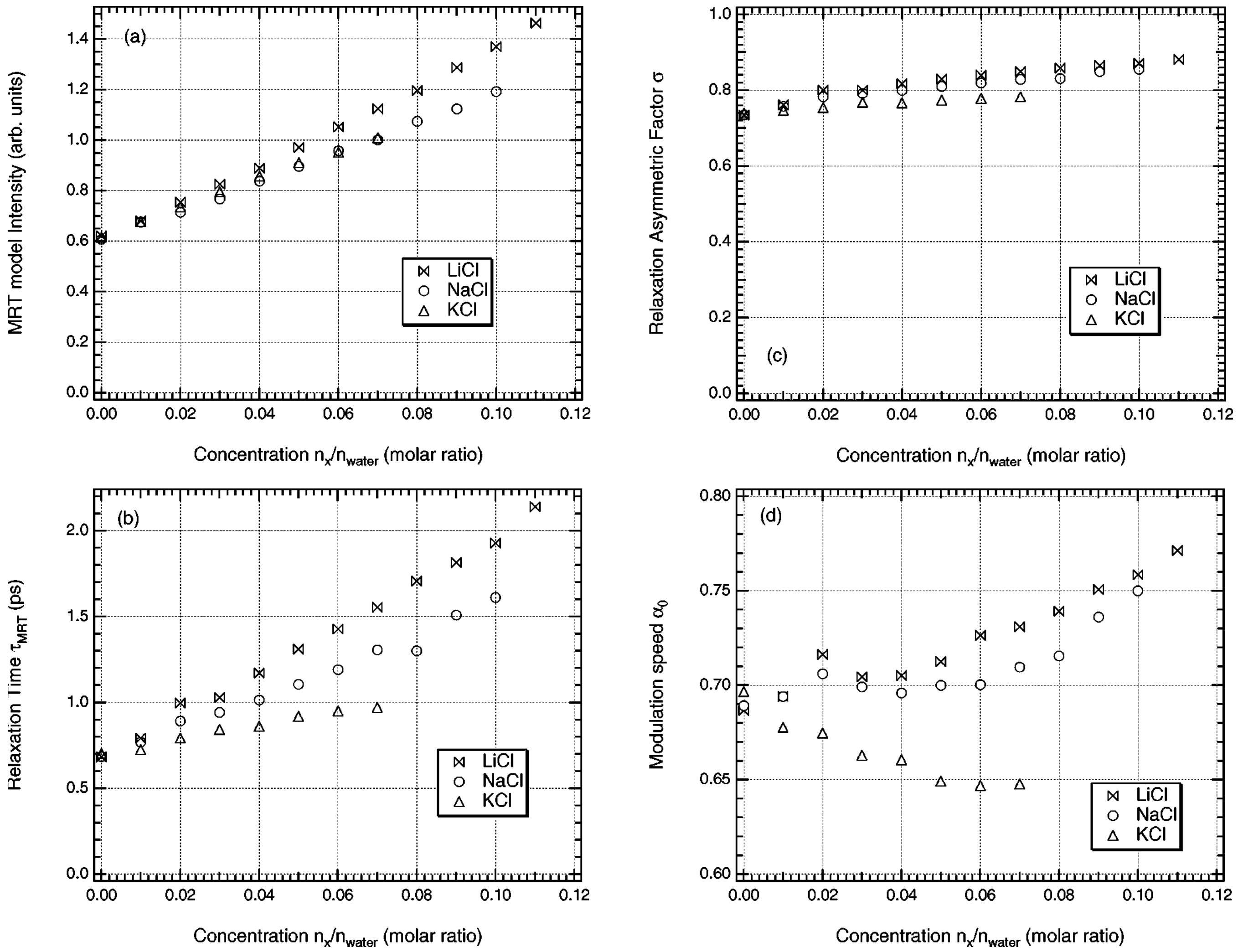

FIG. 3. Fitting results with one MRT model and two damped harmonic oscillations. (a) MRT model intensity as a function of concentration. (b) The relaxation time calculated from the MRT model as a function of concentration. (c) The relaxation asymmetric factor as a function of concentration. (d) The modulation speed as a function of concentration.

constant while in the Cole-Cole type relaxation it increases at low concentration, and then slightly decreases at higher concentrations. The characteristic frequency of the 190 cm^{-1} mode in the MRT model is almost same as the Cole-Cole-type relaxation. The characteristic frequency of the 60 cm^{-1} mode in the MRT model is lower than that in the Cole-Cole-type relaxation. The damping constant $g_{190\mathrm{CC}}$ is larger than $g_{190\mathrm{MRT}}$, while $g_{60\mathrm{CC}}$ is smaller than $g_{60\mathrm{MRT}}$.

IV. DISCUSSION

Due to the large background in the Raman susceptibility of water and aqueous electrolyte solutions, the Cole-Cole function can be applied without discrepancy. The Cole-Cole-type relaxation is interpreted as multiple Debye relaxations in which there are certain distributions of the relaxation times. The Debye function of relaxation is obtained as a solution of the Langevin equation of a rotating dipole under the approximation of the overdamped and narrowing limits. In the case of far-infrared absorption, the high-frequency tail of the Debye relaxation cannot reproduce the experimental spectra [19]. The Debye-type relaxation should be broken down over 30 cm^{-1} because of the inertia effect. We take the same approach as the far-infrared absorption case to analyze the relaxation mode in the low-frequency Raman spectra.

In the case of Brownian motion, we observe the motion of a μm size particle in water. In this case since the particle size is sufficiently larger than water molecules and the specific time of the observation is much longer than the characteristic time of molecular motion, fluctuating forces on the Brownian particle can be treated as an uncorrelated stochastic process. On the other hand, the relaxation process in liquid water and aqueous solutions is quite different from the above Brownian motion. In this case the ''particle'' is considered only to be 10–50 water molecules [20,21] and the specific time of the particle motion is comparable with the characteristic time of molecular motion which corresponds to the duration time of the local structure of hydrogen-bond network. Due to this hydrogen-bond network, a certain correlation exists among water molecules in the liquid state. The fluctuation term in the equation of motion representing the relaxation mode is related to the thermal fluctuations of water molecules themselves. When the correlation length among water molecules can be comparable to the system size which contributes to the relaxation strength, the fluctuation

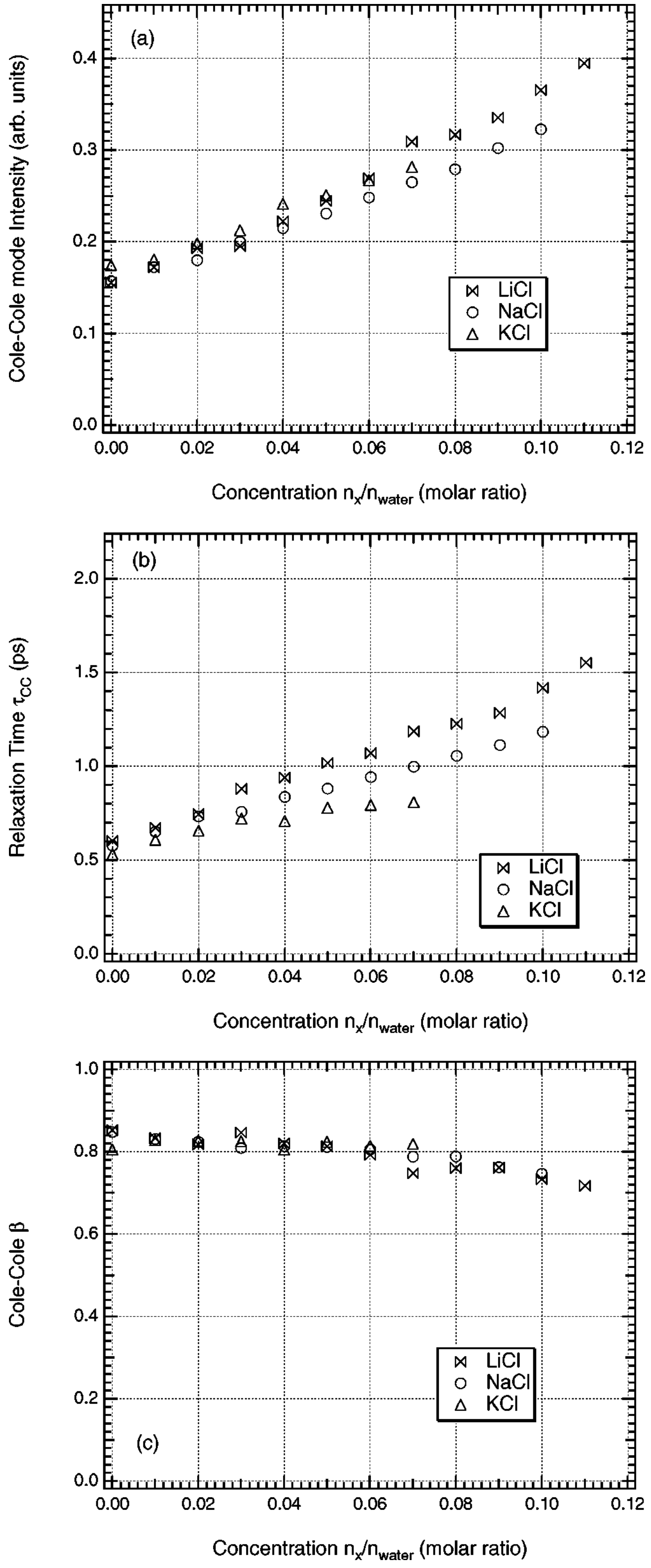

FIG. 4. Fitting results with one Cole-Cole relaxation and two damped harmonic oscillations. (a) Intensity of Cole-Cole relaxation as a function of concentration. (b) The relaxation time as a function of concentration. (c) The concentration dependence of the parameter β.

of the relaxation mode can be considered as colored noise. Based on this consideration we use the imaginary part of the MRT model in the fitting function.

The intensity of the MRT and Cole-Cole-type relaxation modes increases with increasing concentration. Two damped oscillator modes also increased. The origin of the relaxation mode in Raman spectra of water and aqueous solutions has not yet been entirely clarified. For liquid water, the relaxation time observed in low-frequency Raman scattering has been suggested as corresponding to the duration time of creation and annihilation processes of the hydrogen bond-network among water molecules [12,20,21]. The broadband around 190 cm^{-1} corresponds to the stretchinglike vibrations of hydrogen bonds among five water molecules. The broadband around 60 cm^{-1} corresponds to the bendinglike vibrations of hydrogen bonds among at least three water molecules. In salt aqueous solutions, the dynamical structure of water is distorted because of the forming of the hydration shell around ions. This distortion is one of the candidates for the origin to increase the mode intensity of each mode.

For LiCl, NaCl, and KCl aqueous solutions, the characteristic frequency of the stretchinglike mode shifts to the lower side with increasing salt concentration as shown in Figs. 5(c) and 6(c). The results are consistent with the previous work [10,22]. The characteristic frequencies of the bendinglike mode are not changed as shown in Fig. 6(c), but slightly decrease as shown in Fig. 5(c). The distributions of characteristic frequencies in both stretchinglike and bendinglike modes slightly increase with increasing salt concentration as shown in Figs. 5(d) and 6(d). If the intermolecular interaction produce both vibration modes, it is natural that the behaviors of these two modes against salt concentration should be the same. Therefore the results in Fig. 5(c) are reasonable.

Some of the values of the fitting parameters for the stretchinglike and bendinglike modes are different from the results using the MRT model and using the Cole-Cole-type relaxation. Characteristic frequencies and damping constants of stretchinglike modes are nearly equal in both models. The MRT model has smaller values around 190 cm^{-1} than those of the Cole-Cole-type relaxation. The Cole-Cole-type relaxation model produces a nearly constant background around the stretchinglike mode. Peak positions and widths of the stretchinglike mode are not affected by the relaxation component. While for the bendinglike mode, the characteristic frequencies using the Cole-Cole-type relaxation are higher than those using the MRT model. Damping constants using the Cole-Cole-type relaxation are larger than those using the MRT model. The most significant difference of the analysis based on the MRT model from that based on the Cole-Cole function appears at the frequency region around 60 cm^{-1} where the relaxation component overlaps the component of the bendinglike mode. The difference of how to share the strength around 60 cm^{-1} between a relaxation mode and a vibration mode makes a difference in the spectral shape of the bendinglike modes. The strength ratio of the bendinglike mode and the stretchinglike mode are significantly different using the MRT model and using Cole-Cole type relaxation. As shown in Figs. 6(a) and 6(b), the result using the Cole-Cole-type relaxation indicates that the intensity of the bendinglike mode is larger than that of the stretchinglike mode for whole concentration range. On the other hand, as shown in Figs. 5(a) and 5(b) the result using the MRT model indicates that the ratio of the intensity of the stretchinglike mode against that of the bendinglike mode is about 6:1.

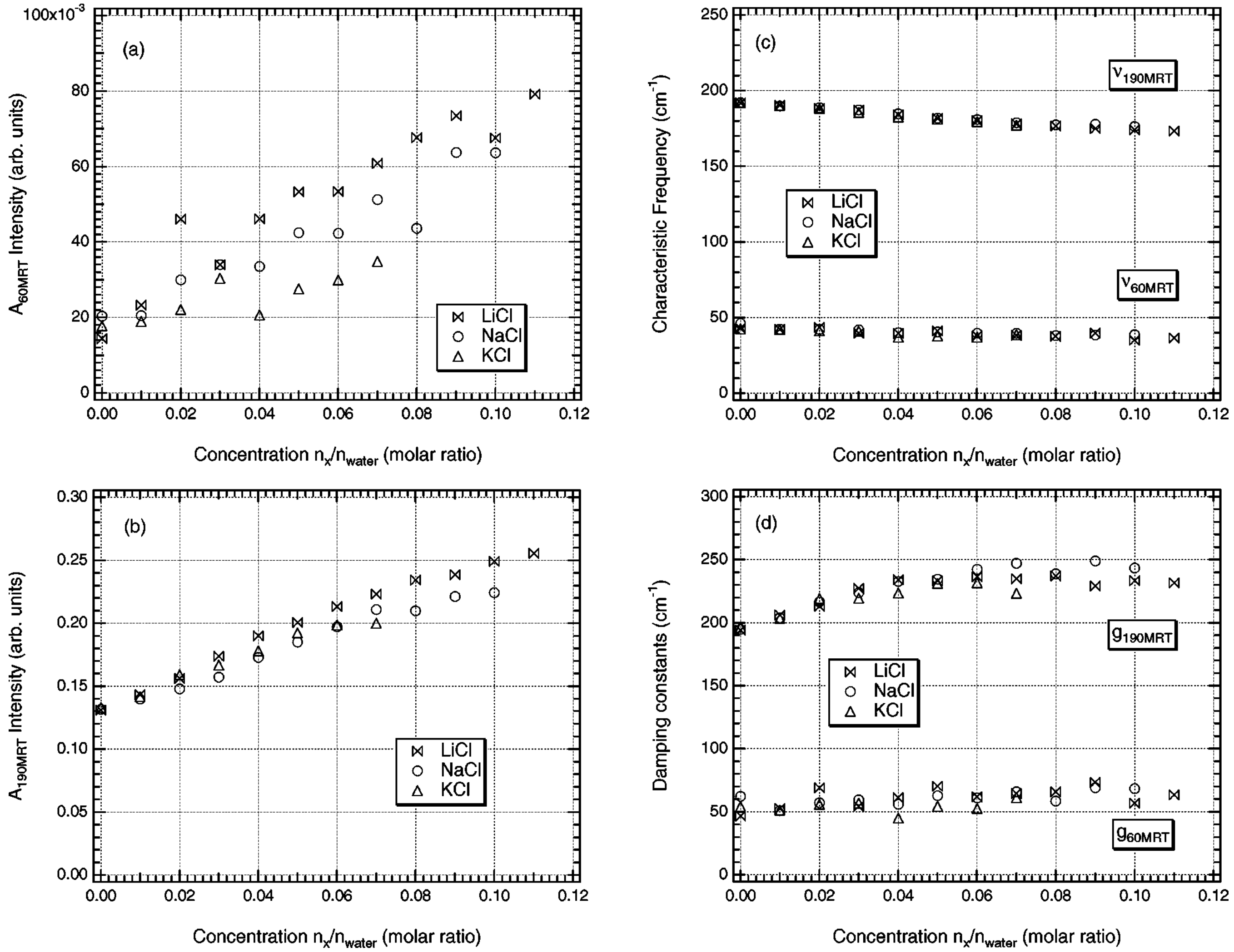

FIG. 5. Fitting results with one MRT model and two damped harmonic oscillation. (a) Intensity of the bending ($60\ \mathrm{cm}^{-1}$) mode as a function of concentration. (b) Intensity of stretching ($190\ \mathrm{cm}^{-1}$) mode as a function of concentration. (c) The characteristic frequencies ν_{190} and ν_{60} as a function of concentration. (d) The damping constants g_{190} and g_{60} as a function of concentration.

In case of ice Ih, there are two vibration modes around 60 and 220 cm^{-1}. The ratio of the intensity of the 220 cm^{-1} mode against that of the 60 cm^{-1} mode is about 10:1 [12]. Due to the hydrogen-bond network, a certain dynamical structure exists even in liquid water. The snapshot of this dynamical structure partially contains the icelike structure. Thus the results shown in Figs. 5(a) and 5(b) which are analyzed by the MRT model are more adequate than those in Figs. 6(a) and 6(b) which are analyzed by the Cole-Cole-type relaxation.

Li^+ and Na^+ ions are usually considered to be structure-making ions and K^+ and Cl^- are categorized as structure-breaking ions. According to the results of NMR, the proton relaxation rates in LiCl and NaCl solutions are larger than that in pure water, while the proton relaxation rates in KCl solution are smaller than that in pure water [23]. The self-diffusion constant of water in LiCl and NaCl aqueous solutions are smaller than that in pure water, while the self-diffusion constant of water in KCl solution is larger than that in pure water [24]. As shown in Fig. 3(d), α_0 in the MRT model varies consistently with the proton relaxation rate and the self-diffusion constant. The α_0 means the correlation rate of the heat bath originating from thermal fluctuation of water molecules. Large α_0 means the existence of the strong correlation in the fluctuating motion of water molecules.

The relaxation times of the aqueous solutions of LiCl, NaCl, and KCl are slower than those of liquid water at any concentration. Concentration and species dependences of τ_{MRT} and τ_{CC} are qualitatively the same. But the τ_{MRT} and τ_{CC} are quantitatively different. The Debye-type relaxation in water through the dielectric relaxation measurement has been reported and the obtained relaxation times are 8.32 and 1.02 ps [25]. Both τ_{MRT} and τ_{CC} in the present work are faster than the dielectric relaxation time. Thus we consider that the relaxation process observed by low-frequency Raman scattering in aqueous solutions does not correspond to the collective rotational motion of water molecules. Salt concentration dependences of α_0 indicate that the relaxation mode observed in low-frequency Raman scattering should contain the information of the reorientational motion in the hydration shell.

Parameter β in the Cole-Cole type relaxation means the distribution of relaxation times. The Cole-Cole band shape is broadened and has a background above 100 cm^{-1} by the

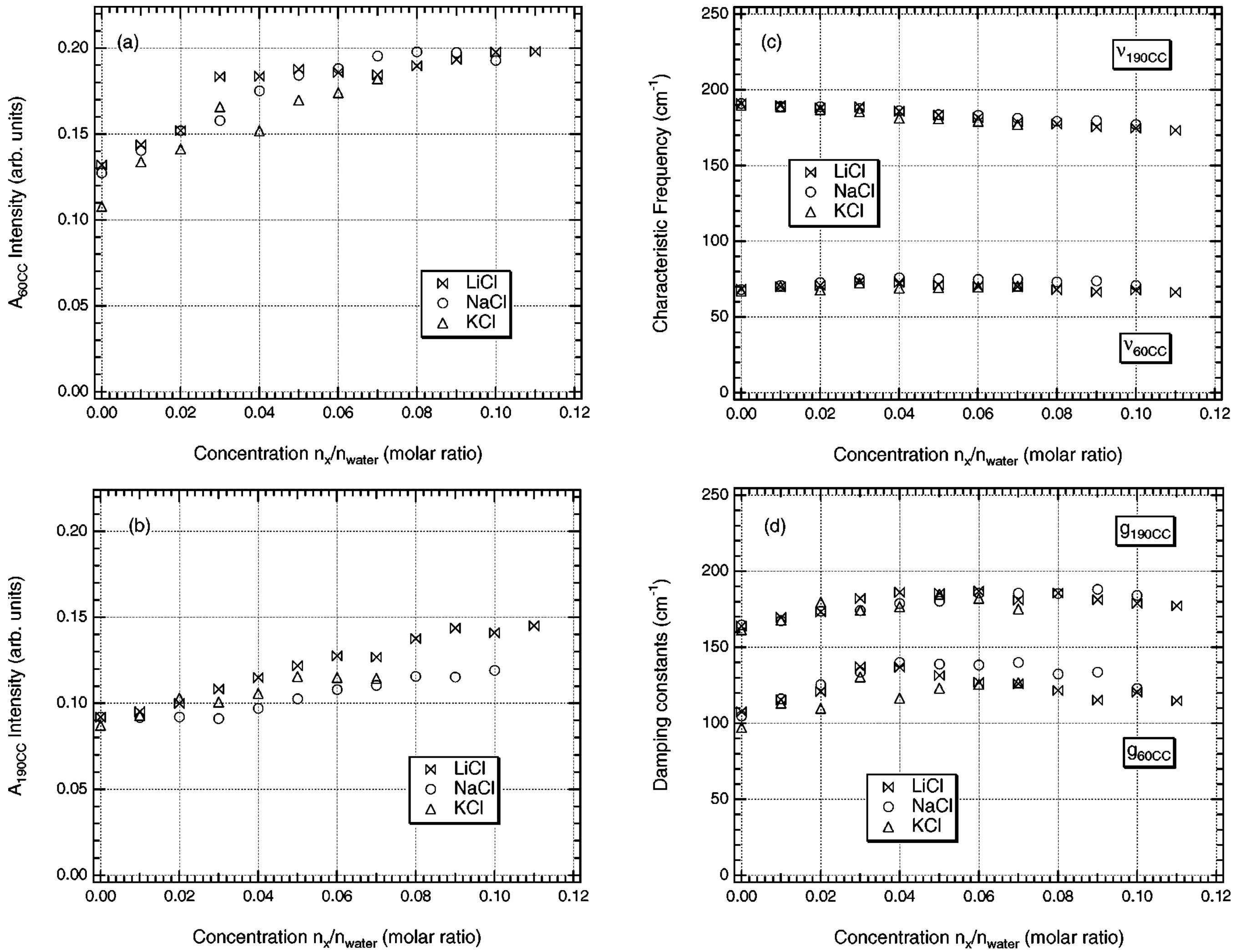

FIG. 6. Fitting results with one Cole-Cole relaxation and two damped harmonic oscillations. (a) Intensity of the bending (60 cm^{-1}) mode as a function of concentration. (b) Intensity of stretching (190 cm^{-1}) mode as a function of concentration. (c) The characteristic frequencies ν_{190} and ν_{60} as a function of concentration. (d) The damping constants g_{190} and g_{60} as a function of concentration.

distributed relaxation times as shown in Fig. 1(a). On the other hand, the MRT model has a single relaxation time and the spectral broadening depends on the α_0 which correlates to the heat bath. Moreover, the MRT model has no background in the high-frequency tail because of the inertial effect.

V. CONCLUDING REMARKS

The low-frequency Raman spectra of aqueous electrolyte solutions were analyzed with the superposition of one relaxation mode and two damped harmonic oscillator modes. We applied two types of relaxation functions, the Cole-Cole relaxation and the MRT model which takes into account the inertia and memory effects. Both models can reproduce well the reduced Raman spectra. In our analysis, the relaxation times of aqueous solutions obtained from both relaxation models are always longer than the relaxation time of liquid water at any concentration. Parameter α_0, the correlation strength of the heat bath, is found to be an indicator of structure-breaking and structure-making effects of each salt.

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