Cations Effects on Rotational Dynamics of Anions and Water Molecules in Alkali

(Li⁺, Na⁺, K⁺, Cs⁺) Thiocyanate (SCN⁻) Aqueous Solutions

Supporting material

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Figure S1. *FTIR spectra of LiSCN aqueous solutions* (D_2O) *in the* $C \equiv N$ *frequency region (A) and OD frequency region in HOD solutions (1% wt D₂O in H₂O) (B) at different bulk concentrations. All the backgrounds are subtracted from the spectra.*



Figure S2. *FTIR spectra of CsSCN aqueous solutions* (D_2O) *in the* $C \equiv N$ *frequency region* (*A*) *and OD frequency region in HOD solutions* (1% wt D_2O *in* H_2O) (*B*) *at different bulk concentrations. All the backgrounds are subtracted from the spectra.*



Figure S3. Concentration dependent rotation anisotropy of SCN (A) and OD (B) measured in the LiSCN solutions as a function of delay. Data is normalized with respect to the value at zero delay. Dots are the experimental results; the lines are the fitting results.



Figure S4. Concentration dependent rotation anisotropy of SCN (A) and OD (B) measured in the NaSCN solutions as a function of delay. Data is normalized with respect to the value at zero delay. Dots are the experimental results; the lines are the fitting results.



Figure S5. Concentration dependent rotation anisotropy of SCN (A) and OD (B) measured in the KSCN solutions as a function of delay. Data is normalized with respect to the value at zero delay. Dots are the experimental results; the lines are the fitting results.



Figure S6. Concentration dependent rotation anisotropy of SCN (A) and OD (B) measured in the CsSCN solutions as a function of delay. Data is normalized with respect to the value at zero delay. Dots are the experimental results; the lines are the fitting results.

	Atom	<i>q</i> (e)	σ (Å)	ε(kJ·mol ⁻¹)
¹ SPC/E	Ow	-0.8476	3.166	0.650
water	Hw	0.4238	0.000	
	S	-0.56	3.52	1.5225
² SCN ⁻	С	0.16	3.35	0.425
	Ν	-0.58	3.31	0.310
${}^{3}\mathrm{K}^{+}$		+1.0	3.33	0.42
$^{3}Na^{+}$		+1.0	2.58	0.42

Table S1. The potential parameters

Table S2. The simulation bulk information						
Concentration	Num	of	Num	of	mixed	Num of water
	KSCN	or	ion			
	NaSCN					
2mol	46					1154
10mol	200					1000
15mol	300					1000

To quantitatively analyze the SCN⁻ anion cluster concentration in LiSCN, NaSCN, KSCN **CsSCN** aqueous 5mol/kg, and solutions we used at а location-energy-exchange kinetic model which was shown in Scheme S1. In the model, vibrational energy can exchange between two closely contacted thiocyanate anions $(SCN_{clu}^{-} \text{ and } S^{13}C^{15}N_{clu}^{-})$. Thiocyanate anions which are separated by water or other anions (SCN_{iso}^{-} and $S^{13}C^{15}N_{iso}^{-}$) can't exchange energy. The two types of thiocyanate anions can exchange locations. The vibrational energy of each species decays with its own lifetime. More details of the kinetic model were described in our previous publications.⁴⁻⁷ From the kinetic model analysis, we can obtain the energy

transfer rate constants, the equilibrium constant and the location exchange rate constants. Detailed fitting parameters for the time dependent intensities of the diagonal peaks and the cross peaks of the mixed MS¹³C¹⁵N/MSCN (M=Li, Na, K, Cs) aqueous solutions at 5mol/kg are shown in Figure S7 to S10. The energy transfer rate and ion cluster concentrations for LiSCN, NaSCN, KSCN and CsSCN solutions at 5mol/kg are listed in Table S3. In the fitting of Fig S7 to S10, we found that the energy transfer rate and equilibrium constant (ion cluster concentration) can't be solely determined. These two parameters are entangled which means that one given energy transfer rate can give one equilibrium constant. It seems that the non-resonant energy transfer fitting can give us arbitrary ion cluster concentrations in the MSCN solutions. However, from the resonance energy transfer measurement, the number of SCN⁻ anions in an energy transfer unit for LiSCN, NaSCN, KSCN and CsSCN can be determined which set a restriction on the cluster concentration value. Thus the energy transfer rates listed in Table 3 were determined by combing with the resonance energy transfer measurements. The details of the resonance energy transfer data can be found in our previous paper.⁶ For comparison, we also compared the ion cluster concentrations when a fixed energy transfer time constant of 140 ps was used in the non-resonant energy transfer fitting for all solutions. The results are listed in Table S4.

$$\xleftarrow{k_{s^{13}c^{15}N^{-}}} S^{13}C^{15}N^{-}_{iso} \xleftarrow{k_{iso \rightarrow clu}}{k_{clu \rightarrow iso}} S^{13}C^{15}N^{-}_{clu} \xleftarrow{k_{s^{13}c^{15}N^{-} \rightarrow SCN^{-}}}{k_{scN^{-} \rightarrow s^{13}c^{15}N^{-}}} SCN^{-}_{clu} \xleftarrow{k_{clu \rightarrow iso}}{k_{iso \rightarrow clu}} SCN^{-}_{iso} \xrightarrow{k_{scN^{-}} \rightarrow SCN^{-}}{k_{scN^{-} \rightarrow s^{13}c^{15}N^{-}}}$$

(Scheme.S1)



Figure S7. Time-dependent intensities of $S^{13}C^{15}N^{-}\Gamma$ and SCN^{-} decay (A) and the energy transfer peaks between $S^{13}C^{15}N^{-}$ and $SCN^{-}\Gamma$ (B) for a 5 mol/kg LiSCN aqueous solution. Dots are data, and lines are calculations. Calculations for (A) and (B) are with input parameters:

$$k_{SCN^{-}fast} = 1/1.55 \ (ps^{-1}); \ k_{SCN^{-}slow} = 1/16.8 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}fast} = 1/1.58 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/20.7 \ (ps^{-1}); \ k_{slsCN^{-}slow} = 1/20.7 \ (ps^{-1}); \ (ps^{-1});$$

with pre-factors of the subgroups and offset of the bi-exponential

$$A_{SCN^{-}fast} = 0.31; \ A_{SCN^{-}slow} = 0.69; A_{S^{13}C^{15}N^{-}fast} = 0.24; \ A_{S^{13}C^{15}N^{-}slow} = 0.76; \ offset = 0.56$$



Figure S8. Time-dependent intensities of $S^{13}C^{15}N^{-1}$ and SCN^{-1} decay (A) and their energy transfer peaks between $S^{13}C^{15}N^{-1}$ and $SCN^{-1}(B)$ for a 5 mol/kg NaSCN

aqueous solution. Dots are data, and lines are calculations. Calculations for (A) and

(B) are with input parameters:

$$k_{SCN^{-}fast} = 1/1.5 \ (ps^{-1}); \ k_{SCN^{-}slow} = 1/23.5 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}fast} = 1/2.6 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/31.6 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/31.6 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/20 \ (ps^{-1}); \ K=1.5; \ k_{SCN^{-}\to S^{13}C^{15}N^{-}} = 1/120 \ (ps^{-1}); \ D=0.70$$

with pre-factors of the subgroups and offset of the bi-exponential

$$A_{SCN^{-}fast} = 0.31; \ A_{SCN^{-}slow} = 0.69; A_{S^{13}C^{15}N^{-}fast} = 0.28; \ A_{S^{13}C^{15}N^{-}slow} = 0.72; \ offset = 0.51.5$$



Figure S9. Time-dependent intensities of $S^{13}C^{15}N^{-}r$ and SCN^{-} decay (A) and their energy transfer peaks between $S^{13}C^{15}N^{-}$ and $SCN^{-}r$ (B) for a 5 mol/kg KSCN aqueous solution. Dots are data, and lines are calculations. Calculations for (A) and (B) are with input parameters:

$$k_{SCN^{-}fast} = 1/1.3 \ (ps^{-1}); \ k_{SCN^{-}slow} = 1/26 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}fast} = 1/2.2 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/33 \ (ps^{-1}); \ k_{slumetric} = 1/10 \ (ps^{-1}); \ K=2.0; \ k_{SCN^{-} \rightarrow S^{13}C^{15}N^{-}} = 1/140 \ (ps^{-1}); \ D=0.70$$

with pre-factors of the subgroups and offset of the bi-exponential

$$A_{SCN^{-}fast} = 0.25; \ A_{SCN^{-}slow} = 0.75; A_{S^{13}C^{15}N^{-}fast} = 0.225; \ A_{S^{13}C^{15}N^{-}slow} = 0.775; \ offset = 0.55; \ A_{SCN^{-}slow} = 0.775; \ A_{SCN^{-}slow} = 0.75; \ A_$$



Figure S10. Time-dependent intensities of $S^{13}C^{15}N^{-}\Gamma$ and SCN^{-} decay (A) and their energy transfer peaks between $S^{13}C^{15}N^{-}$ and $SCN^{-}\Gamma$ (B) for a 5 mol/kg CsSCN aqueous solution. Dots are data, and lines are calculations. Calculations for (A) and (B) are with input parameters:

 $\begin{aligned} k_{SCN^{-}fast} &= 1/2.1 \ (ps^{-1}); \ k_{SCN^{-}slow} = 1/26 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}fast} = 1/1.7 \ (ps^{-1}); \ k_{S^{13}C^{15}N^{-}slow} = 1/27 \ (ps^{-1}); \\ k_{clu \to iso} &= 1/10 \ (ps^{-1}); \ \text{K}=& 2.3; \ k_{SCN^{-} \to S^{13}C^{15}N^{-}} = 1/200 \ (ps^{-1}); \ \text{D}=& 0.70 \end{aligned}$

with pre-factors of the subgroups and offset of the bi-exponential

$$A_{SCN^{-}fast} = 0.24; \ A_{SCN^{-}slow} = 0.76; A_{S^{13}C^{15}N^{-}fast} = 0.31; \ A_{S^{13}C^{15}N^{-}slow} = 0.69; \ offset = 0.56; \ A_{SCN^{-}slow} = 0.69; \ A_{SCN^$$



Figure S11. Rotational time constants of SCN and D_2O in solutions of different cations Vs. viscosity. The viscosity (0.97 centistokes) of pure water is taken to be 1 for the normalization of viscosities of other solutions.



Figure S12. Reorientation correlation functions of SCN⁻ and water in aqueous solutions of (A) 5 mol/kg KSCN and 5 mol/kg CsSCN; and (B) 10 mol/kg NaSCN and 10 mol/kg LiSCN.

	Energy transfer rate (ps)	Equilibrium constant K	Percentage of clustered ions
LiSCN (5mol/kg)	80	1.0	50±4%
NaSCN (5mol/kg)	120	1.5	60±4%
KSCN (5mol/kg)	140	2.0	67±4%
CsSCN (5mol/kg)	200	2.3	$70 \pm 4\%$

Table S3 Experimental cluster concentrations for the LiSCN, NaSCN, KSCN and CsSCN solutions at 5mol/kg.

Table S4 Experimental cluster concentrations for the LiSCN, NaSCN, KSCN and CsSCN solutions at 5mol/kg, the energy transfer rate was fixed at 140 ps.

	Equilibrium constant K	Percentage of clustered ions
LiSCN (5mol/kg)	5.0	83±5%
NaSCN (5mol/kg)	2.2	$69\pm4\%$
KSCN (5mol/kg)	2.0	67±4%
CsSCN (5mol/kg)	1.0	$50\pm4\%$

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