

Electronic supplementary information

Molecular Structure and Ultrafast Dynamics of Sodium Thiocyanate Ion Pairs in Glymes of Different Length

*Susith R Galle Kankanamge, Daniel G. Kuroda**

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States

*Address correspondence to dkuroda@lsu.edu

Figures

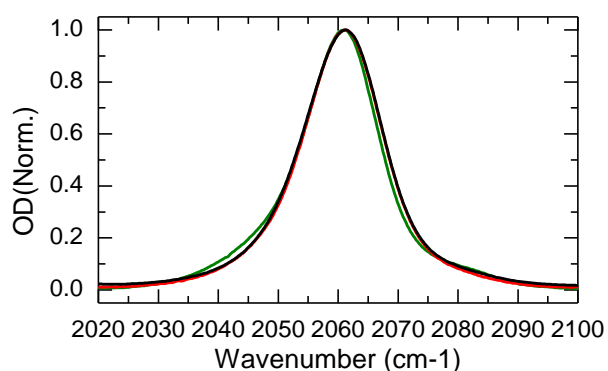


Figure S1. FTIR spectra of 1.5M NaSCN in different glymes, G2 (green), G3 (red) and G4 (black) in the range of 2020 cm⁻¹ to 2100 cm⁻¹.

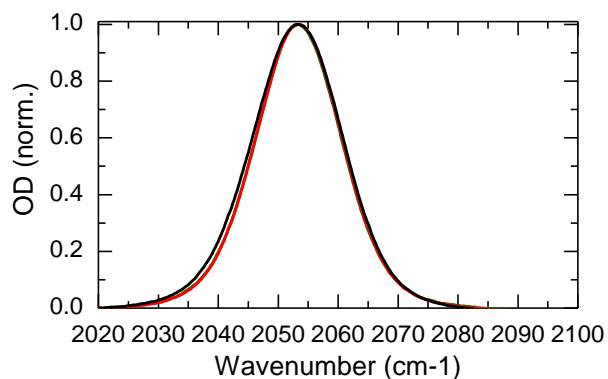


Figure S2. FTIR spectra of 0.5M TBASCN in different glymes, G2 (green), G3 (red) and G4 (black) in the range of 2020 cm⁻¹ to 2100 cm⁻¹.

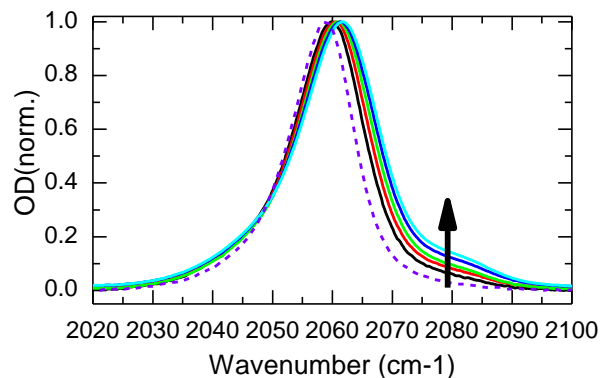


Figure S3. Concentration dependence FTIR spectra of NaSCN on diglyme. Direction of the arrow shows the increase of concentration from 0.5M to 2.5M. Dashed purple line is the 50mM solution.

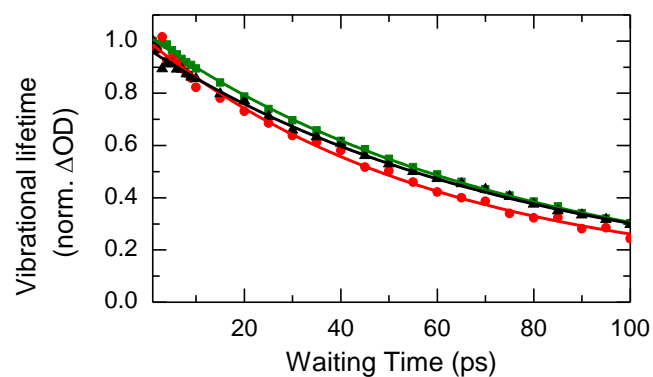


Figure S4. Vibrational lifetime decays of 0.5M NaSCN in G2 (green), G3 (red) and G4 (black)

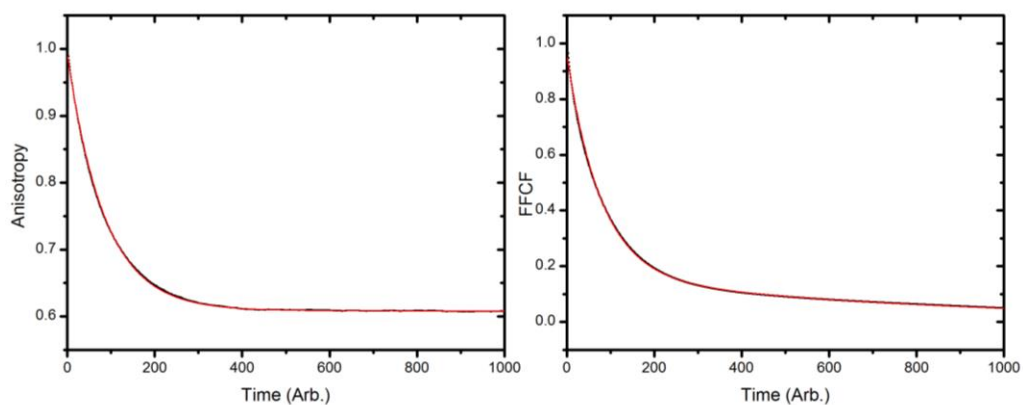


Figure S5. The simulated anisotropy and FFCF when the extent of the cavity along the Na-C direction. The normalized decay time for anisotropy is 7.5 ps and decay times for FFCF are 6.8 ps and 72 ps.

Tables

Table S1. Fitting parameters of FTIR spectra of 0.5M NaSCN in glymes.

		G2	G3	G4
Peak 1	y0	0	0	0
	xc	2054.0±0.8	2054±0.9	2054.0±0.7
	A	6.1±0.9	3.7±0.3	4.0±0.3
	FWHM	27.2	24.9	23.4
Peak 2	y0	0	0	0
	xc	2060.1±0.1	2060.3±0.1	2060.5±0.1
	A	11.6±0.9	013.6±0.3	13.0±0.3
	FWHM	13.7	15.5	15.9
Peak 3	y0	0	0	0
	xc	2078.1±0.6	2078.0±0.7	2078.0±0.4
	A	0.50±0.03	0.31±0.03	0.41±0.03
	FWHM	16.5	14.0	13.8

Table S2. Fitting parameters of FTIR spectra of 1.5M NaSCN in glymes.

		G2	G3	G4
Peak 1	y0	0	0	0
	xc	2055.0±0.7	2056±1	2055.0±0.9
	A	6.6±0.8	7±2	7±2
	FWHM	28.3	25	18.7
Peak 2	y0	0	0	0
	xc	2061.2±0.1	2061.60±0.03	2062.0±0.2
	A	12.3±0.8	13±2	13±2
	FWHM	14.7	15.9	15.5
Peak 3	y0	0	0	0
	xc	2079.9±0.3	2077.1±0.7	2078±1
	A	0.77±0.02	0.9±0.1	0.7±0.2
	FWHM	16.5	18.8	18.7

Table S3. Vibrational lifetime of 0.5M NaSCN in glymes.

	T ₁₀
G2	75±3
G3	60±5
G4	77±6

Table S4. Fitting parameters of CLS data.

	A1	t ₁	A2	t ₂
G2	0.68±0.02	4.6±0.2	0.30±0.02	51±5
G3	0.63±0.02	6.0±0.3	0.36±0.02	68±5
G4	0.68±0.02	4.6±0.2	0.30±0.02	51±5

Table S5. Fitting parameters of anisotropy decays for 0.5M NaSCN in the different glymes.

Sovent	B1	T ₁ (ps)	B2	T ₂ (ps)
Diglyme	0.144±0.009	7.5±0.8	0.217±0.008	114±8
Triglyme	0.134±0.007	9.0±0.9	0.241±0.007	162±13
Tetraglyme	0.12±0.01	7±1	0.30±0.01	152±13

Ion pair association constant

The association constant can be expressed as:

$$K_A = \frac{[A+\cdots B^-]+[AB]}{[A^+][B^-]} = K_{SSIP}(1 + K_{CIP}),$$

where [B⁻], [A⁺...B⁻], [AB] are free, SSIP, and CIP species, respectively.

Given our definition of ion pairing as only contact ion pairs, our data gives an estimate of the molar ratio of CIP over the rest of the species (SSIP and free ions); i.e., $\frac{([A+\cdots B^-]+[B^-])[AB]}{[AB]}$. This ratio is different from the typical ratio, which is the concentration of the free ion over the total concentration of ion pairs; i.e., $\frac{[B^-]}{([A+\cdots B^-]+[AB])}$. The new ratio is needed because IR spectroscopy usually does not distinguish between SSIP and “free” ions (see for example Ref. 40 of the manuscript). Thus, expressing the ratio in terms of what we define as “free”, which are free ions and SSIP, then the ratio of areas can be written as:

$$Ratio = \frac{[A+\cdots B^-]+[B^-]}{[AB]} = \frac{1}{K_{CIP}} + \frac{1}{\sqrt{[AB]K_{CIP}K_{SSIP}}}$$

Note that to derive this expression we have used the following definitions:

$$K_{SSIP} = \frac{[A+\cdots B^-]}{[A^+][B^-]} \text{ and } K_{CIP} = \frac{[AB]}{[A+\cdots B^-]}$$

which is the standard definition of these constants (K_{SSIP} and K_{CIP}). We have also assumed that the extinction coefficients of free ions, SSIP, and CIPS are the same, which according to DFT calculations is a reasonable approximation.

Using equation 5 from Geiger et al., a value of K_{SSIP} of 974 is obtained assuming a dielectric constant of 7.5 for all glymes.¹ With this K_{SSIP} value and the equation previously derived, it is estimated that the value of K_{CIP} to be 2.1 using our experimental data; i.e., the ratio of the sum of the [SSIP] and [free ions] over [CIP] as $\frac{([A+\cdots B^-]+[B^-])}{[AB]}=0.52$ and a [CIP]=0.32 M. Thus, the calculated K_A is $\sim 3 \times 10^3$ for NaSCN in glymes. This association constant shows good agreement with those previously determined for NaSCN in 1-propanol and 2-propanol at 298K of 235 and 778, respectively.² Moreover, the calculated K_A is higher than that found in alcohols, because alcohols have higher dielectric constants (~ 20) than glymes (~ 7). Finally, the estimated K_A is similar to other systems, such as TBAPF₆ in glymes.³

References

1. C. F. Riadigos, R. Iglesias, M. A. Rivas and T. P. Iglesias, *J Chem Thermodyn*, 2011, 43, 275-283.
2. E. N. Tsurko, R. Neueder and J. Barthel, *J Chem Eng Data*, 2000, 45, 678-681.
3. R. J. LeSuer, C. Buttolph and W. E. Geiger, *Anal Chem*, 2004, 76, 6395-6401.

