Electronic Supplementary Information for

Complexation dynamics of CH₃SCN and Li⁺ in acetonitrile

studied by two-dimensional infrared spectroscopy

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1. Kinetics of ion-molecule complexation dynamics

2. 2D Gaussian volume fitting method

1. Kinetics of ion-molecule complexation dynamics

Ion-molecule complexation dynamics observed in the T_w -dependent 2DIR spectra can be described by the two-species exchange kinetic scheme,¹⁻³

$$\xleftarrow{T_{1,F}, \tau_{or,F}}_{decay} CH_3SCN + Li^+ \xleftarrow{k_a}_{k_d} CH_3SCN \cdots Li^+ \xrightarrow{T_{1,C}, \tau_{or,C}}_{decay} \rightarrow \qquad (Scheme 1)$$

where k_a and k_d are the association and dissociation rate constants, $T_{1,F}$ and $T_{1,C}$ are the vibrational lifetimes, $\tau_{or,F}$ and $\tau_{or,C}$ are the orientational relaxation times of free CH₃SCN (F) and CH₃SCN…Li⁺ complex (C), respectively. Here, the activity coefficients of all species in solution are neglected for the sake of simplicity. Then, the equilibrium constant is given by

$$K_{\rm eq} = \frac{[\rm CH_3 SCN \cdots Li^+]}{[\rm Li^+][\rm CH_3 SCN]} = \frac{k_{\rm a}}{k_{\rm d}}$$
(S1)

where $[\cdots]$ represents the equilibrium concentration. The time-dependent changes of $[CH_3SCN\cdots Li^+]$ and $[CH_3SCN]$ obey the following coupled rate equations,²

$$\frac{d[CH_3SCN\cdots Li^+]}{dt} = -k_d[CH_3SCN\cdots Li^+] + k_a[Li^+][CH_3SCN]$$

$$\frac{d[CH_3SCN]}{dt} = k_d[CH_3SCN\cdots Li^+] - k_a[Li^+][CH_3SCN]$$
(S2)

The complexation (association) and dissociation kinetics can be modeled as a pseudo-first order reaction with $k'_a = k_a [Li^+]$. The corresponding equilibrium constant for the pseudo-first order reaction is given by $K'_{eq} = [CH_3SCN\cdots Li^+]/[CH_3SCN] = k_a [Li^+]/k_d = k'_a/k_d$. The analytical solutions of the above rate equations are found to be

$$[CH_{3}SCN \cdots Li^{+}]_{C}(t) = [CH_{3}SCN \cdots Li^{+}] \frac{k_{a}^{'} + k_{d} \exp(-k_{ex}t)}{k_{ex}}$$

$$[CH_{3}SCN]_{F}(t) = [CH_{3}SCN] \frac{k_{d} + k_{a}^{'} \exp(-k_{ex}t)}{k_{ex}}$$

$$[CH_{3}SCN \cdots Li^{+}]_{C \to F}(t) = [CH_{3}SCN \cdots Li^{+}] \frac{k_{d} \left[1 - \exp(-k_{ex}t)\right]}{k_{ex}}$$

$$[CH_{3}SCN]_{F \to C}(t) = [CH_{3}SCN] \frac{k_{a}^{'} \left[1 - \exp(-k_{ex}t)\right]}{k_{ex}}$$
(S3)

where the exchange rate constant is given by the sum of the association and dissociation constants as $k_{ex} = k_d + k'_a$. In the T_w -dependent 2DIR spectra, $[CH_3SCN\cdots Li^+]_C(t)$ and $[CH_3SCN]_F(t)$ are the concentrations determining the diagonal peak amplitudes, whereas $[CH_3SCN\cdots Li^+]_{C\to F}(t)$ and $[CH_3SCN]_{F\to C}(t)$ correspond to the concentrations associated with the cross-peaks. Now, by including the vibrational population and orientational relaxation process, the analytic equations for the diagonal and cross-peak amplitudes as a function of T_w are obtained as⁴⁻⁵

$$I_{C}(T_{w}) = C_{C}\mu_{C}^{4} \left\{ \frac{4}{9} e^{-\alpha T_{w}} \left[\cosh(\beta T_{w}) - \gamma \sinh(\beta T_{w}) \right] + \frac{5}{9} e^{-\phi T_{w}} \left[\cosh(\xi T_{w}) - \eta \sinh(\xi T_{w}) \right] \right\}$$

$$I_{F}(T_{w}) = C_{F}\mu_{F}^{4} \left\{ \frac{4}{9} e^{-\alpha T_{w}} \left[\cosh(\beta T_{w}) + \gamma \sinh(\beta T_{w}) \right] + \frac{5}{9} e^{-\phi T_{w}} \left[\cosh(\xi T_{w}) + \eta \sinh(\xi T_{w}) \right] \right\}$$

$$I_{C \to F}(T_{w}) = C_{C}\mu_{C}^{2}\mu_{F}^{2} \left\{ \frac{4}{9} \frac{k_{a}}{\beta} e^{-\alpha T_{w}} \sinh(\beta T_{w}) + \frac{5}{9} e^{-\phi T_{w}} \frac{k_{a}}{\xi} \sinh(\xi T_{w}) \right\}$$

$$I_{F \to C}(T_{w}) = C_{F}\mu_{F}^{2}\mu_{C}^{2} \left\{ \frac{4}{9} \frac{k_{a}}{\beta} e^{-\alpha T_{w}} \sinh(\beta T_{w}) + \frac{5}{9} e^{-\phi T_{w}} \frac{k_{a}}{\xi} \sinh(\xi T_{w}) \right\}$$
(S4)

where

$$\alpha = \frac{1}{2} \left(D_{\rm C} + D_{\rm F} + k_{\rm C} + k_{\rm F} + k_{\rm a}^{'} + k_{\rm d} \right)$$

$$\beta = \sqrt{\alpha^2 - \left(D_{\rm C} D_{\rm F} + D_{\rm F} k_{\rm C} + D_{\rm F} k_{\rm a}^{'} + D_{\rm C} k_{\rm F} + k_{\rm C} k_{\rm F} + k_{\rm a}^{'} k_{\rm F} + D_{\rm C} k_{\rm d} + k_{\rm C} k_{\rm d} \right)}$$

$$\gamma = \frac{\alpha - \left(D_{\rm C} + k_{\rm C} + k_{\rm a}^{'} \right)}{\beta}$$

$$\varphi = \frac{1}{2} \left(k_{\rm C} + k_{\rm F} + k_{\rm a}^{'} + k_{\rm d} \right)$$
$$\xi = \sqrt{\varphi^2 - \left(k_{\rm C} k_{\rm F} + k_{\rm a}^{'} k_{\rm F} + k_{\rm C} k_{\rm d} \right)}$$
$$\eta = \frac{\varphi - \left(k_{\rm C} + k_{\rm a}^{'} \right)}{\xi}$$

Here, *C* denotes the concentration and μ the transition dipole moment. $D_{\rm F} = 1/\tau_{\rm or,F}$ and $D_{\rm C} = 1/\tau_{\rm or,C}$ are related to the orientational diffusion coefficients, and $k_{\rm F} = 1/T_{\rm 1,F}$ and $k_{\rm C} = 1/T_{\rm 1,C}$ are the vibrational population relaxation rates of free CH₃SCN (F) and CH₃SCN…Li⁺ complex (C), respectively.

In the two-species exchange kinetic scheme (Scheme 1), the IR PP signal, $S_{C}^{PP}(t)$, can be expressed as

$$S_{\rm C}^{PP}(t) = I_{\rm C}(t) + I_{\rm F \to C}(t)$$

$$S_{\rm F}^{PP}(t) = I_{\rm F}(t) + I_{\rm C \to F}(t)$$
(S5)

In this case, IR PP signal is equivalent to the integration of 2DIR spectra along the ω_{τ} axis onto the ω_{t} axis (the probing frequency). $S_{C}^{PP}(t)$ results from the population decay and orientational relaxation. Therefore, the population decay, P(t), can be obtained by neglecting the effect of the orientational relaxation in Eq. (S5).

$$P_{\rm C}(t) = I_{\rm C}(t) + I_{\rm F \to C}(t)$$

$$P_{\rm F}(t) = I_{\rm F}(t) + I_{\rm C \to F}(t)$$
(S6)

where $D_{\rm C} = D_{\rm F} = 0$ in Eq. (S4). As shown in Eq. (S6), P(t) decays due to the pure vibrational population decay and chemical exchange.

2. Two-dimensional (2D) Gaussian volume fitting method

The diagonal and cross-peaks in the 2DIR spectrum at a given T_w are successfully fitted with rotated 2D Gaussian functions so that the peak volumes can be determined. The long axis of the rotated 2D Gaussian function is parallel to the diagonal. The rotated 2D Gaussian function for a given diagonal peak is given by

$$G(\omega_{\tau},\omega_{t}) = \mathbf{A} \cdot \exp\left[-\frac{\left(\omega_{\tau}-\omega_{t}-\omega_{\tau0}+\omega_{t0}\right)^{2}}{4\sigma_{\tau}^{2}} - \frac{\left(\omega_{\tau}+\omega_{t}-\omega_{\tau0}-\omega_{t0}\right)^{2}}{4\sigma_{t}^{2}}\right] - \mathbf{A} \cdot \exp\left[-\frac{\left(\omega_{\tau}-\omega_{t}+\Delta\omega-\omega_{\tau0}+\omega_{t0}\right)^{2}}{4\sigma_{\tau}^{2}} - \frac{\left(\omega_{\tau}+\omega_{t}-\Delta\omega-\omega_{\tau0}-\omega_{t0}\right)^{2}}{4\sigma_{t}^{2}}\right]$$
(S7)

where ω_{r0} and ω_{t0} are the peak positions along the ω_r axis and ω_t axis, σ_r and σ_r are the diagonal and anti-diagonal widths, respectively, and $\Delta \omega$ is the vibrational anharmonicity. The first term in Eq. (S7) represents the 2D Gaussian peak for the $v = 0 \rightarrow 1$ transition and the second term is the 2D Gaussian peak for the $v = 1 \rightarrow 2$ transition. For a cross-peak, their amplitudes are varied for 2D Gaussian function fitting, since those parameters obtained from the analyses of diagonal peaks can be used again. For a complete numerical fitting analysis, there are 13 parameters that are to be determined for the 2D Gaussian fits to the 2DIR spectrum. Among them, the peak positions and vibrational anharmonicities could be easily determined from the 2DIR spectrum. The vibrational lifetimes and orientational relaxation times are measured using the polarization-controlled IR pump-probe spectroscopy. The concentrations, transition dipole moments, equilibrium constant are determined from the FTIR spectroscopy. Then, the remaining seven parameters that are related to peak amplitudes and widths are iteratively varied until the fitting results converge to the experimental 2DIR spectra. The fitted 2DIR spectra are shown in Figure S2 and compared with the experimental 2DIR spectra shown in Figure 2.

Once the 2D Gaussian volume fitting analysis is completed, the peak volumes are plotted as a function of T_w and the analytical equations in Eq. (S4) are used to fit to the peak volume data. Here, the only remaining parameter that should be determined from the kinetic fitting analyses is the dissociation rate constant, k_d . By using the k_d value, the association rate constant ($k'_a = K'_{eq}k_d$) and the exchange rate constant ($k_{ex} = k_d + k'_a$) are readily obtained.

References

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Figure S1



Figure S1. By analyzing the cross-peaks in T_w -dependent 2DIR spectra, the forward (k_a') and backward (k_d) rate constants can be extracted.

Figure S2



Figure S2. The 2D Gaussian volume fit results. Numerically calculated 2DIR spectra with the fitting parameters are plotted here and they are to be compared with the experimental results presented in Figure 2 in the main text.

Figure S3



Figure S3. (A) Temperature-dependent FTIR spectra of free CH₃SCN. (B) Temperaturedependent FTIR spectra of the sample solution with $[Li^+]=2.0$ M. (C) Decomposition of FTIR spectrum into the nitrile stretch bands of free CH₃SCN and CH₃SCN…Li⁺.

Figure S4



Figure S4. (A) Parallel and (B) perpendicular IR PP signals.