Electronic Supplementary Information for

Effect of ion-ligand binding on ion pairing dynamics studied by two-dimensional infrared spectroscopy

YoungAh Kwon,§ Junho Lee,§ and Sungnam Park*

Department of Chemistry, Korea University, Seoul, 02841, Korea.

*Author to whom correspondence should be addressed.

Email addresses: spark8@korea.ac.kr

§ Y. K. and J. L. contributed equally to this work.
Contents

1. Polarization-controlled IR PP spectroscopy
2. Two-dimensional infrared (2DIR) spectroscopy
3. Kinetics of chemical exchange dynamics
4. Two-dimensional (2D) Gaussian volume fitting method
5. Raman spectroscopy
6. Figure S1. Concentration-dependent FTIR spectra
7. Figure S2. Raman spectra measured with 0.5 M AgSCN and 0.5 M CuSCN in DMTF
8. Figure S3. Polarization-controlled IR PP signal measured with AgSCN in DMTF
9. Figure S4. Polarization-controlled IR PP signal measured with CuSCN in DMTF
10. Figure S5. Experimental and fitted 2DIR spectra of AgSCN in DMTF
11. Figure S6. Experimental and fitted 2DIR spectra of CuSCN in DMTF
12. Figure S7. Illustration of the center line slope method to extract the FFCF from 2DIR spectrum
13. Figure S8. The FFCF extracted from our 2DIR spectra by the center line slope method
1. Polarization-controlled IR pump-probe spectroscopy

The femtosecond laser system has been described elsewhere. In brief, a train of 800 nm pulses with ~45 fs duration and ~1.0 mJ per pulse was generated by a Ti:sapphire oscillator (Tsunami, Spectra-Physics) and regenerative amplifier (Spitfire, Spectra-Physics) laser system operating at 1 kHz. An optical parametric amplifier (OPA, Spectra-Physics) was pumped with the 800 nm pulses to produce near-IR pulses at ~1.4 and ~1.9 μm which were used to generate mid-IR pulses at 2050 cm\(^{-1}\) in a 0.5 mm thick AgGaS\(_2\) crystal (type II) by difference frequency generation. The power spectrum of the mid-IR pulses had a Gaussian envelope with an ~250 cm\(^{-1}\) bandwidth (full width at half-maximum). The dielectric materials in the setup such as a Ge Brewster plate and ZnSe beam splitters cause the linear dispersion, and this dispersion was compensated with the CaF\(_2\) plates with different thicknesses. The mid-IR pulses were nearly transform-limited at the sample position.

Experimental details of the IR pump-probe spectroscopy have described elsewhere. In the experiments, the IR pulses were split into the pump and probe beams with a 9:1 intensity ratio and were focused onto the sample. The probe beam was collimated after the sample and was dispersed through a spectrometer onto the 64-element MCT array detector. The IR pump-probe signal \(S(t)\) was collected by measuring the transmission of the probe beam through the sample by chopping the pump beam at 500 Hz. For a given delay time \(t\), the IR pump-probe signal was defined by \(S(t) = \frac{T_{\text{pump on}} - T_{\text{pump off}}}{T_{\text{pump off}}} = \frac{\Delta T(t)}{T}\), where \(T\) is the transmission of the probe beam. For polarization-controlled IR pump-probe experiments, the wiregrid polarizers were placed in the pump and probe beam pathways before the sample and their polarization states were set to be 0 and 45° with respect to the normal to the optical table, respectively. A wiregrid analyzer polarizer on a motorized rotational stage was placed after the sample, and the parallel and perpendicular polarizations of the probe beam were selectively measured by setting the analyzer polarizer to be 0 and 90° by the computer-controlled
motorized rotational stage. The parallel and perpendicular IR pump-probe signals, \( S_{\parallel}(\omega_{pr}, t) \) and \( S_{\perp}(\omega_{pr}, t) \), were consecutively measured for every two scans with the polarization of the probe beam parallel and perpendicular to that of the pump beam, respectively.

2. 2DIR spectroscopy

The principles and experimental details of 2DIR spectroscopy have been described in detail elsewhere.\(^4\)\(^{,}\)\(^6\)\(^-\)\(^8\) In brief, the mid-IR beam with a pulse energy of ~800 nJ was split into three excitation beams and a local oscillator \((k_1, k_2, k_3, \text{ and } k_{LO})\). Three mid-IR beams \((k_1, k_2, \text{ and } k_3)\) were focused onto the sample in a boxcar geometry with a parabolic mirror (focal length = 10 cm) and after the sample the beams were collimated with another parabolic mirror (focal length = 10 cm). The spot size of the IR beams at the sample position was estimated to be less than 100 \(\mu\)m in diameter. The relative time delays between the three mid-IR pulses were varied with computer-controlled linear translational stages. The signal field emitted from the sample in a unique phase-matching direction was combined with a local oscillator pulse for subsequent heterodyne detection. The heterodyne-detected signal was spectrally-resolved in a monochromator onto a 64-element MCT (Mercury-Cadmium-Telluride) array detector (InfraRed Associates Inc.) equipped with a high-speed data acquisition system (Infrared Systems Development Corp.). A small portion of the mid-IR beam was sampled and went around the sample and used as a reference beam to correct the fluctuation of the laser intensity during the experiment.

In 2DIR experiments, there are three time variables: evolution time \( (\tau) \), waiting time \( (T_w) \), and detection time \( (t) \). The time period between the first and the second pulses are called the evolution time \( (\tau) \), and during this time period, the molecules are excited to a coherence state oscillating at their initial frequencies \( (\omega_{r}) \). During the waiting time \( (T_w) \) between the second and the third pulses, the molecules get to a population state and undergo the chemical exchange.
After the third pulse, the detection time \((t)\) begins and the molecules end up on another coherence state oscillating at their final frequencies. These frequencies are read out during this time period.\(^6\,9\) In principle, 2DIR signals collected in the experiments should be doubly Fourier-transformed along the \(\tau\)-axis and \(t\)-axis to give the 2D spectra with the initial and final frequencies of \(\omega_\tau\) and \(\omega_t\), respectively. In practice, Fourier-transformation along \(t\)-axis was performed by the spectrometer during the experiments. Therefore, 2DIR signals, \(S(\tau,T_w,\omega)\) were obtained at individual spectrometer frequencies \((\omega)\) by scanning the \(\tau\)-axis for a given \(T_w\) time. The temporal interferograms as a function of \(\tau\) at the spectrometer frequencies \((\omega)\) were Fourier-transformed to give the \(\omega_\tau\) axis. To obtain purely absorptive part of the 2DIR signals, rephasing and nonrephasing 2DIR signals were measured by using two different pulse sequences in our beam geometry and they were added in the frequency domain after Fourier-transformation.\(^9\) Finally, 2DIR spectra with two frequency axes of \(\omega_\tau\) and \(\omega_t\) were displayed as a function of \(T_w\) time, \(S(\omega_\tau,T_w,\omega)\) or \(S(\omega_\tau,\omega;T_w)\). By examining \(T_w\)-dependent 2DIR spectra, all structural and dynamic information on the molecular system under study can be obtained.\(^10\,12\)

3. Kinetics of chemical exchange dynamics

Ion-molecule complexation dynamics observed in the \(T_w\)-dependent 2DIR spectra can be described by the two-species exchange kinetic scheme,\(^4\,7\,13\)

\[
\begin{align*}
\text{M}^+ + \text{SCN}^- &\quad \xrightleftharpoons{\tau_{d,F}, \tau_{a,F}} \quad \text{CIP} \quad \xrightarrow{\frac{k_a}{k_d}} \quad \frac{\tau_{d,C}, \tau_{a,C}}{\text{decay}}
\end{align*}
\]

(Scheme S1)

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 SCN\(^-\) (F) and CIP (M-SCN or M-NCS, 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
\[ K_{eq} = \frac{[\text{CIP}]}{[\text{M}^+][\text{SCN}^-]} = \frac{k_a}{k_d} \quad (S1) \]

where \([\cdots]\) represents the equilibrium concentration. The time-dependent changes of \([\text{M-SCN}]\) and \([\text{SCN}^-]\) obey the following coupled rate equations,\(^7\)

\[
\frac{d[\text{CIP}]}{dt} = -k_a[\text{CIP}] + k_s[\text{M}^+][\text{SCN}^-] \quad (S2) \\
\frac{d[\text{SCN}^-]}{dt} = k_d[\text{CIP}] - k_s[\text{M}^+][\text{SCN}^-] 
\]

The complexation (association) and dissociation kinetics can be modeled as a pseudo-first order reaction with \(k_s = k_s[\text{M}^+]\). Thus, the chemical exchange kinetic scheme can be re-written as

\[
\text{SCN}^- \xrightarrow{\text{decay}} \frac{k_d-k_s}{k_s} \xrightarrow{\text{decay}} \text{CIP} \quad \text{(Scheme S1')} 
\]

The coupled rate equations in Eq. (S2) are rewritten as

\[
\frac{d[\text{CIP}]}{dt} = -k_d[\text{CIP}] + k_s'[\text{SCN}^-] \quad (S3) \\
\frac{d[\text{SCN}^-]}{dt} = k_d[\text{CIP}] - k_s'[\text{SCN}^-] 
\]

where \(k_s' = k_s[\text{M}^+]\) and the association reaction is written as the pseudo-first order reaction.

The corresponding equilibrium constant for the pseudo-first order reaction is given by

\[ K_{eq} = [\text{CIP}] / [\text{SCN}^-] = k_s[\text{M}^+] / k_d = k_s'/k_d \]

The analytical solutions of the above rate equations are found to be

\[
[\text{CIP}]_{t_c}(t) = [\text{CIP}] \frac{k_s' + k_d \exp(-k_{ex}t)}{k_{ex}} \\
[\text{SCN}^-]_{t_c}(t) = [\text{SCN}^-] \frac{k_d + k_s' \exp(-k_{ex}t)}{k_{ex}} \\
[\text{CIP}]_{t_{c-1}}(t) = [\text{CIP}] \frac{k_d \left[ 1 - \exp(-k_{ex}t) \right]}{k_{ex}} \\
[\text{SCN}^-]_{t_{c-1}}(t) = [\text{SCN}^-] \frac{k_s' \left[ 1 - \exp(-k_{ex}t) \right]}{k_{ex}}, \quad (S4)
\]
where the exchange rate constant is given by the sum of the association and dissociation constants as \( k_{ex} = k_d + k_d'. \) In the \( T_w \)-dependent 2DIR spectra, \([\text{CIP}]_c(t)\) and \([\text{SCN}^-]_c(t)\) are the concentrations determining the diagonal peak amplitudes, whereas \([\text{CIP}]_{c\to r}(t)\) and \([\text{SCN}^-]_{r\to c}(t)\) 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 as\(^{14-15}\)

\[
I_c(T_w) = C_c \mu_c^4 \left\{ \frac{4}{9} e^{-\alpha T_w} \left[ \cosh(\beta T_w) - \gamma \sinh(\beta T_w) \right] + \frac{5}{9} e^{-\varphi T_w} \left[ \cosh(\xi T_w) - \eta \sinh(\xi T_w) \right] \right\}
\]

\[
I_r(T_w) = C_r \mu_r^4 \left\{ \frac{4}{9} e^{-\alpha T_w} \left[ \cosh(\beta T_w) + \gamma \sinh(\beta T_w) \right] + \frac{5}{9} e^{-\varphi T_w} \left[ \cosh(\xi T_w) + \eta \sinh(\xi T_w) \right] \right\}
\]

\[
I_{c\to r}(T_w) = C_c \mu_c^2 \mu_r^2 \left\{ \frac{4}{9} k_d \frac{1}{\beta} e^{-\alpha T_w} \sinh(\beta T_w) + \frac{5}{9} e^{-\varphi T_w} \frac{k_d'}{\xi} \sinh(\xi T_w) \right\}
\]

\[
I_{r\to c}(T_w) = C_r \mu_r^2 \mu_c^2 \left\{ \frac{4}{9} k_d \frac{1}{\beta} e^{-\alpha T_w} \sinh(\beta T_w) + \frac{5}{9} e^{-\varphi T_w} \frac{k_d'}{\xi} \sinh(\xi T_w) \right\}
\]

(S5)

where

\[
\alpha = \frac{1}{2} \left( D_C + D_F + k_C + k_F + k_a + k_d \right)
\]

\[
\beta = \sqrt{\alpha^2 - \left( D_C D_F + D_F k_C + D_F k_a + D_C k_F + k_C k_F + k_a k_F + D_C k_d + k_C k_d \right)}
\]

\[
\gamma = \frac{\alpha - (D_C + k_C + k_a)}{\beta}
\]

\[
\varphi = \frac{1}{2} \left( k_C + k_F + k_a + k_d \right)
\]

\[
\xi = \sqrt{\varphi^2 - \left( k_C k_F + k_a k_F + k_C k_d \right)}
\]

\[
\eta = \frac{\varphi - (k_C + k_a)}{\xi}
\]
Here, \( C \) denotes the concentration and \( \mu \) the transition dipole moment. \( D_F = 1 / \tau_{or,F} \) and \( D_C = 1 / \tau_{or,C} \) are related to the orientational diffusion coefficients, and \( k_F = 1 / T_{1,F} \) and \( k_C = 1 / T_{1,C} \) are the vibrational population relaxation rates of free SCN\(^-\) and CIP, respectively.

In the two-species exchange kinetic scheme (Scheme S1'), the IR PP signal, \( S_{CP}^{PP}(t) \), can be expressed as

\[
S_{CP}^{PP}(t) = I_C(t) + I_{F \rightarrow C}(t) \\
S_{FP}^{PP}(t) = I_F(t) + I_{C \rightarrow F}(t)
\]  

(S6)

In this case, IR PP signal is equivalent to the integration of 2DIR spectra along the \( \omega_t \) axis onto the \( \omega \) axis (the probing frequency). \( S_{CP}^{PP}(t) \) 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).

\[
P_C(t) = I_C(t) + I_{F \rightarrow C}(t) \\
P_F(t) = I_F(t) + I_{C \rightarrow F}(t)
\]  

(S7)

where \( D_C = D_F = 0 \) in Eq. (S5). As shown in Eq. (S7), \( P(t) \) decays due to the vibrational population decay and chemical exchange.

4. 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
\[ G(\omega_r, \omega_t) = A \cdot \exp \left[ \frac{-(\omega_r - \omega_t - \omega_{r0} + \omega_{t0})^2}{4\sigma_r^2} - \frac{(\omega_r + \omega_t - \omega_{r0} - \omega_{t0})^2}{4\sigma_t^2} \right] \]

\[ - A \cdot \exp \left[ \frac{-(\omega_r - \omega_t + \Delta\omega - \omega_{r0} + \omega_{t0})^2}{4\sigma_r^2} - \frac{(\omega_r + \omega_t - \Delta\omega - \omega_{r0} - \omega_{t0})^2}{4\sigma_t^2} \right] \tag{S8} \]

where \( \omega_{r0} \) and \( \omega_{t0} \) are the peak positions along the \( \omega_r \) axis and \( \omega_t \) axis, \( \sigma_r \) and \( \sigma_t \) are the diagonal and anti-diagonal widths, respectively, and \( \Delta\omega \) is the vibrational anharmonicity. The first term in Eq. (S8) represents the 2D Gaussian peak for the \( \nu = 0 \rightarrow 1 \) transition and the second term is the 2D Gaussian peak for the \( \nu = 1 \rightarrow 2 \) 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.

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. (S5) 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.

5. Raman spectroscopy
Our Raman experimental setup consists of a 100 mW 532 nm green laser (MGL-III-532, Changchun New Industries Optoelectronics Tech. Co., Ltd) and a monochromator (Shamrock SR-303i-B, Andor Technology) coupled with a CCD camera (iDus DU-401A-BV, Andor Technology). A Raman edge filter (Edmund optics) was placed in front of the monochromator to attenuate the intense Rayleigh scattering. Raman spectra were measured down to \( \sim 100 \text{ cm}^{-1} \) with a frequency resolution of \( \sim 1.7 \text{ cm}^{-1} \).
References


Figure S1. Concentration-dependent FTIR spectra of (A) AgSCN, (B) CuSCN, and (C) Bu$_4$N(SCN) in DMTF. The path length of the cell was set to 12 μm.
Figure S2. Raman spectra measured with 0.5 M AgSCN and 0.5 M CuSCN in DMTF. Raman spectra were decomposed into the free SCN\(^-\) at a low frequency and Ag-SCN (or Cu-NCS) at a high frequency.
Figure S3. Polarization-controlled IR PP signals, $S_{\parallel}(\omega_{pr}, t)$ and $S_{\perp}(\omega_{pr}, t)$, measured with 0.5 M AgSCN in DMTF
Figure S4. Polarization-controlled IR PP signals, $S_{||}(\omega_p, t)$ and $S_{\perp}(\omega_p, t)$, measured with 0.5 M CuSCN in DMTF
Figure S5. 2DIR spectra at a series of $T_w$ times measured experimentally with 0.5 M AgSCN in DMTF and the corresponding multiple 2D Gaussian fitting results.
Figure S6. 2DIR spectra at a series of $T_w$ times measured experimentally with 0.5 M CuSCN in DMTF and the corresponding multiple 2D Gaussian fitting results.
Figure S7. Illustration of the center line slope (CLS) method to extract the frequency-frequency correlation function (FFCF) from 2DIR spectrum. For the CIPs, we used the positive peaks but for free SCN\(^-\) ions, we used the negative peaks.
Figure S8. The frequency-frequency correlation function (FFCF) extracted from our 2DIR spectra by the center line slope (CLS) method. (A) CIP. The FFCF decays faster for AgSCN than CuNCS. The lines are the bi-exponential fit to the FFCF. For AgSCN in DMTF,
\[ C(T_w) = 0.37 \exp(-T_w / 4.9) + 0.46 \exp(-T_w / 33.8) \]
and for CuNCS in DMTF,
\[ C(T_w) = 0.32 \exp(-T_w / 4.7) + 0.42 \exp(-T_w / 61.1) \]. (B) Free SCN\(^-\) ions in two solutions. The FFCFs for SCN\(^-\) are similar and decay much faster than those for the CIPs.