Supporting Information

Conducting Excitation and Emission Spectra in IR Regime: Frequency-Domain Time-Resolved Vibrational Four Wave Mixing Spectroscopy

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I. Experimental details

A solution of 1.0 M magnesium perchlorate in acetonitrile was chosen as a model system. The solution contains free, uncoordinated CH₃CN species and coordinated CH₃CN species in the form of Mg(CH₃CN)_x²⁺ (x=4-6).^{1, 2} For the FMW measurement, the mixture was diluted in chloroform CHCl₃ with a volume ratio of 1:4. The resulting solution was hosted in a 100 μ m pathlength CaF₂ cell.



Figure S1. The diagram categorizes the different time orderings of three excitation pulses for the $\mathbf{k}_{4} = \mathbf{k}_{1} - \mathbf{k}_{2} + \mathbf{k}_{2}$ phase matching condition. The excitation frequencies (ω_{1} , ω_{2} , and ω_{2}) may be equal or different. Each time ordering corresponds to different coherence pathways. The x and y axes are $\tau_{2'1}=T_{2'}-T_{1}$ and $\tau_{21}=T_{-2}-T_{1}$, respectively, and zero delay is in the center.³⁻⁵ The dashed black arrow indicates the delay scan direction adopted for Figure 2 in the text.

The FWM experiment uses a mode-locked Ti:sapphire oscillator regenerative amplifier to pump two independently tunable optical parametric amplifiers (OPAs).⁴⁻⁷ The OPAs create two mid-infrared laser pulses in frequencies of ω_1 and ω_2 with pulse width of 900 fs and bandwidth of 23 cm⁻¹. The ω_2 beam is split to create a third beam, designated ω_3 , and all beams are identically polarized. The beams are focused into the sample with an off-axis parabolic mirror at angles defined by phase matching, $\mathbf{k}_4 = \mathbf{k}_1 - \mathbf{k}_{-2} + \mathbf{k}_{2'}$ in the time frame $\tau_{21}=T_{-2}-T_1$ vs $\tau_{2'1}=T_{2'}-T_1$ where

 τ_i 's refer to actual pulse positions in time; subscripts *i*=1, 2, 2' refer to different laser pulses, not time ordering. The signal is spectrally resolved with a McPherson 0.3 meter monochromator (ω_m) and a MCT detector. The monochromator slits are adjusted to provide 25 cm⁻¹ resolution. The monochromator is also used to calibrate the spectral scanning of the OPAs. For this calibration, the slits were adjusted to provide a resolution of 5 cm⁻¹. The excitation pulse frequencies are identical when measured before and after the sample. The output intensity is recorded as a function of ω_1 , ω_2 , ω_m , τ_{21} , and $\tau_{2'1}$. By scanning $\omega_1=\omega_m$ and $\omega_2=\omega_{2'}$ with fixed τ_{21} and $\tau_{2'1}$ in the temporal regions of I, II and III which relate to DOVE-IR processes,^{4, 8} 2D spectra are acquired, such as Figure 1 and Figure S2. The existence of a cross peak indicates mode coupling between the two vibrational states.⁸ By scanning τ_{21} and $\tau_{2'1}$ with fixed ω_1 , ω_2 , ω_m , 1D delay scan can be made such as Figure 2. One-dimensional, one color CT spectra can be obtained by scanning ω_m with fixed $\omega_1=\omega_2=\omega_{2'}$, τ_{21} and $\tau_{2'1}$ as those of Figures 3 and 4, or two color CT spectra can be generated by scanning ω_m with fixed ω_1 and $\omega_2=\omega_{2'}$, and $\tau_{2'1}$ as that of Figure S4.

II. Spectra showing the coupling between the v2 mode and the v3 +v4 mode of CH3CN



Figure S2. 2D spectrum of CH₃CN in CHCl₃ (v:v=1:11) with a path length of 160 μ m with $\tau_{21}=0$ ps and $\tau_{2'1}=1.0$ ps, a temporal sequence set between regions I and II in Figure S1. The cross peaks suggest the coupling between v_2 and v_3+v_4 . The 1D infrared spectrum of the mixture appears on the top side for comparison. The color bar is a logarithmic depiction of the output intensity.



Figure S3. One-dimensional scan by increasing the detection sensitivity for the cross peak at $(\omega_1, \omega_2)=(2290, 2254)$ cm⁻¹ for free acetonitrile species in the mixture of CH₃CN-Mg(ClO₄)₂. The scan was set $\tau_{21}=0$ ps, $\tau_{2'1}=1.0$ ps, $\omega_2=\omega_{2'}=2254$ cm⁻¹ while scanning $\omega_1=\omega_m$.

III. Spectra showing strong coherence transfer between the v_2 mode and the $v_3 + v_4$ mode of coordinated CH₃CN



Figure S4. The abscissa shows the $\tau_{21} = \tau_{2'1}$ time delay dependence of the output intensity and the ordinate shows spectral dependence using a monochromator to resolve the output frequency. Phase matching requires the output signal to appear at 2280 cm⁻¹. The feature at 2310 cm⁻¹ arises from coherence transfer and is modulated at the frequency difference between the two states.



Figure S5. One-dimensional scan for cross peak at $(\omega_1, \omega_2)=(2290, 2317)$ cm⁻¹ and the associated CT peak for the mixture of CH₃CN-Mg(ClO₄)₂. The scan was set at $\tau_{21}=\tau_{2'1}=-1.2$ ps, $\omega_1=2290$, $\omega_2=\omega_{2'}=2317$ cm⁻¹ while scanning ω_m . The main peak at 2290 cm⁻¹ is the cross peak and the peak at 2317 cm⁻¹ is the CT peak. The intensity ratio of 2290 to 2317 cm⁻¹ is 17, indicating very strong coherence transfer between the v₂ mode and the v₃ +v₄ mode of coordinated CH₃CN.

IV. Examples of selected coherence and population pathways for Figure 3 and Figure 4



Figure S6. Energy level and Liouville diagrams showing one of the pathways for the flow of coherences and populations from the initial ground state population, aa, to the output coherence, ca (diagonal peak) or ba (CT peak) in (A) for Figure 3, and ba (diagonal peak) or ca (CT peak) in (B) for Figure 4.

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