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

Wei Zhao,[*,†] Andrei V. Pakoulev,[‡,⊥] John C. Wright [*,‡]

[†]Department of Chemistry, University of Arkansas at Little Rock, Little Rock, Arkansas 72204, and [‡]Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Supporting Information Placeholder

ABSTRACT: We report new features of recently developed ultrafast coherent multidimensional spectroscopy (CMDS), an optical analogue to multidimensional NMR. By using both frequency and time domain nonlinear four wave mixing methods, CMDS is able to directly observe coherence transfer (CT), the coherent quantum mechanical analogue of population relaxation. Using a mixture of acetonitrile and magnesium perchlorate (1.0 M) as a model system, we demonstrated that this one color, population involving CT process makes CMDS capable of measuring samples with features that mimic excitation and emission spectral measurements in fluorescence spectroscopy. With the new capabilities, CT-based vibrational resonance energy transfer (VRET) methods may be developed for label-free biosensing and imaging, such as those demonstrated by fluorescence resonance energy transfer (FRET).

Recently, there has been great interest in using coherence in complex chemical systems,[1] where coherence phenomena arise from interference, or the addition, of wave-like amplitudes with fixed phase differences.[1] Ultrafast coherent multidimensional spectroscopy (CMDS) is an optical analogue to multidimensional NMR[2-9] that provides unique capabilities for molecular dynamics and structural studies by using both frequency and time domain nonlinear four wave mixing (FWM) methods.[2, 8, 9] The methods involve a 5-dimensional variable space with three spectral and two temporal dimensions (Figure S1 in the Supporting Information).[8, 9] One of unique features of CMDS is allowing one to directly observe coherence transfer (CT). CT is the coherent analogue of population relaxation.[8, 9] The CT process makes CMDS capable of measuring samples with coherent relaxation that mimics the incoherent excitation and emission spectra conducted in fluorescence measurements. Although there are similarities in how relaxation creates new peaks, fluorescence is very different because it involves the incoherent dephasing of a coherence while CT is fully coherent and involves the interaction with the environment. The coherent states created by CMDS experiments are quantum mechanically entangled states. CT occurs when an entangled state evolves to a different state without destroying the entanglement. Fluorescence occurs after the initially excited coherence dephases to form an excited state population that can itself fluoresce or relax incoherently to a fluorescent state.[10, 11] CT provides a direct probe of the coherent coupling between a molecule and the thermal bath. Here we present the unique capabilities of frequency domain time-resolved vibrational FWM spectroscopy for creating excitation and emission-like spectral features in the infrared regime with a coherent relaxation. The excitation and emission spectra-like features may enable CMDS methods as a versatile tool for broad applications.[1]

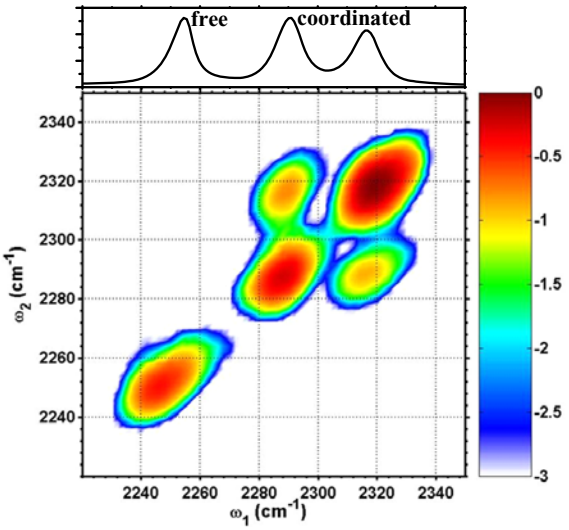

Figure 1. 2D spectrum showing the log (FWM intensity) vs the two excitation frequencies at τ_{21}=0 ps and $\tau_{2'1}$=1.0 ps. The 1D infrared spectrum of the mixture appears on the top side for comparison.

The model system in this work is a mixture of acetonitrile CH_3CN and magnesium perchlorate $Mg(ClO_4)_2$ (1.0 M) diluted in chloroform $CHCl_3$ (v:v=1:4). The solution contains free, uncoordinated CH_3CN species and coordinated CH_3CN species in the form of $Mg(CH_3CN)_x^{2+}$ (x=4-6).[12, 13] In the spectral range of 2100-2400 cm^{-1}, the free species contains an environmentally-sensitive C≡N stretch mode (ν_2 at 2253 cm^{-1}) and a 2292-cm^{-1} combination band (ν_3 +ν_4) involving the C-C bend (ν_3 at 1375 cm^{-1}) and C-C stretch (ν_4 at 918 cm^{-1}).[12, 14-16] The ν_2 mode is coupled with the ν_3 +ν_4 mode as evidenced by their cross peaks (2253, 2292) and (2292, 2253) cm^{-1} in Figure S2 of the Supporting Information. When CH_3CN is mixed with magnesium perchlorate, the interaction between Mg^{2+} and CH_3CN, mainly due to the electrophilicity of Mg^{2+}, causes large blue shifts in ν_2 and ν_4 of CH_3CN. The ν_4 frequency for coordinated CH_3CN shifts to

938 cm^{-1} (not shown),[17] ν_2 to 2290 cm^{-1}, and $\nu_3+\nu_4$ to 2317 cm^{-1} (Figure 1). The ν_2 and $\nu_3+\nu_4$ modes of coordinated species are much more strongly coupled to each other as shown by their strong cross peaks (2290, 2317) and (2317, 2290) cm^{-1} in Figure 1. In comparison, the cross peaks of free species do not appear in Figure 1 under the same intensity scale and are only weakly seen with increased detection sensitivity (Figure S3). The strong mode coupling between the ν_2 mode and the $\nu_3+\nu_4$ mode of coordinated species provides us with a unique opportunity to explore the fluorescence-like CMDS involving CT.

The FWM measurements are detailed in the Supporting Information. Briefly, three mid-infrared laser pulses with frequencies of ω_1 and $\omega_2=\omega_{2'}$, pulse widths of 900 fs, and a bandwidth of 23 cm^{-1} are focused into the sample with an off-axis parabolic mirror at angles defined by the phase matching condition, $\mathbf{k}_4=\mathbf{k}_1-\mathbf{k}_2+\mathbf{k}_{2'}$ in the time frame τ_{21} vs $\tau_{2'1}$ (Figure S1). The signal is spectrally resolved with a monochromator (ω_m) and a MCT detector.[8, 9]

There is strong CT between the ν_2 mode and the $\nu_3+\nu_4$ mode of coordinated species as shown by the characteristic CT temporal modulation in Figure 2a, which shows the one dimensional scan of the sample by fixing $\omega_1=\omega_2=\omega_{2'}$=2290 cm^{-1} and monitoring output at ω_m=2317 cm^{-1} while scanning the delays $\tau_{21}=\tau_{2'1}$ along the dashed black arrow direction shown in Figure S1. The observed temporal modulation is due to CT, not quantum beating since possible spectral overlapping among the laser beams could not produce such the large signal shown in Figures 3, 4, S4, and S5. It results because of the interference among several equivalent coherence pathways [8, 9] and has a ~1.2 ps interval between two nearby maxima. The modulated signal has a frequency of 27 cm^{-1} as shown in Figure 2b, matching the frequency difference between the ν_2 mode and the $\nu_3+\nu_4$ mode of coordinated species.

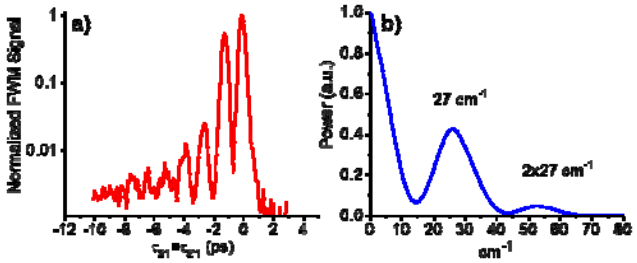

Figure 2. (a) One-dimensional scan of delays τ_{21} and $\tau_{2'1}$ along the dashed black arrow direction ($\tau_{21}=\tau_{2'1}$) shown in Figure S1. $\omega_1=\omega_2=\omega_{2'}$=2290 cm^{-1}, ω_m=2317 cm^{-1}. The interval between two nearby maxima is ~1.2 ps. (b) Direct Fourier transform of data in (a). 27 cm^{-1} matches the difference of $\omega_{\nu_3+\nu_4}-\omega_{\nu_2}$ = (2317-2290) cm^{-1} of coordinated species.

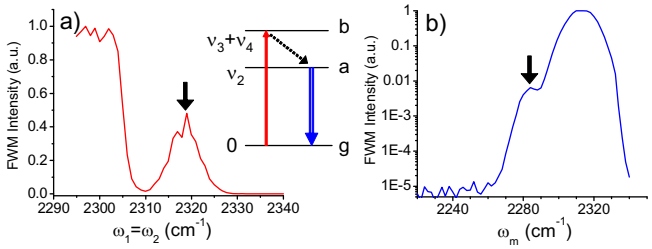

Figure 3. a) Excitation-like FMW spectrum by monitoring FWM output at 2290 cm^{-1} while scanning ω_1 and ω_2 and b) Emission-like FWM spectrum by tuning ω_1 and ω_2 at 2317 cm^{-1} while scanning ω_m. Here $\tau_{21}=\tau_{2'1}$=-1.2 ps. The arrows indicate the CT peaks.

Since CT is the analogue of population relaxation, we take advantage of the unique frequency and time domain features of CMDS to explore the fluorescence-like features (the insets shown in Figures 3 and 4. The actual coherence and population flow process is shown in Figure S5) by tuning ω_i (i=1,2,2′, and m) while fixing τ_{21} and $\tau_{2'1}$ at -1.2 ps. In Figure 3a, the ω_m is fixed at the 2290 cm^{-1} frequency of the ν_2 mode of coordinated species while the excitation frequencies are scanned such that $\omega_1=\omega_2=\omega_{2'}$. This scan is similar to fluorescence excitation spectra measurement. Surprisingly, in addition to the observation of the strong diagonal 2290 cm^{-1} peak, which is expected, a well-separated peak appears at 2317 cm^{-1}, belonging to the $\nu_3+\nu_4$ mode of the coordinated species, occurs. By fixing $\omega_1=\omega_2=\omega_{2'}$=2317 cm^{-1} in one color at the frequency of the $\nu_3+\nu_4$ mode while scanning ω_m, a process similar to fluorescence emission spectra measurement, an emission band at 2290 cm^{-1}, with a signal intensity about one hundredth of the main diagonal 2317 cm^{-1} peak, is observed (Figure 3b). The CT peak intensity is usually on the order of 10^{-4}–10^{-5} of the main diagonal peak.[18] The results suggest strong coherence transfer from the $\nu_3+\nu_4$ mode to the ν_2 mode.

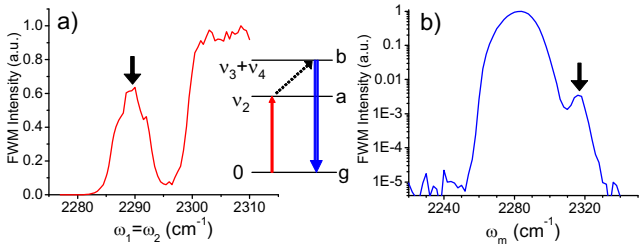

Figure 4. a) Excitation-like FWM spectrum by monitoring FWM output at 2317 cm^{-1} while scanning ω_1 and ω_2 and b) Emission-like FWM spectrum by tuning ω_1 and ω_2 at 2290 cm^{-1} while scanning ω_m. Here $\tau_{21}=\tau_{2'1}$=-1.2 ps. The arrows indicate the CT peaks.

Furthermore, an up-conversion fluorescence-like excitation process is also observed by fixing ω_m at 2317 cm^{-1} and scanning $\omega_1=\omega_2=\omega_{2'}$ in one color. As shown in Figure 4a, a well-separated peak at 2290 cm^{-1} from the main diagonal peak is observed. By fixing $\omega_1=\omega_2=\omega_{2'}$=2290 cm^{-1} while scanning ω_m, a process similar to up-conversion fluorescence emission spectra measurement, an emission peak at 2317 cm^{-1} occurs, which has an intensity 10^{-2}~10^{-3} of the main diagonal peak at 2290 cm^{-1} (Figure 4b). The results suggest strong coherence transfer from the ν_2 mode to the $\nu_3+\nu_4$ mode. One of striking observations is the fact that the coherence transfer violates the secular approximation. The secular approximation assumes the thermal bath correlation time is much shorter than the coherence dephasing time. The destructive interference between the two coherences involved in the transfer then eliminates transfer of coherence. The existence of coherent transfer then requires a non-Markovian bath with a longer correlation time.[19, 20] The entanglement between the bath and the molecular system must then be considered in understanding the nature of CT. The entanglement with the bath may result from the increased bath correlation time that might be expected from solvation with the divalent metal ion. It would be interesting to explore the nature of the solvent and metal ion on the CT efficiency. Similar non-Markovian effects have been observed in photosynthetic complexes[21] and other molecular systems.[18, 22-24]

The above results demonstrate that CMDS is capable of providing measurement capabilities in a way similar to fluorescence excitation and emission spectra measurements based on CT-involving, one-color frequency domain time-resolved vibrational FWM spectroscopic methods. These features enable one to develop CMDS into versatile vibrational tools for revealing

the role of coherence as a design element in realizing function,[1] such as probing the nature of the solvent and metal ion on measuring the CT efficiency, in addition to molecular structure and interaction studies. As fluorescence-based tools have numerous applications, fluorescence-like, CT-based vibrational CMDS may offer unique features for broad applications extending to those systems where fluorescence may not be available in the IR regime. In particular, since coherence transfer is related to thermal bath induced coupling, which could occur inter-molecularly and be distance-sensitive, CT-based vibrational resonance energy transfer (VRET) methods may be developed with new capabilities for a wide range of applications such as label-free biosensing and imaging,[25] with capabilities similar to those demonstrated by fluorescence resonance energy transfer (FRET).[26]

ASSOCIATED CONTENT

Supporting Information

Figures S1-S6, experimental details, 2D spectrum of CH_3CN, 1D scan of CH_3CN-$Mg(ClO_4)_2$ showing mode coupling, time delay dependence of the output intensity, 1D scan of CH_3CN-$Mg(ClO_4)_2$ showing strong CT, CT pathways involved in Figures 3 and 4. This material is available free of charge via the internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: wxzhao@ualr.edu, wright@chem.wisc.edu

Notes

The authors declare no competing financial interests.

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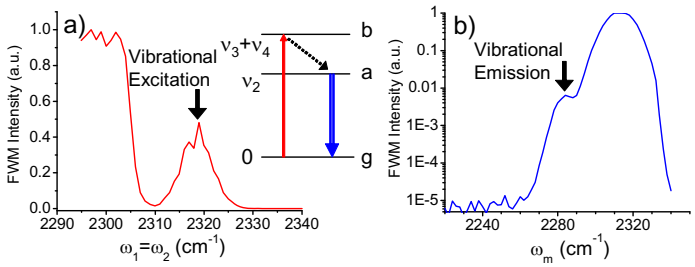

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