Monitoring Intramolecular Proton Transfer with Two-Dimensional Infrared Spectroscopy: A Computational Prediction

Z. L. Terranova and S. A. Corcelli*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556
* Email: scorcell@nd.edu

Supporting Information

A. Infrared Absorption Spectra

Infrared (IR) absorption spectra were computed solely from knowledge of the fluctuating frequency trajectory, $\omega(t)$, using a semiclassical formalism,[1,2]

$$I(\omega-\omega_0)=\int_{-\infty}^{\infty} dt\; e^{-i\omega t}\left\langle \exp\left[i\int_0^t d\tau\,\delta\omega(\tau)\right]\right\rangle, \tag{1}$$

where ω_0 is the average frequency, $\delta\omega(t)=\omega(t)-\omega_0$, is the fluctuation of the frequency from its average value, and $\langle\cdots\rangle$ represents a classical ensemble average.

B. Two-Dimensional Infrared (2D IR) Spectra

In two-dimensional infrared (2D IR) spectroscopy, three separate femtosecond IR pulses interact with the sample, and the subsequent response is measured. The three pulses have specific wave vectors labeled $\boldsymbol{k_1}$, $\boldsymbol{k_2}$, and $\boldsymbol{k_3}$ corresponding to the their sequence. The rephasing signal is observed in the $\boldsymbol{k_{RP}} = \boldsymbol{-k_1} + \boldsymbol{k_2} + \boldsymbol{k_3}$ direction, while the non-rephasing signal is described as $\boldsymbol{k_{NR}} = \boldsymbol{k_1} - \boldsymbol{k_2} + \boldsymbol{k_3}$ direction. Within the Condon approximation and assuming that only two vibrational states are relevant, the three-pulse echo response functions are given by[1,3]

$$R_1(t_3,t_2,t_1)=R_2(t_3,t_2,t_1)=\exp\left[-i\omega_0 t_3+i\omega_0 t_1\right]\phi_{RP}(t_3,t_2,t_1), \tag{2}$$

and

$$R_4(t_3,t_2,t_1)=R_5(t_3,t_2,t_1)=\exp\left[-i\omega_0 t_3-i\omega_0 t_1\right]\phi_{NR}(t_3,t_2,t_1), \tag{3}$$

where

$$\phi_{RP}(t_3,t_2,t_1)=\exp\left[i\int_0^{t_1} d\tau\,\delta\omega(\tau)-i\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau\,\delta\omega(\tau)\right], \tag{3}$$

and

$$\phi_{NR}(t_3,t_2,t_1)=\exp\left[-i\int_0^{t_1} d\tau\,\delta\omega(\tau)-i\int_{t_1+t_2}^{t_1+t_2+t_3} d\tau\,\delta\omega(\tau)\right], \tag{4}$$

The 2D IR signal, $S(\omega_3,t_2,\omega_1)$, is given by

$$S(\omega_3,t_2,\omega_1)=\mathrm{Re}\left[\sum_{i=1}^{6}S_i(\omega_3,t_2,\omega_1)\right], \tag{5}$$

where

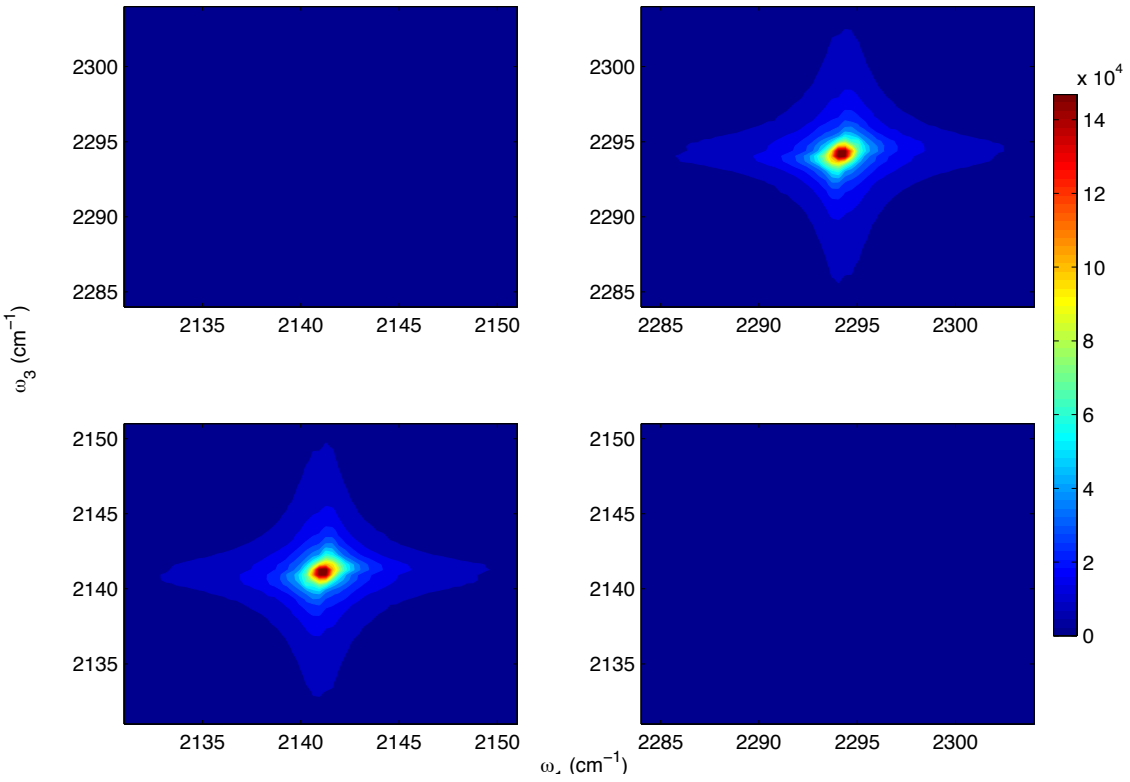
$$S_i(\omega_3,t_2,\omega_1)=\int_0^\infty dt_1\int_0^\infty dt_3\exp(i\omega_3t_3-i\omega_1t_1)R_i(t_3,t_2,t_1)\qquad i=1-3\,, \tag{6}$$

and

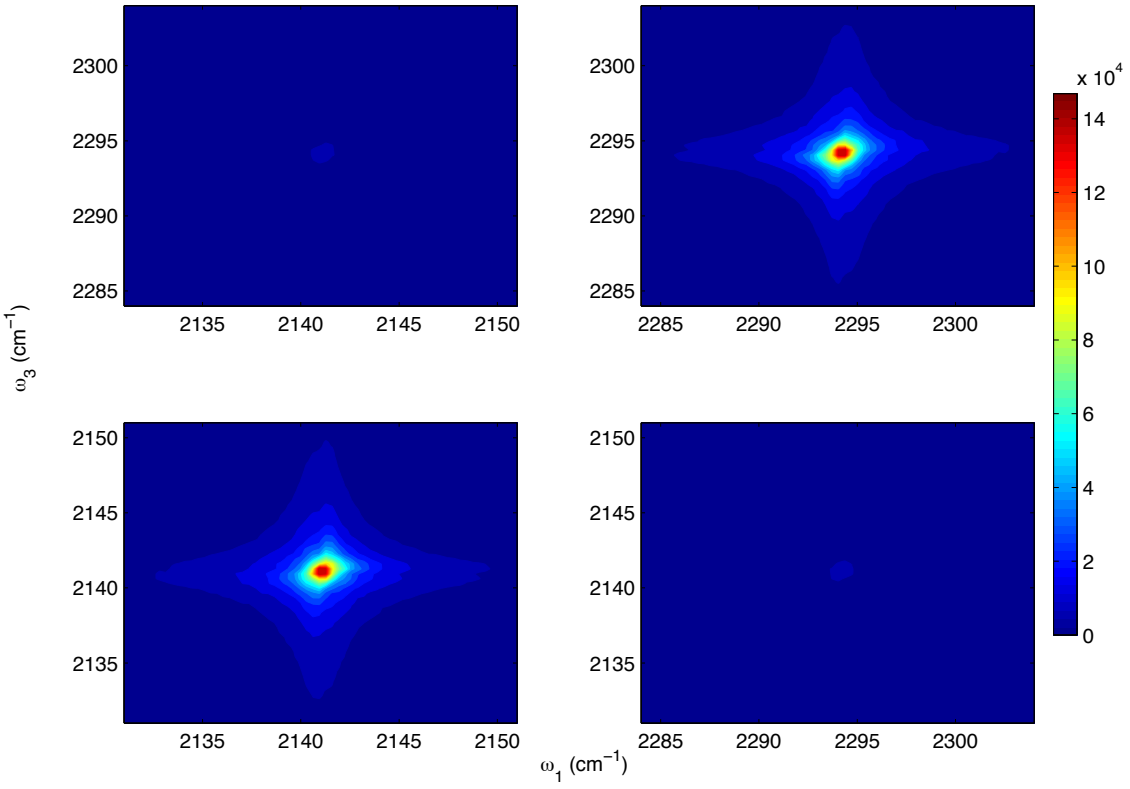
$$S_i(\omega_3,t_2,\omega_1)=\int_0^\infty dt_1\int_0^\infty dt_3\exp(i\omega_3t_3+i\omega_1t_1)R_i(t_3,t_2,t_1)\qquad i=4-6\,, \tag{7}$$

For a two-level system, $R_3 = R_6 = 0$. The waiting time, T_W, is synonymous with t_2 in the equations above. Note that the 2D IR spectra can also be computed solely from knowledge of the fluctuating frequency trajectory, $\omega(t)$. Shown below are chemical exchange 2D IR spectra for the C–D stretch of labeled malonaldehyde in aqueous solution for waiting times in the range 0 to 500 ps.

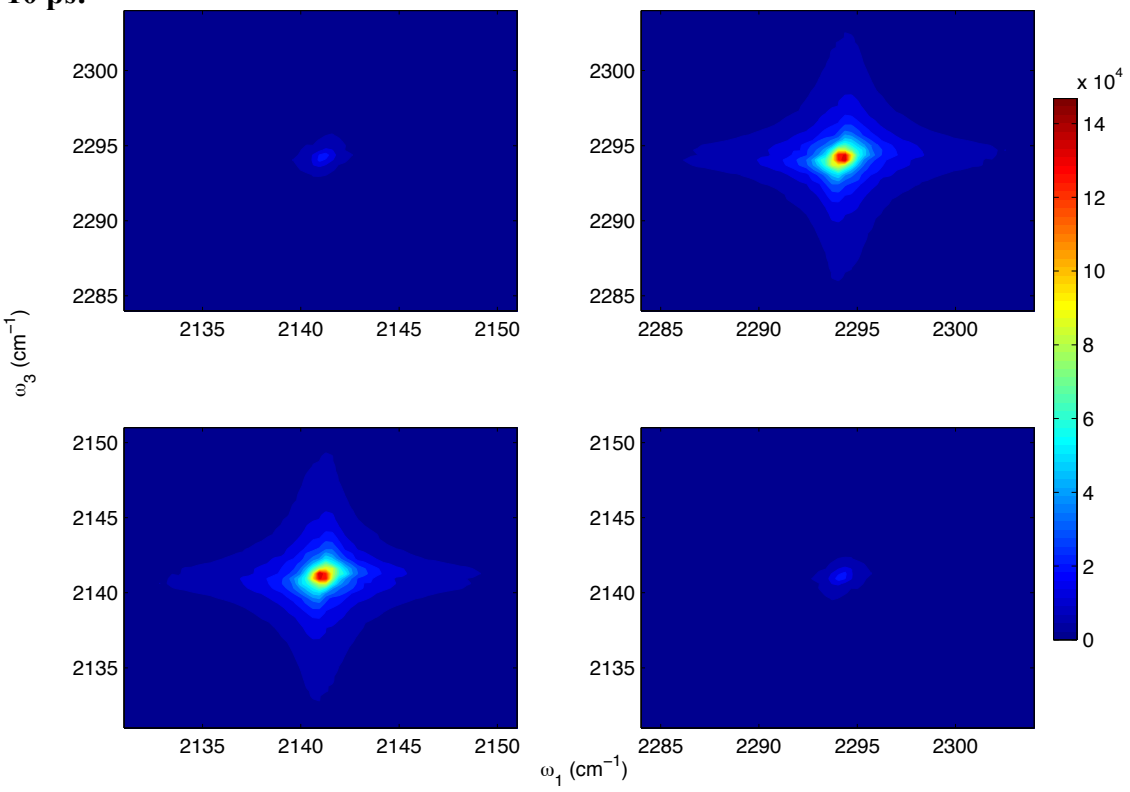
T_w = 0 ps:



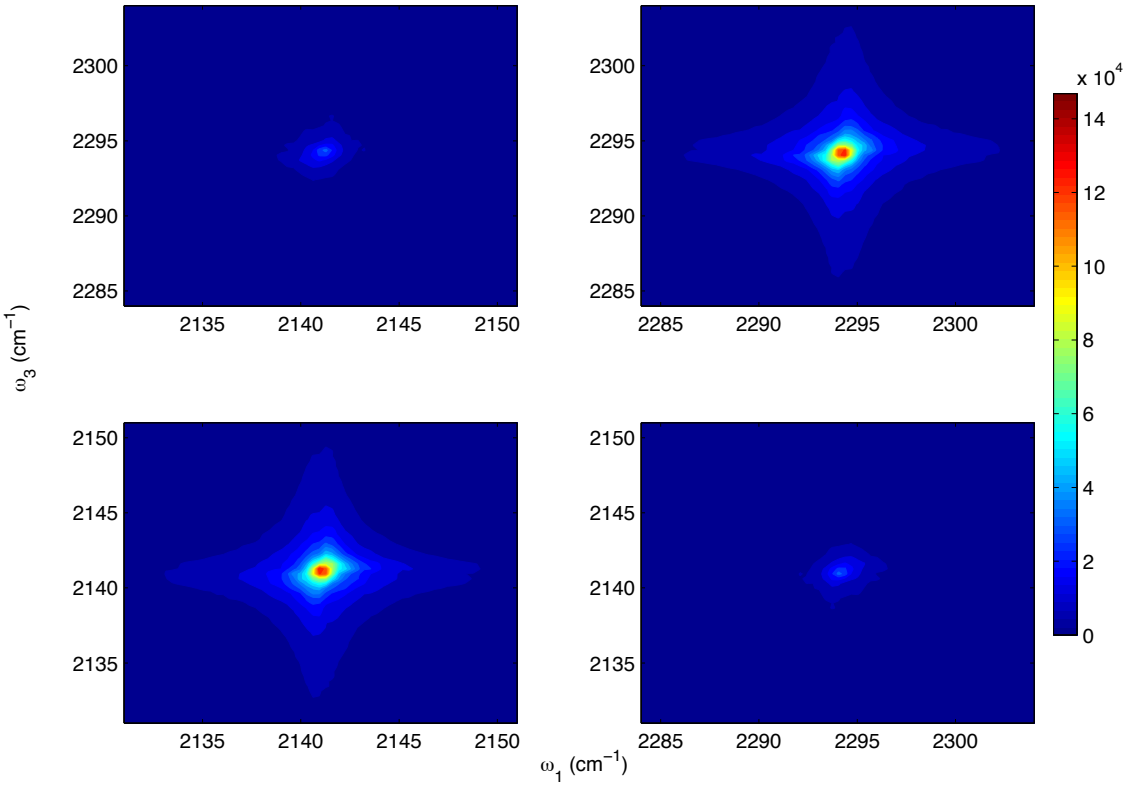
T_w = 5 ps:



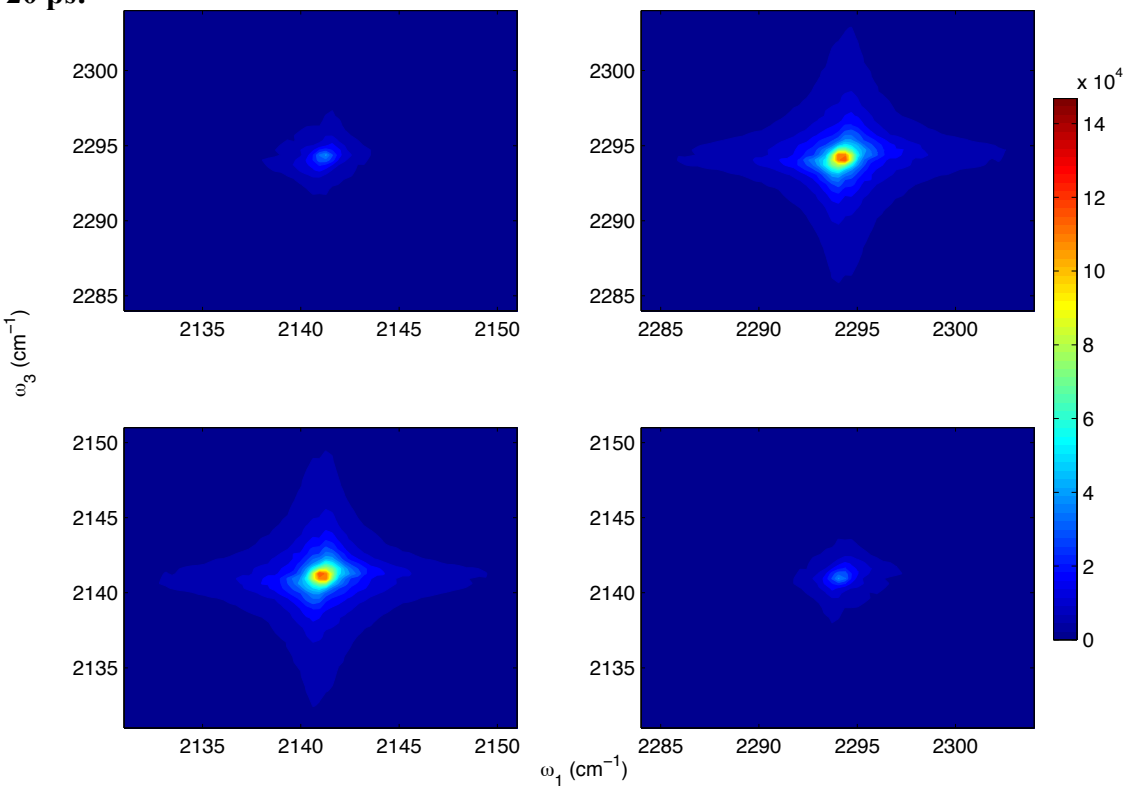
T_w = 10 ps:



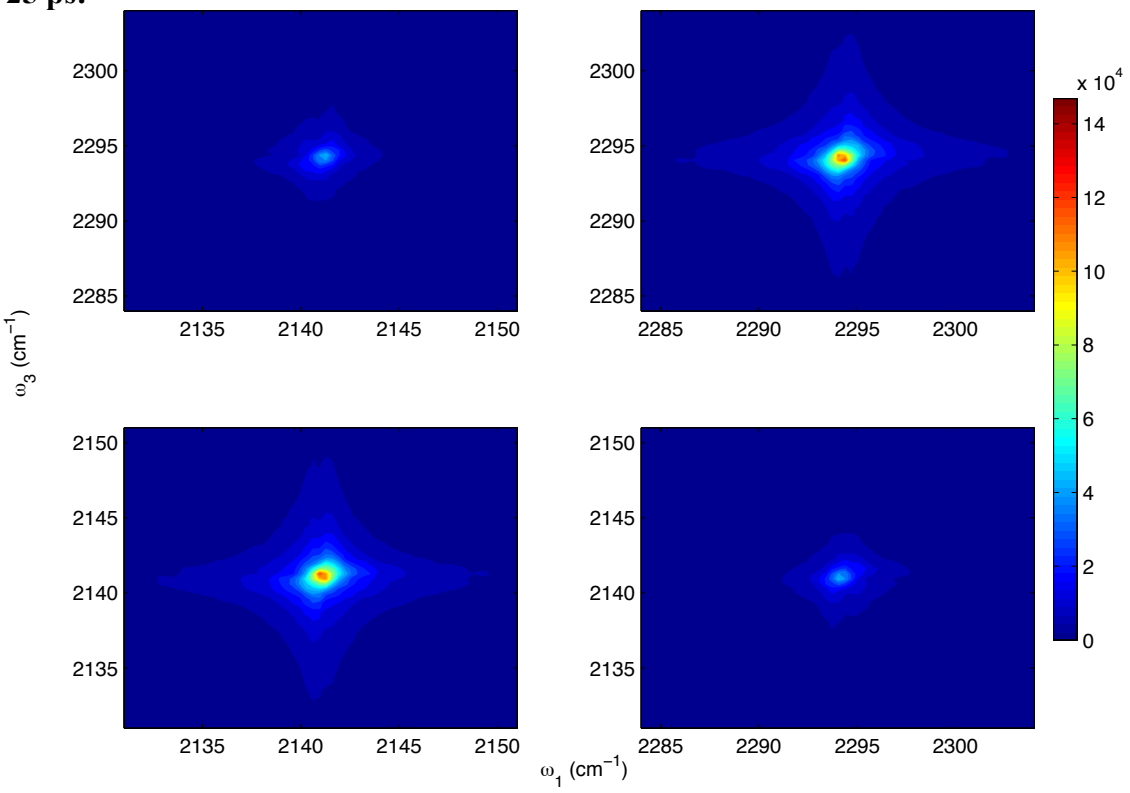
T_w = 15 ps:



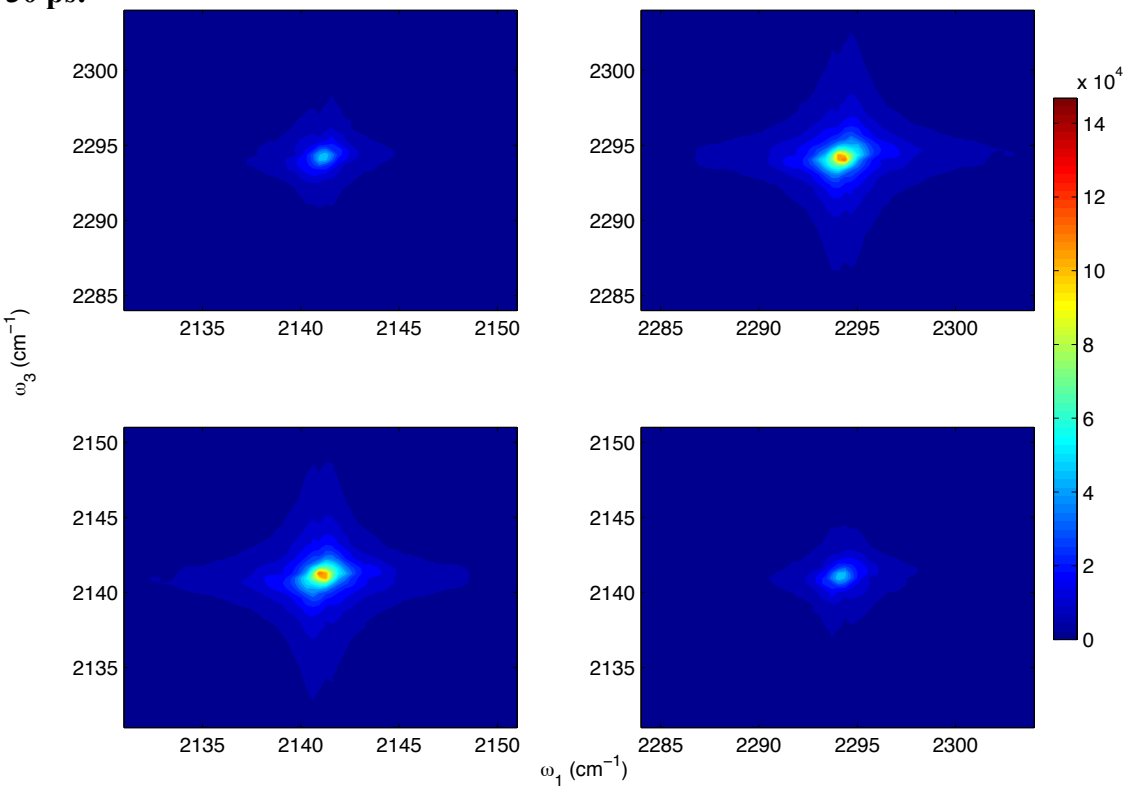
T_w = 20 ps:



T_w = 25 ps:



T_w = 30 ps:



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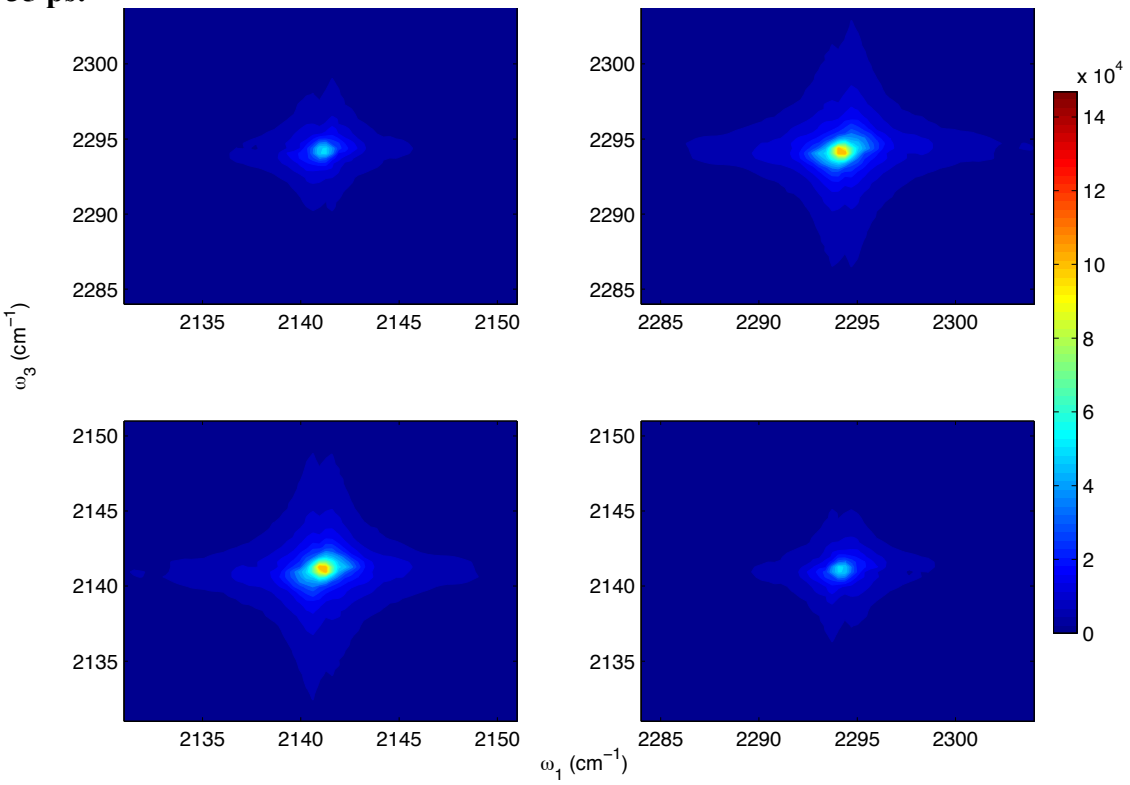

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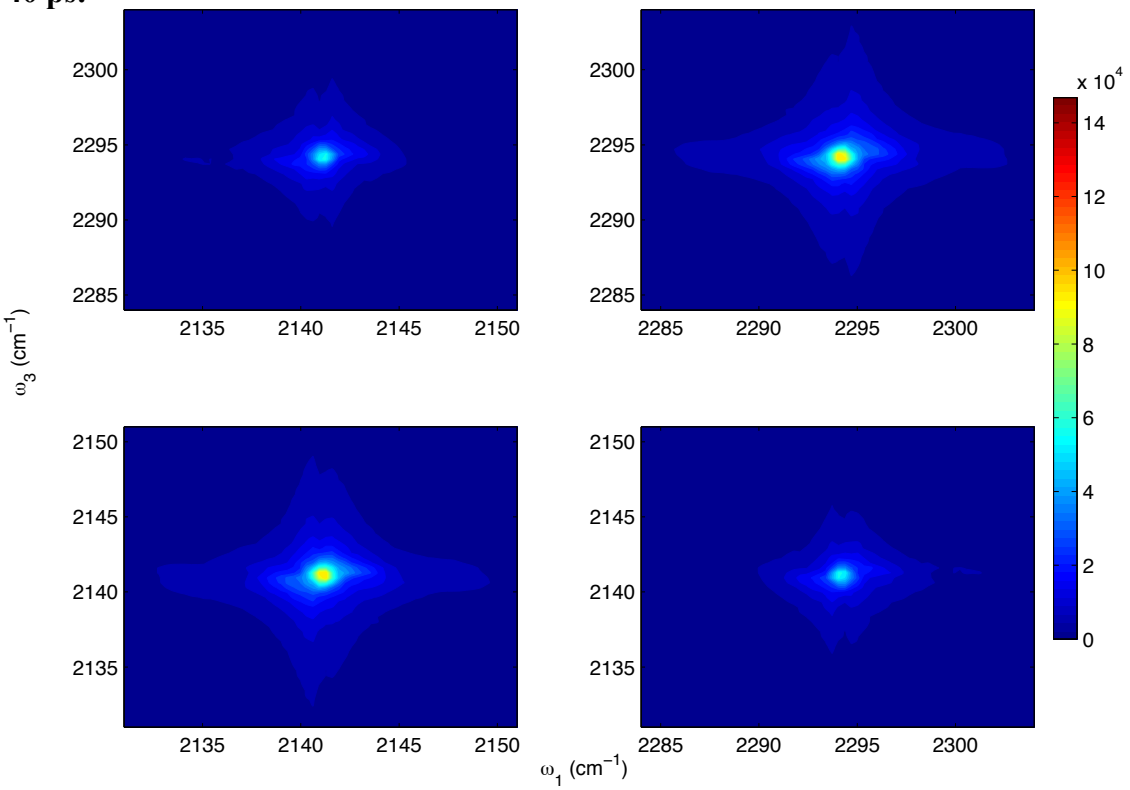
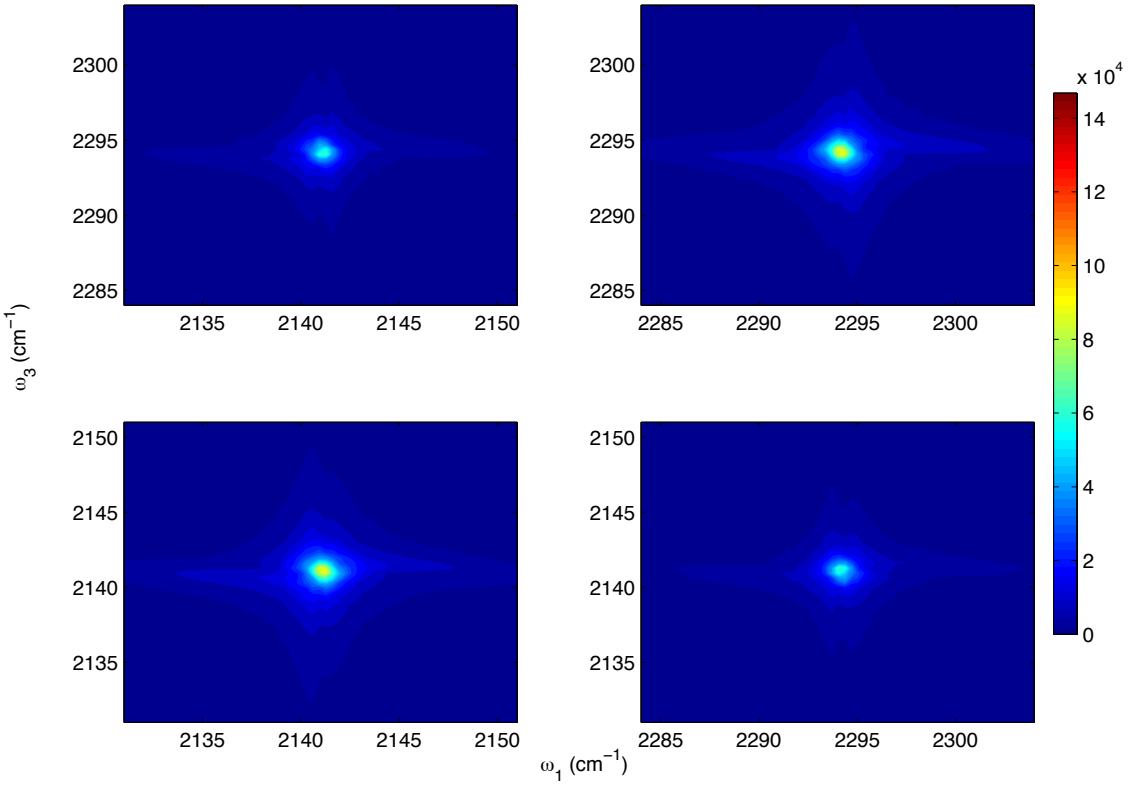
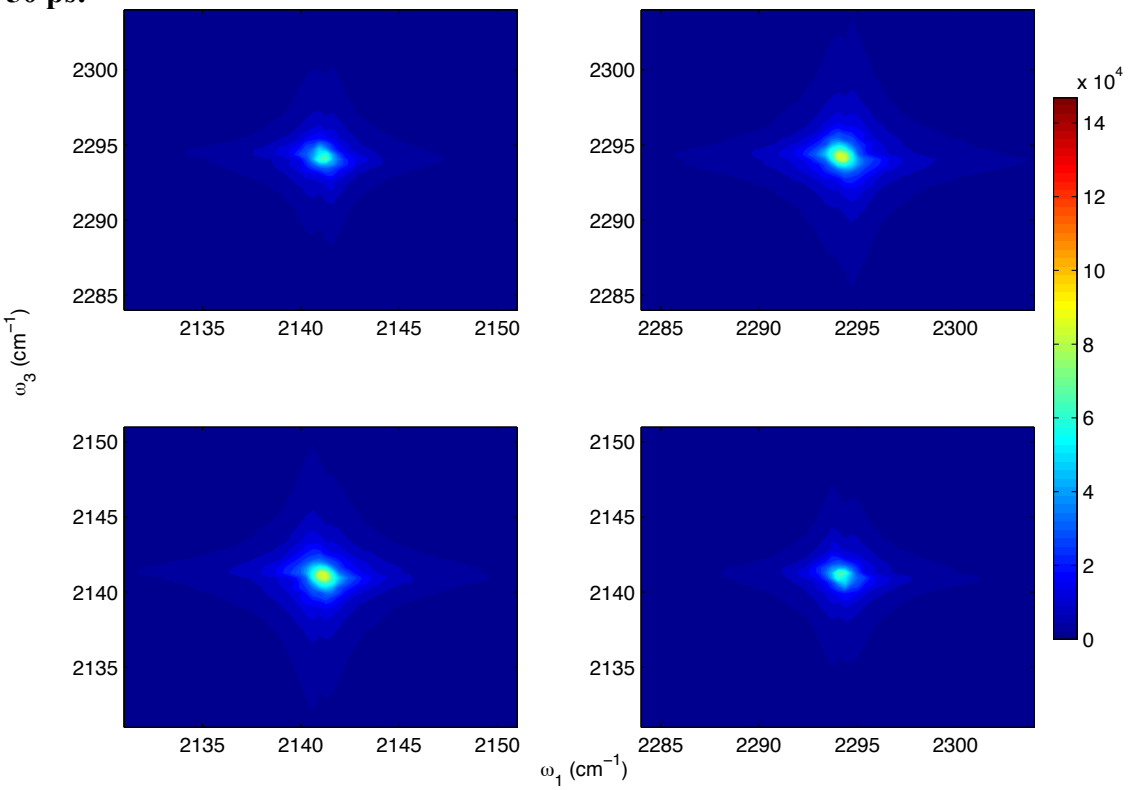


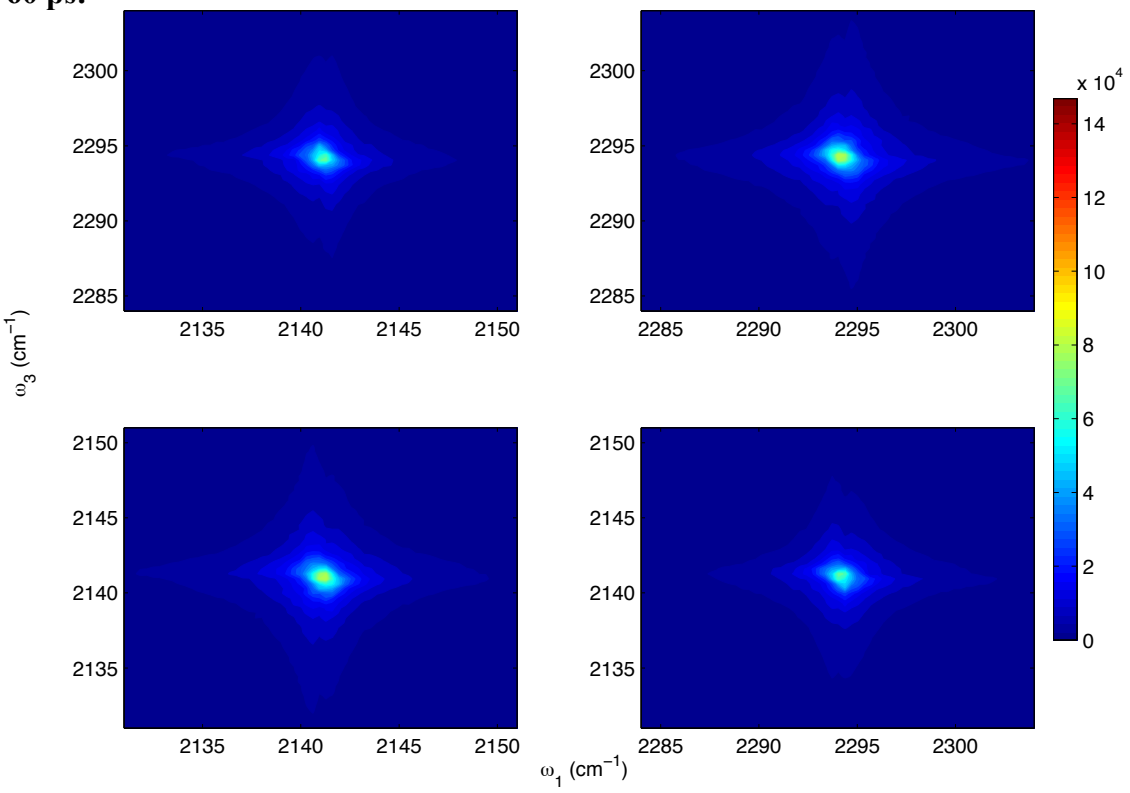
T_w = 45 ps:



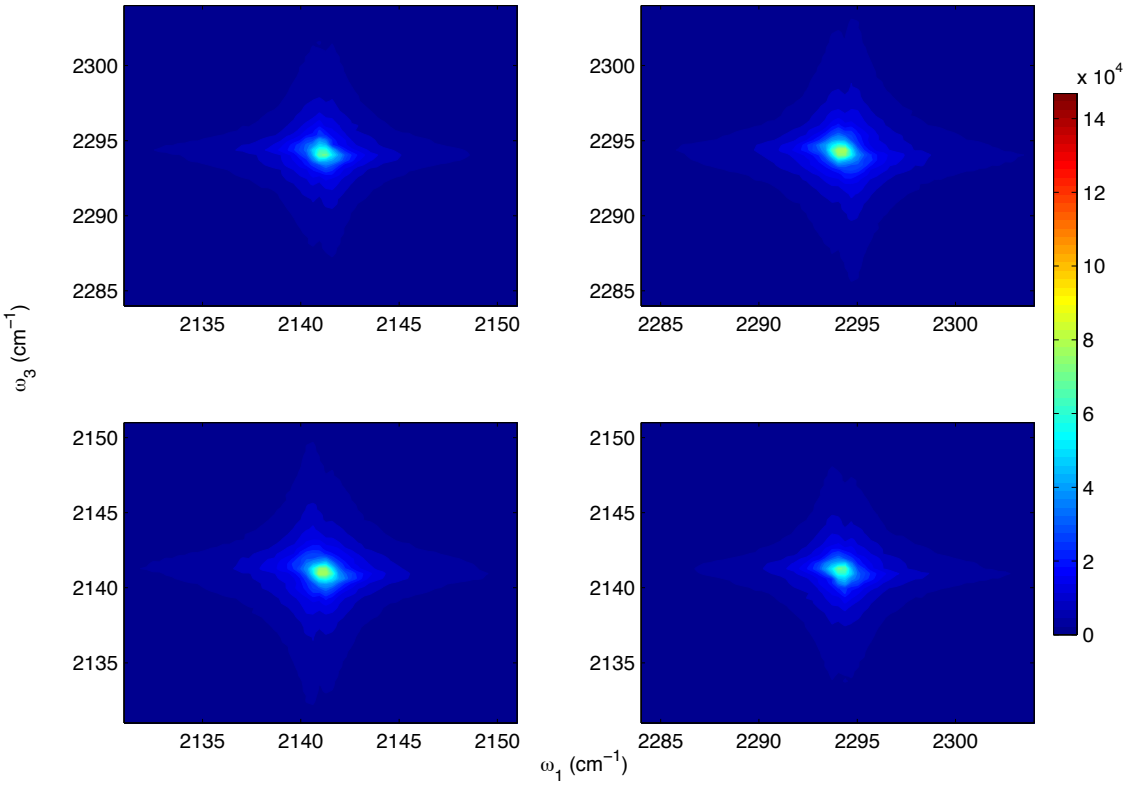
T_w = 50 ps:



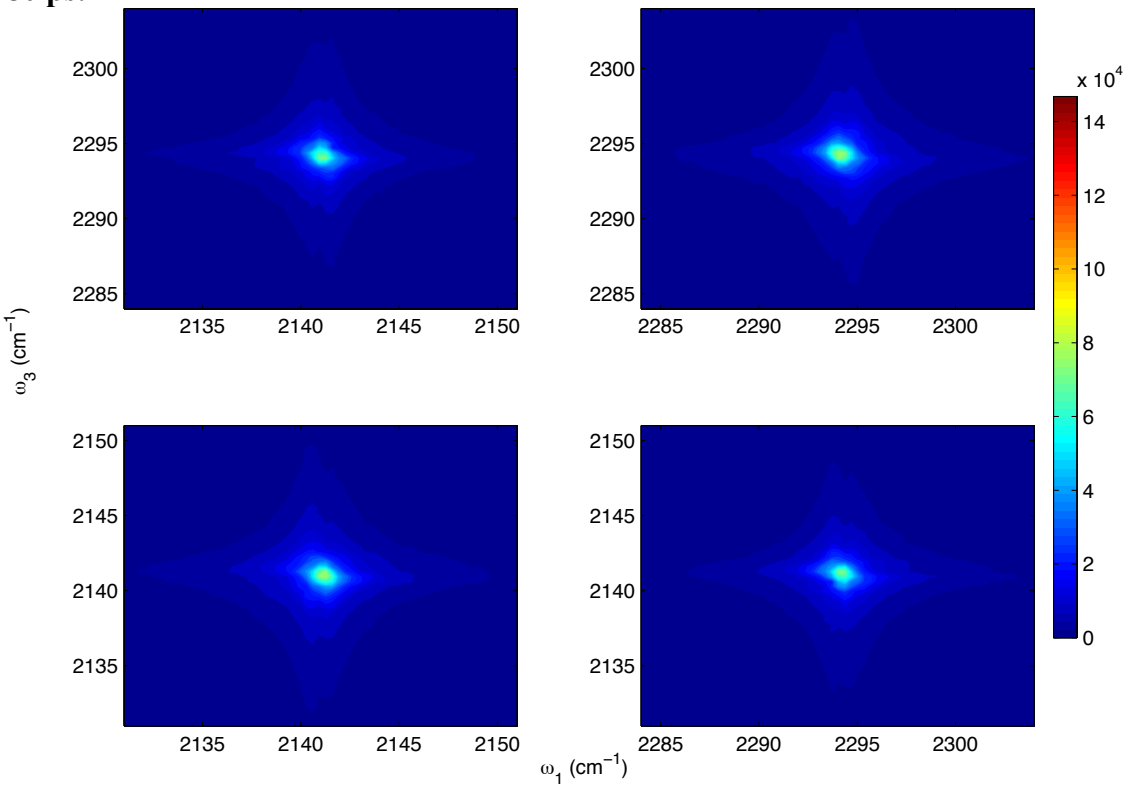
T_w = 60 ps:



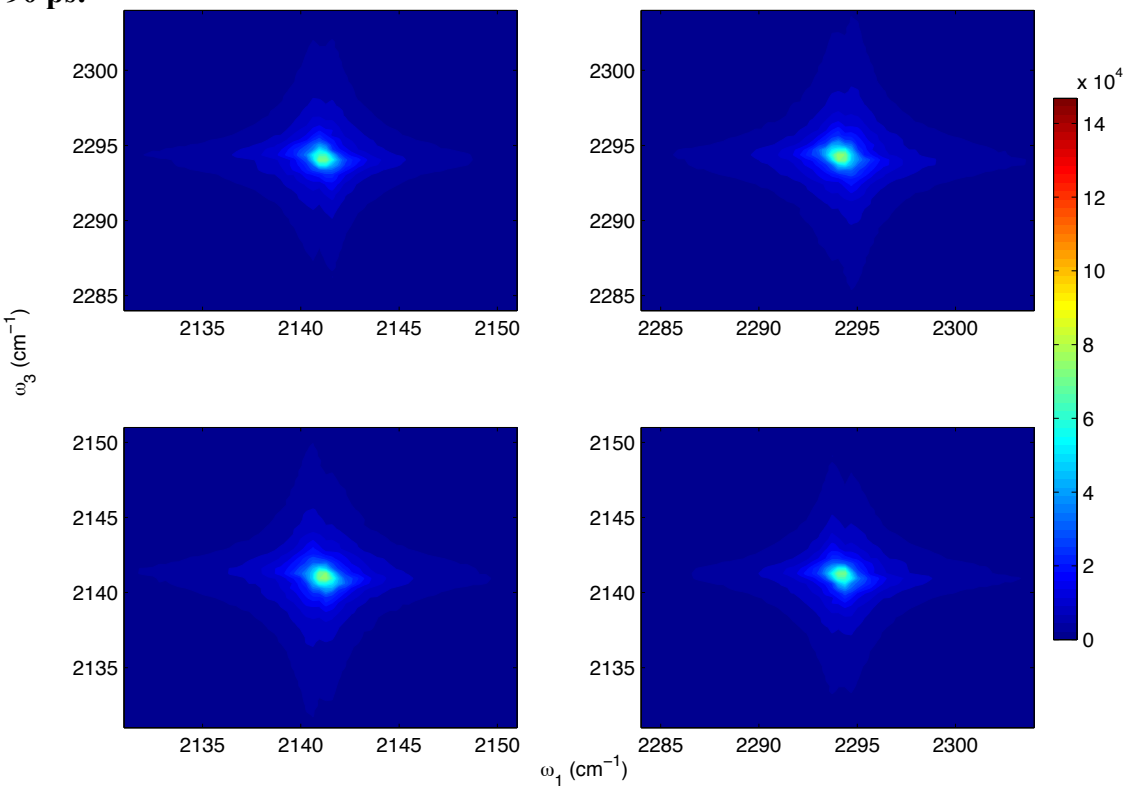
T_w = 70 ps:



T_w = 80 ps:



T_w = 90 ps:



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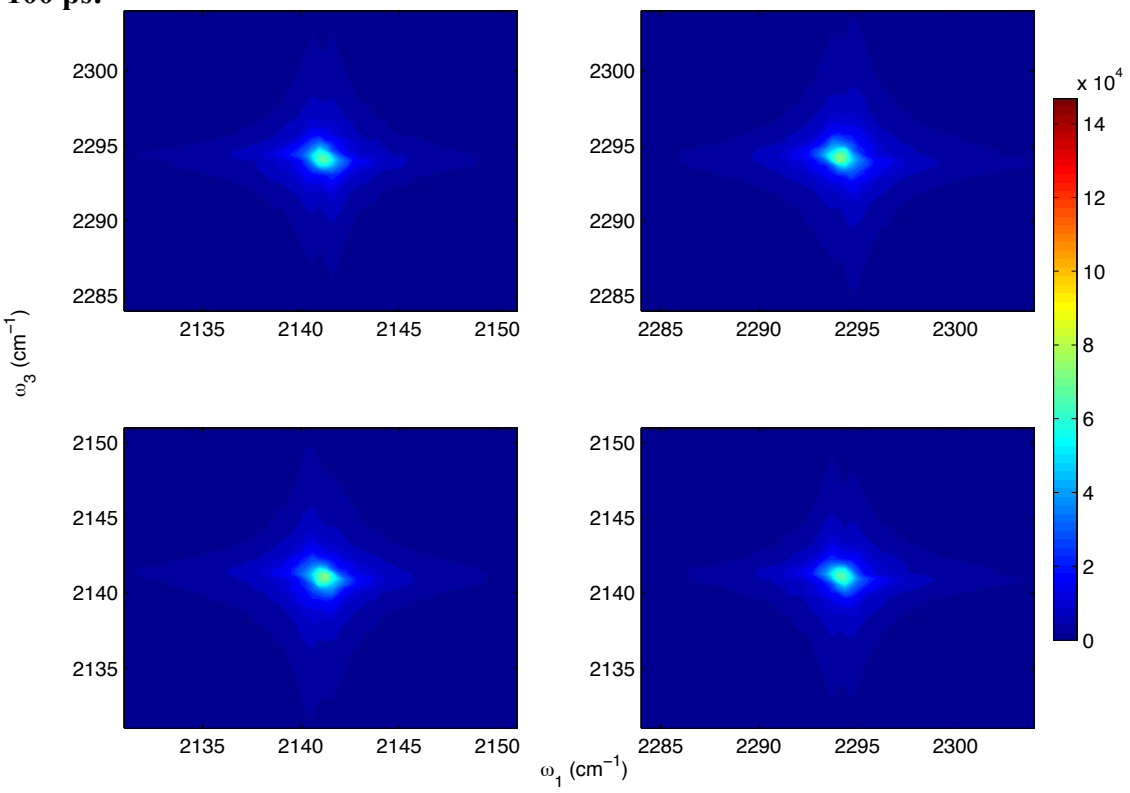

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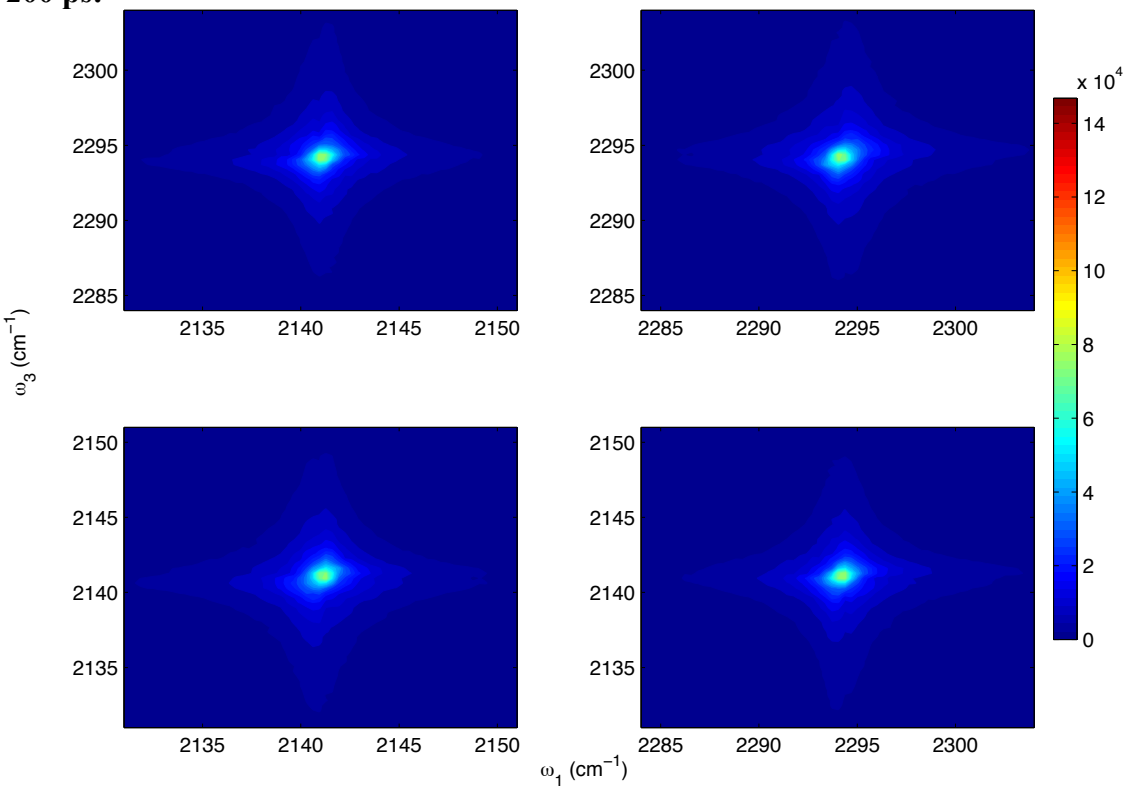

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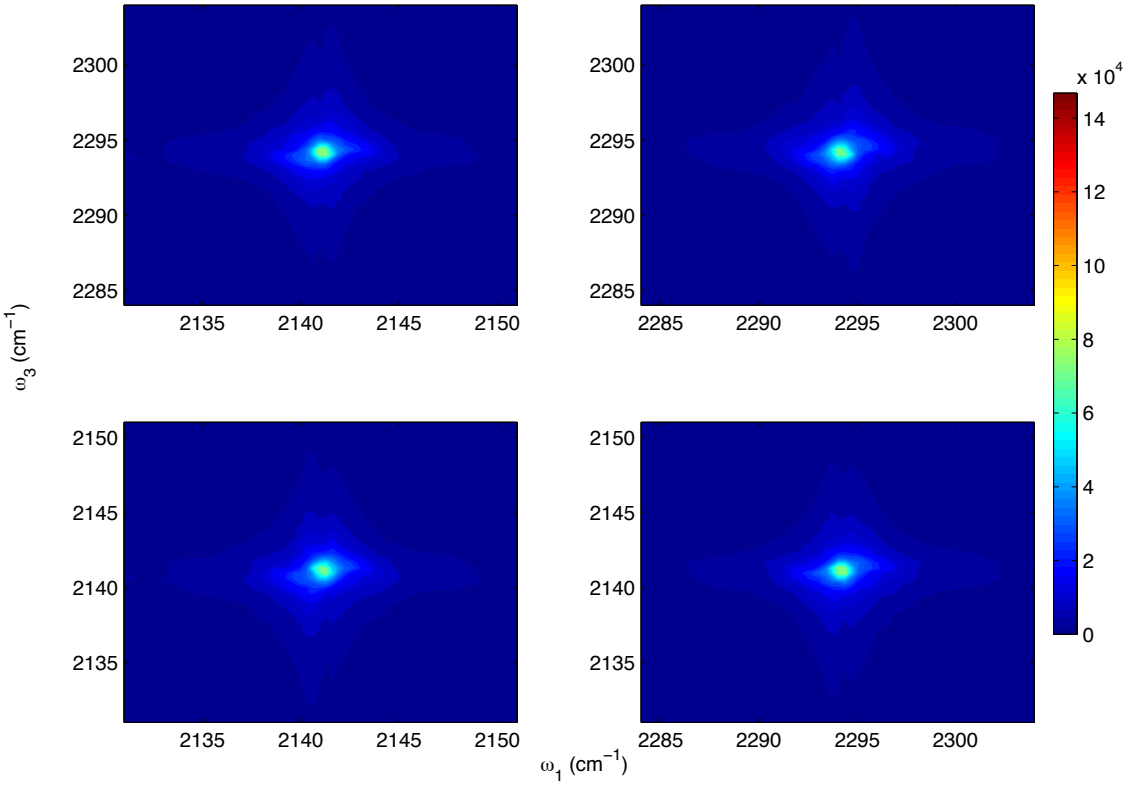

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(2) Schmidt, J. R.; Corcelli, S. A. *J. Chem. Phys.* **2008**, *128*, 184504.
(3) Schmidt, J. R.; Corcelli, S. A.; Skinner, J. L. *J. Chem. Phys.* **2005**, *123*, 044513.