Abstract Submitted
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Two-Dimensional Line Shapes in Electronic-Vibrational Spectroscopy as a Measure of Correlated Spectral Dynamics of Electronic and Vibrational Degrees of Freedom NICHOLAS LEWIS, HUI DONG, THOMAS OLIVER, GRAHAM FLEMING, University of California, Berkeley — 2D optical spectroscopies in many different frequency regimes have been useful to study the correlated spectral behavior for many different types of system degrees of freedom. The slope of the center-line of a feature in 2D electronic and 2D infrared spectroscopy has been shown to provide detailed information about the correlation functions that describe the system-bath coupling for the system degrees of freedom.[1] Recently, we have demonstrated a new spectroscopic technique, 2D electronic-vibrational spectroscopy, that is capable of directly measuring the correlation between spectral motion of the electronic and vibrational degrees of freedom.[2] Here we demonstrate that the center-line slope of a 2DEV resonance can be directly related to the correlation function for the vibrational degrees of freedom on the electronic excited state. We show experimentally that this can be observed in 2DEV spectra of the dye DTTCI. Finally, we show how 2DEV spectra can be used to directly measure the strength of system-bath coupling for the vibrational degrees of freedom on the electronic excited state versus those on the electronic ground state.

[1]K. Kwac and M. Cho, **J. Phys. Chem. A** 107, 5903
[2]T.A.A. Oliver, N.H.C. Lewis and G.R. Fleming, **PNAS** 111, 0927

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