Fully Coherent Electronic-Vibrational Spectroscopy of Transition Metal Complexes

John C. Wright*, Erin Boyle, Nathan Neff-Mallon, and Jonathan Handali

Department of Chemistry, University of Wisconsin-Madison, 1001 University Ave Madison WI 53706 USA, *wright@chem.wisc.edu

Three independently tunable OPAs create multiple quantum coherences (MQCs) using fully coherent pathways involving vibrational and electronic states. The MQCs create 3D electronic/vibrational spectra that can serve as multidimensional spectral signatures of transition metal complexes in complex biological systems. We report experiments using different methodologies to probe different biological systems.

The application of CMDS to following the dynamics in complex biological samples requires high selectivity for extracting the multidimensional spectra of specific moieties within the samples. The requisite selectivity can be with multiple quantum coherences (MQCs) containing distinctive vibrational and electronic states. This paper reports the use of two different fully coherent methods that form MQCs containing two vibrational states and an electronic state. The MQCs are formed by resonance with three independently tunable optical parametric amplifiers. The emission from the MQCs is cooperative and multiplicatively enhanced by the three resonances. The directional emission is defined by either a $\vec{k}_4 = \vec{k}_1 + \vec{k}_2 + \vec{k}_3$ and $\vec{k}_4 = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$ phase matching geometry. The output frequency is spectrally resolved from the excitation frequencies so scattered light is not important. Since the selection rules for the vibrational transitions are the same as those in infrared spectroscopy, these fully coherent pathways provide a resonance infrared absorption spectroscopy that is analogous to resonance Raman spectroscopy. The methods are applied to benzene [1], a Styryl 9M dye [2], copper phthalocyanine tetrasulfonate [3], chlorophyll, and photosystem II.

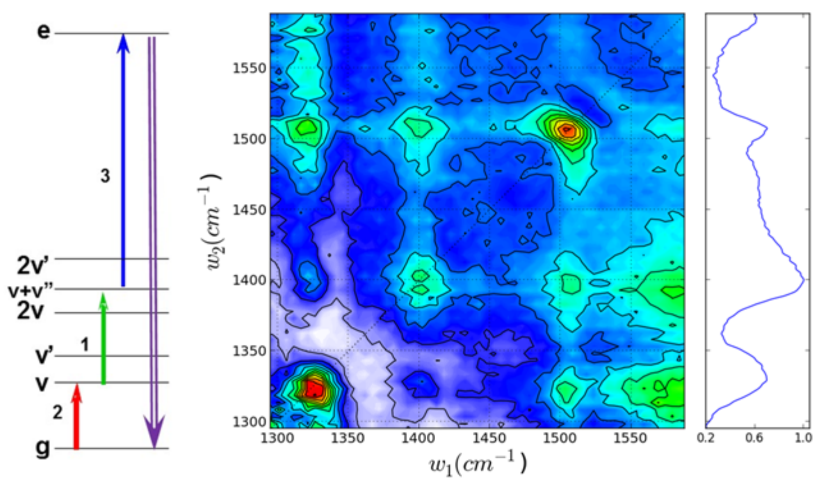

Fig. 1 2D spectrum of copper phthalocyanine. The IR spectrum appears on the right and the fully coherent pathway appears on the left.

[1] Erin S. Boyle, Andrei V. Pakoulev, and John C. Wright, J. Phys. Chem. A **117**, 5578-5588 (2013).
[2] Erin S. Boyle, Nathan Neff-Mallon, and John C. Wright, J. Phys. Chem. A. **117**, 12401-12408 (2013).
[3] Erin S. Boyle, Nathan A. Neff-Mallon, Jonathan D. Handali, and John C. Wright, J. Phys. Chem. A **118**, 3112–3119 (2014).