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### **Elucidation of Chemical Reactions by Two-Dimensional Resonance Raman Spectroscopy**

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Two-dimensional (2D) Raman spectroscopies were proposed by Mukamel and Loring in 1985 as a method for resolving line broadening mechanisms of vibrational motions in liquids. Significant technical issues challenged the development of both five- and seven-pulse 2D Raman spectroscopies. For this reason, 2D Raman experiments were largely abandoned in 2002 following the first demonstrations of 2D infrared spectroscopies (i.e., an alternate approach for obtaining similar information). We have recently shown that 2D Raman experiments conducted under electronically resonant conditions are much less susceptible to the problems encountered in the earlier 2D Raman work, which was carried out off-resonance. In effect, Franck-Condon activity obviates the problematic selection rules encountered under electronically off-resonant conditions. In this presentation, I will discuss applications of 2D resonance Raman spectroscopies to photodissociation reactions of triiodide and myoglobin. It will be shown that vibrational resonances of the reactants and products can be displayed in separate dimensions of a 2D resonance Raman spectrum when the photo-dissociation reaction is fast compared to the vibrational period. Such 2D spectra expose correlations between the nonequilibrium geometry of the reactant and the distribution of vibrational quanta in the product, thereby yielding insight in the photo-dissociation mechanism. Our results suggest that the ability of 2D resonance Raman spectroscopy to detect correlations between reactants and products will generalize to other ultrafast processes such as electron transfer and energy transfer.