Relating action- and transmission-detected multidimensional wave-packet interferometry signals

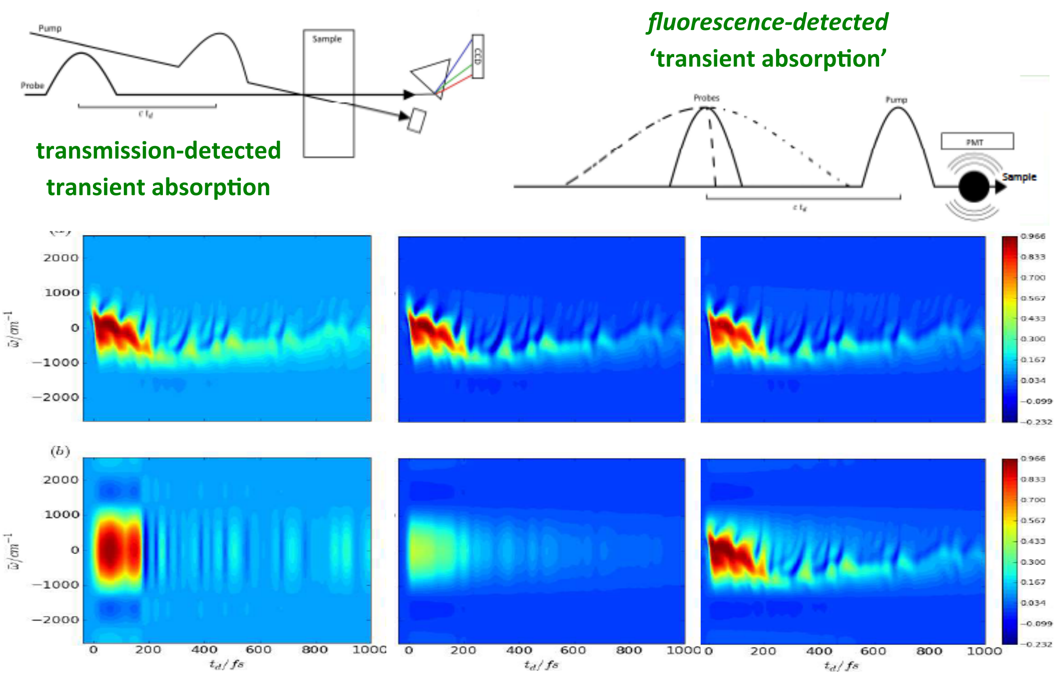
Jeffrey A. Cina*

Department of Chemistry & Biochemistry and Oregon Center for Optical, Molecular, and Quantum Science, University of Oregon, Eugene, Oregon, USA, 97403 *cina@uoregon.edu

We report on our recent comparative studies of calculated fluorescence-detected wave-packet interferometry and heterodyne-detected four-wave-mixing signals. Special attention is given to the possible use of pulse-shaping methods to render more nearly equivalent differently measured time-resolved nonlinear optical signals.

Several methods have become standard for measuring 2D electronic spectroscopy signals. While evidently closely related, these measurements—loosely encompassing action-detected and transmission-detected versions—also differ in several significant respects. For purposes of meaningful comparison, it is worthwhile to explicate the origins of these differences and to identify strategies for making the different approaches more nearly equivalent.

We begin by comparing the ordinary spectrally resolved transmission approach to ultrafast transient-absorption (TA) with a proposed fluorescence-detected version. Fluorescence-detection would not require an extended sample and could in principle be carried out by accumulating data from a single chromophore. The figure [1] shows calculated transmission- and fluorescence-detected TA signals from a 13-mode system modeled on the algal light-harvesting complex of PC577. [2]



On the left are the 'conventional' and 'out-of-order' signal contributions under fluorescence detection. It can be seen in the middle panels that an abruptly initiated spectrally filtered probe pulse minimizes the out-of-order term. The right-hand panels compare the resulting net fluorescence-detect signal (bottom) with ordinary transmission-detected TA (top).

[1] Kelly S. Wilson and Jeffrey A. Cina, *unpublished* (2015).

[2] J. A. Cina, P. A. Kovac, C. C. Jumper, J. C. Dean, and G. D. Scholes, "Ultrafast transient absorption

revisited: Phase-flips, fingers, and other dynamical features," *submitted* (2016).