

Intramolecular Vibrations in 2D Electronic Spectroscopy (2D-ES) under Different Excitation Conditions

Franco V. A. Camargo^{1,2}, Harry L. Anderson³, Stephen R. Meech¹ and Ismael A. Heisler^{1,*}

¹School of Chemistry, Norwich Research Park, University of East Anglia, Norwich NR4 7TJ, UK

²CAPES Foundation, Ministry of Education of Brazil, Brasilia DF 70040-202, Brazil

³Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Oxford OX1 3TA, UK

* i.heisler@uea.ac.uk

2D-ES is ideally suited to study electronic or vibrational molecular couplings. However, unravelling the origin of the ensuing coherences can prove challenging, as similar features arise from distinct physical processes. Vibrations coupled to electronic transitions are ubiquitous and here we explore their signatures in 2D spectra under different excitation conditions.

Studying coupled transitions with 2D-ES is convenient because spreading the information along an extra (excitation) axis means that cross-peak structures form as a result of coupling. 2D-ES has thus been employed to study a variety of molecular systems, which established that couplings associated with very different physical origins (e.g., vibrational or electronic) result in similar spectroscopic features [1].

Analogously to transient absorption, 2D-ES signals also present oscillatory amplitude over population time (T) if there is coherent wavepacket motion. Therefore, further information about couplings can be obtained by studying coherent dynamics with a 3D measurement, that is, a series of 2D-ES maps for various values of T . A Fourier transform over T then allows identification, in the excitation-detection plane, where different beating frequencies have amplitude [2]. Analyzing rephasing and nonrephasing signals as well as positive and negative frequencies during T allows further selection of pathways.

Here we employ 2D-ES on zinc-porphyrin molecules to explore and benchmark a rich landscape of different features in amplitude and phase of coherent dynamics that arise from vibrations coupled to the electronic transitions under different excitation and temperature conditions (Fig.1).

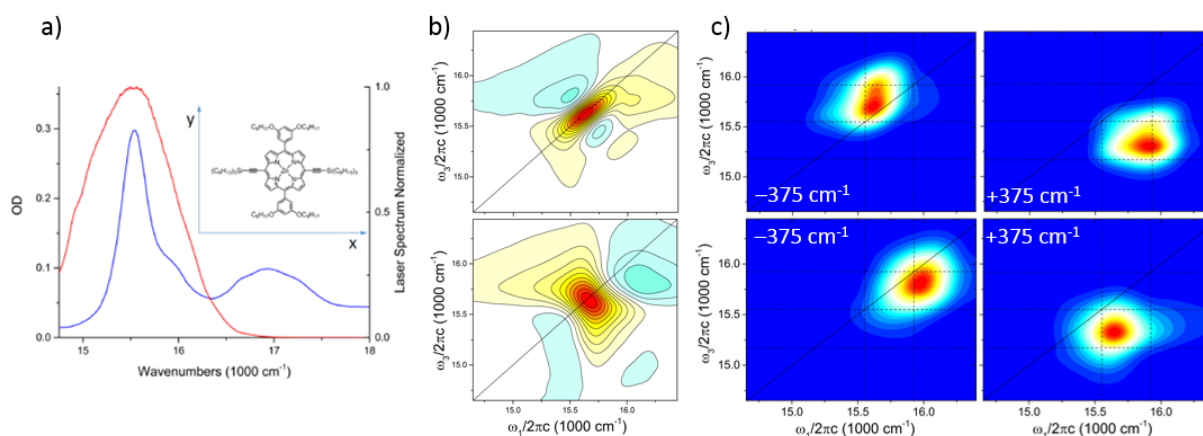


Fig.1 (a) Molecular structure (inset), linear absorption (blue) of the zinc-porphyrin monomer and laser spectrum (red). (b) Rephasing (top) and Nonrephasing (bottom) 2D spectra of the monomer at 120 fs. (c) Rephasing (top) and Nonrephasing (bottom) oscillation amplitude maps for a vibrational mode at ± 375 cm⁻¹. Excitation defined by the laser spectrum, hot ground state contributions and overlapping lineshapes of coupled states (causing interference effects [2]) can combine to cause either the presence or the absence of some peaks.

[1] N. Christensson *et al.*, JPCB **115**, 5383 (2011).

[2] F. V. A. Camargo *et al.*, JPCA **119**, 95 (2015).