Time-frequency methods for coherent spectroscopy

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Time-frequency decomposition techniques, borrowed from the signal-processing field, are adapted and applied to the analysis of 2D oscillating signals. Synthetic signals are used to optimize and benchmark the performances of several time-frequency approaches. The methods are applied on sample 2D electronic spectroscopy data of a common dye.

2D electronic spectroscopy (2DES) has now become a mature experimental technique to study electronic relaxation and energy transfer dynamics of molecules, nanomaterials and biological molecules. One of the most appealing characteristics of this technique is its capability of capturing coherent dynamics manifested as oscillations of the optical signal as a function of time. In recent years, Fourier-analysis techniques and especially Fourier transform amplitude maps have proved to be a valuable tool to interpret the oscillating component of the signal, see for example ref. [1]. One important limit of this approach is the extraction of information only in the frequency domain.

The time-frequency transforms (TFT) can overcome this limit providing simultaneously frequency and time resolution [2], unveiling explicitly the dynamics of the relevant beating components, and supplying a valuable help in their interpretation.

In order to fully exploit the potentiality of this method, several TFTs are tested in the analysis of sample 2D data [3], both synthetically generated and experimental. The construction of a theoretical TFT for signals with exponentially decaying oscillations is proposed as a benchmark for the investigated time-frequency methods [4] (Fig. 1).

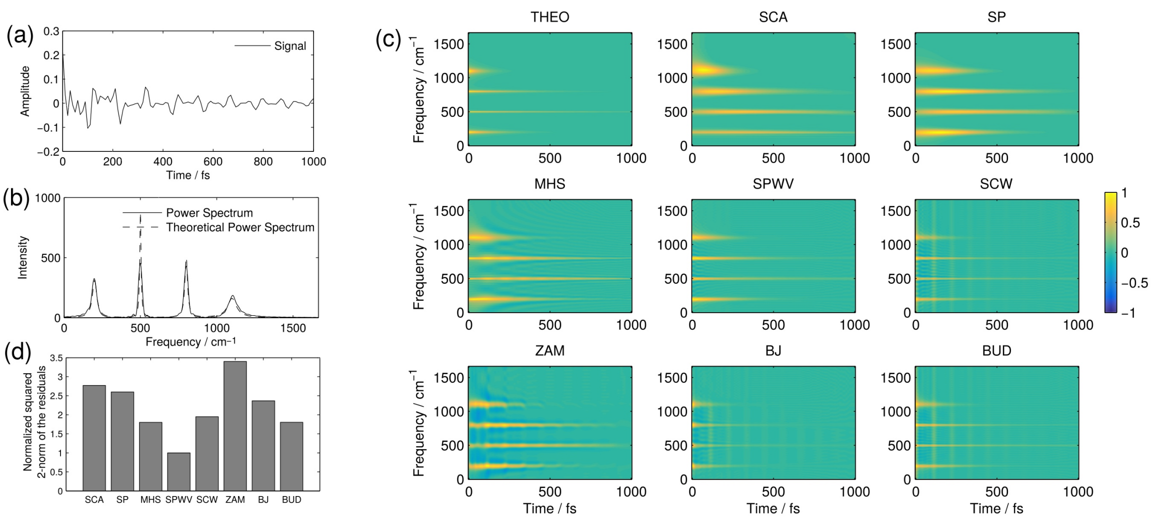

Fig. 1 – Synthetic signal with four oscillating decaying components (a) and its power spectrum (b). Time-frequency transforms of the signal (c); THEO = theoretical TFT, SCA = scalogram, SP = spectrogram, MHS = Margenau-Hill spectrogram distribution, SPWV = smoothed pseudo-Wigner-Ville distribution, SCW = smoothed Choi-Williams distribution, ZAM = Zao-Atlas-Marks distribution, BJ = Born-Jordan distribution, BUD = Butterworth distribution [5]. Normalized squared 2-norm of the residual with respect to the theoretical TFT (d).

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