Finite Pulse Effects in 2D Electronic Spectroscopies

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When modelling experimental 2D spectra, the effects of finite pulse durations are usually neglected to optimize computational costs. We present analytic treatment of finite pulse duration effects on electronic 2D spectra. While $\mathbf{k_i}$ and $\mathbf{k_{ii}}$ signals are rather robust, the double quantum signal $\mathbf{k_{iii}}$ shows unexpected but readily interpreted dependencies.

We address the convolution problem for two-dimensional (2D) coherent spectroscopy, and investigate how finite durations of excitation laser pulses affect the coherent response. The implementation of the full convolution procedure connecting third order response functions R with the third order polarization P generated by the sample with delay t_3 after three laser pulses at intervals t_1, t_2 [1]

$$P(t_1 + t_2 + t_3) = \int_{-\infty}^{t_1+t_2+t_3} d\tau_a \int_{\tau_a}^{t_1+t_2+t_3} d\tau_b \int_{\tau_b}^{t_1+t_2+t_3} d\tau_c \; E(\tau_a)E(\tau_b - t_1)E(\tau_c - t_1 - t_2) \times R(\tau_b - \tau_a, \tau_c - \tau_b, t_1 + t_2 + t_3 - \tau_c) \quad (1)$$

is costly and numerically challenging, and it is thus rarely used for simulating 2D spectra. Instead, in the enumeration of response functions the dipole strengths are modified along the scheme $\mu_{eg} \to \mu_{eg} \int_{-\infty}^{\infty} E(t) e^{-i\omega_{eg}t}$ where ω_{eg} is central frequency of transition [1], or the pulse duration is neglected at all, $E(t) \to \delta(t)$.

Such procedures usually work satisfactorily for the standard $\mathbf{k_i}$ and $\mathbf{k_{ii}}$ signals, however, they are not exact. We noticed that pulse related artifacts often persist in double quantum (2Q) signal $\mathbf{k_{iii}}$ despite all efforts to avoid them, especially for weak electronic resonances [2]. In an effort to model and eventually overcome these effects, we have revisited finite pulse analysis based on the full convolution approach of Eq. (1), considering a simple toy model for both the material response and pulse profiles [3]. Tedious, but closed formulas are then obtained, enumerated and further analyzed. Preliminary calculations shows that the $\mathbf{k_{iii}}$ signal has larger sensitivity toward pulse durations than $\mathbf{k_i}$ and $\mathbf{k_{ii}}$ signals. Finally, we discuss some recent 2Q-2D experiments where such artifacts are superimposing the spectra.

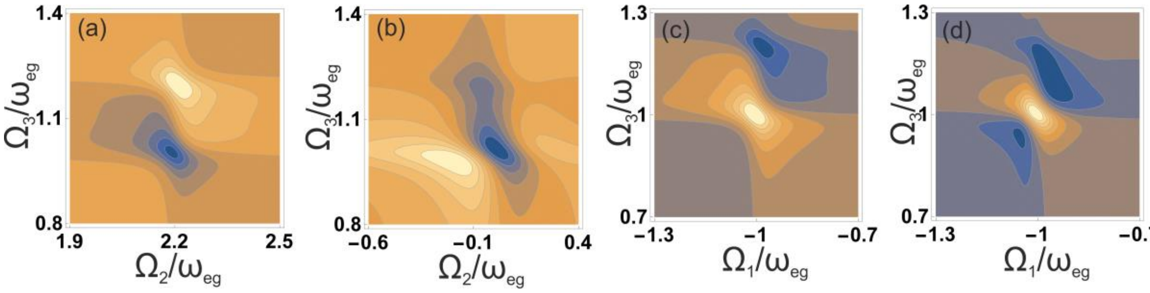

Fig.1 2Q-2D signal $S_{\mathbf{k_{iii}}}(t_1 = 0, \Omega_2, \Omega_3)$ for a three level molecule (levels g, e, f) with transition frequency and ω_{fe}/ω_{eg}=1.2, and dephasing rates $\gamma/\omega_{eg} = 0.05$ for variable pulse durations. Panel (a) with pulse duration $2\sigma = 0.06/\omega_{eg}$ represents standard theoretical calculation with $E(t) \to \delta(t)$, while the (b) panel $2\sigma = 6.0/\omega_{eg}$ represents real finite pulses. Figs (c),(d) are the same for photon echo $S_{\mathbf{k_i}}(\Omega_1, t_2 = 0, \Omega_3)$ signal.

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