Exciton-exciton annihilation dynamics in six-wave mixing 2DES spectra

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Two dimensional electronic spectroscopy (2DES) is a powerful spectroscopic tool that allows to study dynamics of excited states. The type of signal can be categorized by the phase matching condition of optical pulses interacting with the molecular aggregate. The $\mathbf{K}_1$-$\mathbf{K}_2$+$\mathbf{K}_3$ signal, where K corresponds to each pulse wavevector, allows to study single exciton dynamics. While the $2\mathbf{K}_1$-$2\mathbf{K}_2$+$\mathbf{K}_3$ signal allows to probe double exciton dynamics.

Exciton – exciton annihilation (EEA) is a process that involves interaction of 2 excitation. EEA is the process when two separate molecular excitations form a high energy short lived state. After fast internal conversion the molecule returns back into singly excited state, the remaining energy of other excitation gets dissipated in its vibrational manifold. It has been shows that EEA can be studied by $2\mathbf{K}_1$-$2\mathbf{K}_2$+$\mathbf{K}$ type of signal[1].

EEA is a process that depends on density of excitations. This nonlinear dependence requires accounting of optical field intensity. In our earlier work[2] we have developed EEA terms for nonlinear exciton equations (NEE). NEE allow calculating nonlinear polarization at order of our choosing. We apply phase cycling technique[3] to extract nonlinear 2DES signals. We show that significant changes in 2DES spectra can be observed when annihilation is allowed (Figure 1).

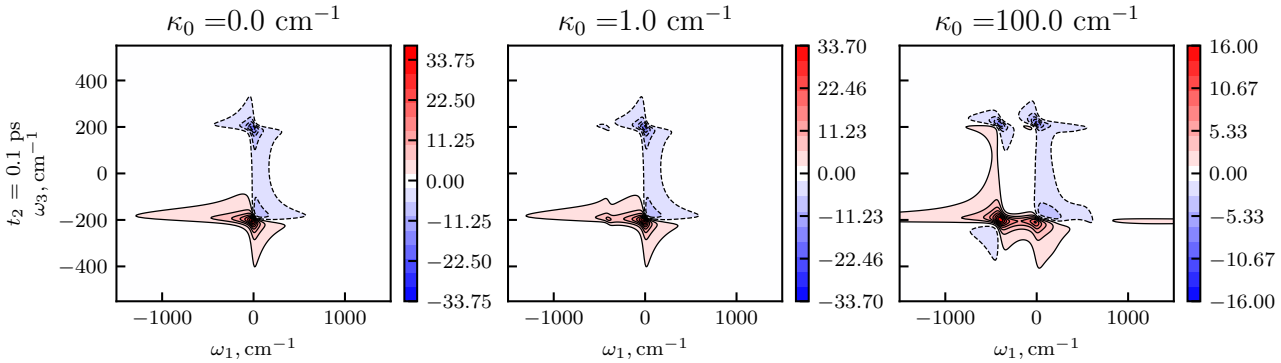

Figure 1: $2\mathbf{K}_1$-$2\mathbf{K}_2$+$\mathbf{K}_3$ 2DES spectra of a J type dimer, for paulionic particles, at delay time t_2 = 0.1 ps, at different annihilation parameter κ_0 values

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References

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