

Theory of Femtosecond Double-Pulse Single-Molecule Spectroscopy

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We have performed simulations of single-molecule fluorescence signals, excited by a pair of phase-locked pump pulses, for several models with strong intramolecular electronic and electron-vibrational couplings. It is shown that the signals can be decomposed into population and coherence contributions. We have explored how the initial preparation of the molecular system manifests itself in the fluorescence signal.

Recently, the van Hulst group has developed the novel technique of femtosecond single-molecule spectroscopy [1]. In this technique, a pair of phase-locked femtosecond pump pulses excites a single molecule to an excited electronic state. The integral fluorescence is detected as a function of the time delay between the pulses.

We present a theoretical description of femtosecond single-molecule spectroscopy. The signals are simulated for a series of model systems with two or three electronic levels and several vibrational modes, using a method which is similar to that described in Ref. [2]. The signal excited by temporally well separated phase-locked pulses can be written as a function of the pulse delay time τ and the phase difference φ as follows:

$$I_F(\tau, \varphi) = A(\tau) + \text{Re}[B(\tau)e^{i\varphi} + C(\tau)e^{2i\varphi}]e^{-\tau/\tau_d} \quad (1)$$

where $A(\tau)$ describes wave-packet evolution in the electronic populations of the density matrix, $B(\tau)$ and $C(\tau)$ are contributions due to electronic single and double coherences, and τ_d is the electronic dephasing time. In the leading order in the system-field interactions, $A(\tau)$ is τ -independent and the signal solely contains information about the decay of electronic coherences. If, on the other hand, the pump pulses are strong (that is, non-perturbative), the signal exhibits beatings reflecting vibrational wave-packet dynamics (Fig. 1a). It is suggested that monitoring of the fluorescence signal as a function of the phase φ (for fixed τ) can be used to distinguish between two- and three-level systems (Fig. 1b).

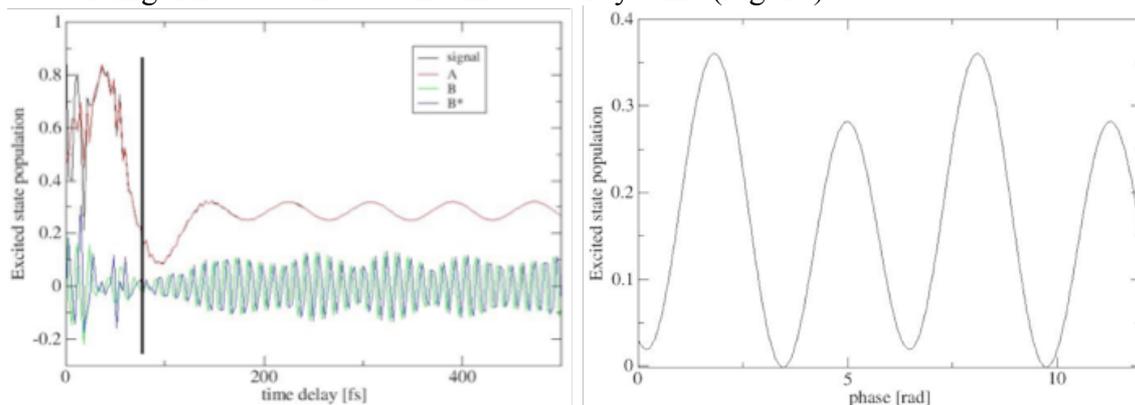


Fig. 1 (a) Fluorescence signal for an electronic two-level system with a single vibrational mode, excited by strong resonant pump pulses. The dephasing time is $\tau_d = 30$ fs. The population contribution (A) and the coherence contribution (B) are also shown. (b) Phase-dependence of the signal for a three-electronic-level system with a single vibrational mode, excited by strong resonant pump pulses with a delay of $\tau = 200$ fs. The dephasing time is $\tau_d = 300$ fs.

- [1] R. Hilder *et al.*, Phys. Chem. Chem. Phys. **13**, 1888 (2011).
[2] M. F. Gelin *et al.*, J. Chem. Phys. **139**, 214302 (2013).