

# Femtosecond Optical Spectroscopies of Solvated Polyatomic Molecules

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**Abstract.** A multimode Brownian oscillator model is developed for third order nonlinear optical spectroscopies in condensed phases, taking into account molecular dynamics of coherent nuclear motions of the absorber and the dephasing and reorganization processes of solvent molecules. Calculations of femtosecond photon echo are discussed.

In this paper we present a generalized Brownian oscillator model which illustrates various aspects of molecular dynamical processes during time resolved nonlinear optical measurements.[1-5] Our description of molecular dynamics is based on the time evolution of density matrix in Liouville (or phase) space.

Let us consider an optical measurement of a solvated chromophore. We assume that only two electronic states,  $|g\rangle$  and  $|e\rangle$ , of the chromophore are relevant for the optical excitation. All four wave mixing spectroscopies of this molecular system can be expressed in terms of the molecular response function which is the sum of four-time correlation functions of the chromophore dipole moment  $\mu$ . The typical form of these four-time correlation functions is  $\text{Tr} [G_{eg}(t_3)G_{mm}(t_2)G_{ge}(t_1)\rho_0]$  with  $m=g$  or  $e$ . Here  $\rho_0$  describes the initial thermal distribution of the material system in the ground electronic state  $|g\rangle$ . The molecular dynamics during the optical measurement are completely described by the Liouville space Green function  $G_{mn}(t)$ , which is defined by its action on an arbitrary dynamical variable  $A$ :

$$G_{mn}(t) A = \exp(-iH_m t/\hbar) A \exp(iH_n t/\hbar); \quad m,n=e \text{ or } g. \quad (1)$$

The diagonal Green function  $G_{mm}(t)$  describes the molecular dynamics in the potential surface  $V_m$  (corresponding to  $H_m$ ) and is governed by the single molecular nuclear Hamiltonian  $H_m$ . Its phase space representation  $G_{mm}(p,q,t; p_0,q_0)$  has a well defined classical analogue, i.e. the conditional probability of finding the system in phase space point  $(p,q)$  at time  $t$ , assuming it evolved in the potential surface  $V_m$  from  $(p_0,q_0)$  at time  $t=0$ . Since  $G_{mm}$  describes the coupled dynamics of the chromophore and the solvent, the complete phase space has a macroscopic number of degrees of freedom. However, we consider explicitly only a few relevant degrees of freedom, denoted as the system modes, by using the generalized Langevin equation:

$$q(t) = p(t) \quad (2)$$

$$\dot{p}(t) = \partial V / \partial q - \int_0^t \hat{\gamma}(t-\tau) p(\tau) dt + f(t). \quad (2b)$$

Here  $V$  is the effective potential surface for the system modes in the  $m = c$  or  $g$  electronic state. The friction kernel and the random force satisfy the fluctuation-dissipation relation:  $\langle f(t)f(0) \rangle = k_B T \gamma(t)$ . The quantum dynamics in state  $|m\rangle$  can be obtained by considering eqs.(2) as operator equations. A Fokker-Planck equation for  $G_{mm}(p,q,t; p_0,q_0)$  can then be obtained from eqs.(2). The off-diagonal Green function, e.g.  $G_{cg}(p,q,t; p_0,q_0)$ , describes the molecular dynamics during an optical transition and depends on both of the electronic state Hamiltonians,  $H_g$  and  $H_c$ . This Green function has no classical analogue due to its quantum nature which involves two electronic states.[3]

It is obvious that all the optically active modes of the chromophore should be considered explicitly in eqs.(2). In addition, the *solvation coordinate* should also be considered explicitly. Physically, the solvation coordinate originates from the collective nuclear response of the solvent upon optical excitation of the chromophore. This solvation coordinate is described by a strongly overdamped oscillator governed by the Smoluchowski equation of motion. In a frequency-resolved experiment, the optically active modes contribute to the Franck-Condon progressions and the solvation coordinate contributes to the line broadening. In a time-resolved experiment, the optically active modes show quantum beats with the vibronic dephasing and relaxation induced by the solvent friction and fluctuations, whereas the strongly overdamped solvation coordinate is responsible for spectral diffusion, e.g. the time-dependent Stokes shift and broadening, as well as homogeneous and inhomogeneous electronic dephasing.

Let us consider an ideal stimulated photon echo experiment in which the system is subject to three impulsive pulses with wavevectors  $\underline{k}_1$ ,  $\underline{k}_2$  and  $\underline{k}_3$ , separated by  $\tau_{21}$  and  $\tau_{32}$ , subsequently. The echo signal is then generated after the third pulse at the phase matching direction of  $\underline{k}_3 + \underline{k}_2 - \underline{k}_1$  as a function of  $\tau_{21}$  and  $\tau_{32}$ :

$$SSPE(\tau_{21}, \tau_{32}) = \text{Tr} \{ G_{cg}(\tau_{21}) [G_{cc}(\tau_{32}) + G_{gg}(\tau_{32})] G_{gc}(\tau_{21}) \rho_0 \}^2. \quad (3)$$

The physical picture of the stimulated photon echo described by eq.(3) as follows: At time  $t=0$ , the initially equilibrated system  $\rho_0$  is excited by the first pulse to an optical coherence  $\rho_{ge}$ , which then evolves freely, as described by the Green function  $G_{ge}(\tau_{21})$ , until  $t=\tau_{21}$ . The system is then subjected to the second impulsive pulse, which transfers the system to either the electronic ground  $\rho_{gg}$  or the excited  $\rho_{cc}$  state. The system then evolves freely as described either by  $G_{gg}(\tau_{32})$  or by  $G_{cc}(\tau_{32})$  until it interacts with the third impulsive pulse. After the third pulse the system is again in an optical coherence and the echo arises due to the free rephasing processes described by the Green function  $G_{cg}(\tau_{21})$ , which is the Hermitian conjugate of  $G_{ge}(\tau_{21})$ . The ordinary (two-pulse) photon echo is a limiting case of the stimulated echo when  $\tau_{32}=0$  and  $\underline{k}_3=\underline{k}_2$ . In this case all the relevant molecular dynamics are related to the optical coherence and described by[4]

$$SSPE(\tau_{21}) = \text{Tr} \{ G_{cg}(\tau_{21}) G_{gc}(\tau_{21}) \rho_0 \}^2. \quad (4)$$

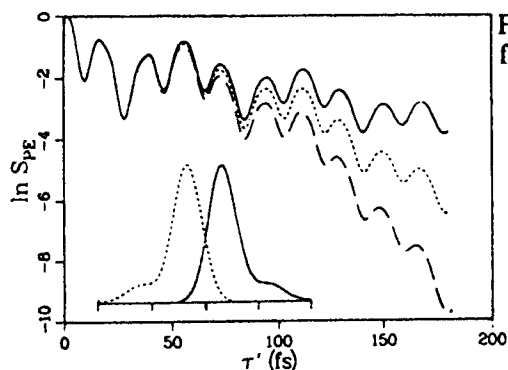


Fig.1: The impulsive two pulse echo for a three mode system [1b].

Figure 1 presents the ordinary photon echo signal for a three mode system (two coherent vibrations and a single solvation coordinate). The various curves correspond to a different choice of solvent timescale. Details of the calculations are given in Reference 1b. The calculations demonstrate the capacity of the present Brownian oscillator model to describe the coherent nuclear motion as well as the solvation dynamics which couple to optical transitions, as measured recently.[6]

The present Brownian model provides a unified description of the molecular dynamics, which include the coherent nuclear motion, electronic and nuclear dephasing and solvent relaxation, as probed in nonlinear optical measurements of polyatomic molecules in solution. The electronic solvation dynamics (spectral diffusion, homogeneous and inhomogeneous electronic dephasing) is described by a macroscopic solvation coordinate, which undergoes an overdamped motion. The stochastic lineshape model[7] is a special limit case of the present model obtained by considering an overdamped oscillator and neglecting the time dependent Stokes shift. The present Brownian solvation model can describe the complete picture of solvent reorganization processes, which include spectral (Stokes) shift as well as line broadening.

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