Kubo's Lineshape Function for a Linear-Quadratic Chromophore-Solvent Coupling

Dmitry V. Matyushov *

Department of Physics and Department of Chemistry & Biochemistry, Arizona State University, PO Box 871504, Tempe, AZ 85287-1504

E-mail: dmitrym@asu.edu

*To whom correspondence should be addressed

Abstract

An exact, closed-form solution is obtained for the lineshape function of an optical transition with the transition frequency depending linearly plus quadratically on a Gaussian coordinate of the thermal bath. The dynamical modulation of the lineshape involves two parameters corresponding to the linear and quadratic components of the transition frequency. The increase of the second component results in a non-Gaussian lineshape which splits into two Lorenzian lines in the limit of fast modulation.

Keywords: Time-resolved spectroscopy, stochastic functional integrals, quadratic chromophore-bath coupling.

Introduction

The question addressed here is how the modulation of the spectroscopic transition frequency $\Omega(t)$ by fluctuations of the thermal bath is related to the observed spectral lineshape.[1–4] The lineshape depends on both the magnitude and the rate of the modulation. The modulation magnitude is characterized by the variance $\Delta = \langle(\delta\Omega)^2\rangle^{1/2}$, while the modulation rate is characterized by the relaxation time τ_c of the stochastic bath on which $\Omega(t)$ depends. Two limits are commonly distinguished. The slow modulation, $\tau_c\Delta \gg 1$, leads to an essentially static lineshape fully determined by the statistical distribution of the bath variables. The fast modulation, $\tau_c\Delta \ll 1$, results in the line narrowing (motional narrowing). The lineshape depends in this limit on both the statistics and the dynamics of the bath.

This general framework is known as Kubo's stochastic theory of the lineshape.[4] Specific calculations within this theory require finding the lineshape function $g(t)$ by averaging over the trajectories of the spectroscopic transition frequency $\Omega(\tau)$ in the equation[5,6]

$$\Psi(t) = e^{-g(t)} = \left\langle \exp\left(i\int_0^t \Omega(\tau)d\tau \right) \right\rangle \tag{1}$$

For brevity, we assume that $\Omega(t)$ is the random part of the frequency, that is $\langle\Omega\rangle = 0$. A non-zero average frequency only shifts the position of the spectral maximum.[3,5]

Typical calculations in the Kubo model are performed assuming the linear coupling between $\Omega(t)$ and a stochastic bath variable $x(t)$:

$$\Omega(x) = ax \tag{2}$$

where $\langle x\rangle = 0$ is assumed. If, additionally, $x(t)$ is a Gaussian variable, only the second cumulant contributes to the lineshape function in eq (1) and a simple result for $g(t)$ follows[5,7]

$$g(t) = (\Delta\tau_c)^2 \left[\gamma t - 1 + \chi(t)\right] \tag{3}$$

In this equation, $\chi(t)$ denotes the exponential time autocorrelation function of the variable $x(t)$

$$\langle x(t)x(0)\rangle = \langle x(0)^2\rangle\chi(t), \quad \chi(t) = e^{-\gamma t} \tag{4}$$

where $\gamma = 1/\tau_c$ and $t > 0$.

Fourier transform of eq (1) results in the spectral lineshape. With the use of eq (3), it is mostly a Lorenzian line in the fast modulation limit, with a faster than Lorenzian decay of the spectral wings away from the maximum. In the opposite limit of slow modulation, the lineshape is a Gaussian line.

The goal of this paper is to understand observable consequences of non-Gaussian dynamics of $\Omega(t)$.[7] Obviously, the two-cumulant approximation is not applicable for such stochastic processes. Estimates of higher-order cumulants can help to quantify deviations from the Gaussian lineshape in the static[8] and noise-modulated[9,10] limits. It is, however, desirable to produce exact results involving the summation of an infinite series of cumulants. An example of such solution is presented here within the model that considers a linear plus quadratic dependence of $\Omega(x(t))$ on the bath variable $x(t)$. Specifically, the lineshape function in eq (1) is exactly calculated by assuming a linear-quadratic[10–15] functionality for $\Omega(x)$

$$\Omega(x) = ax + \tfrac{1}{2}bx^2 \tag{5}$$

If $x(t)$ is still a Gaussian variable, the variance of Ω becomes $\langle\Omega^2\rangle = \Delta^2 + (3/4)\Pi^2$, where we keep Δ to specify the variance of the linear component of the transition frequency $\Delta = a\langle x^2\rangle^{1/2}$ and $\Pi = b\langle x^2\rangle$. Since two parameters now control the spectral width, it is expected that at least two parameters should determine the dynamical modulation of the lineshape as well. The derivation presented here indeed confirms that $\Delta\tau_c$ and $\Pi\tau_c$ are two separate modulation parameters.

Even when $x(t)$ is still a Gaussian variable, the stochastic variable $\Omega(t)$ given by eq (5) is not Gaussian any longer.[12] The second-cumulant expansion becomes an approximation. In order to avoid truncated cumulant expansions, the problem is solved here exactly by direct stochastic path integration[16] over the trajectories $x(t)$. The result is a new lineshape function

$$g(t) = \frac{(\Delta\tau_c)^2}{\epsilon^3}\left[\tilde{t} - \frac{2(1-\chi(\tilde{t}))}{1+\chi(\tilde{t})+\epsilon(1-\chi(\tilde{t}))}\right] \quad (6)$$

in which $\tilde{t} = \epsilon\gamma t$. The parameter ϵ in this equation is a complex variable with its imaginary part proportional to $\Pi\tau_c$

$$\epsilon^2 = 1 - 2i\Pi\tau_c \quad (7)$$

At $\epsilon = 1$, which corresponds to $b = 0$ in eq (5), eq (6) reduces to Kubo's function in eq (3). In a more general case, the spectral lineshape shows significant and non-trivial dynamic modulation not reducible to the traditional transformation from the Lorenzian to the Gaussian lineshape.

Stochastic path integral for the lineshape

The exponential form of the time correlation function in eq (4) describes a Brownian harmonic oscillator, or Ornstein-Uhlenbeck process.[17] We, therefore, consider $x(t)$ as a stochastic Ornstein-Uhlenbeck variable, which satisfies the Langevin equation

$$\dot{x}(t) + \gamma x(t) = y(t) \quad (8)$$

Here, $y(t)$ is a random force with stochastic properties of white noise (delta-function for the time correlation function).

The average over the stochastic trajectories in eq (1) can be re-written in terms of the propagator describing the probability of reaching the position $x = x(t)$ at the time t given that the bath variable was $x_0 = x(0)$ at time $t = 0$. The propagator is then integrated over all possible realizations of x_0 consistent with the equilibrium Boltzmann distribution $P_{\mathrm{eq}}(x_0)$

$$\Psi(t) = \int dx dx_0 P(x,t|x_0,0)P_{\mathrm{eq}}(x_0) \quad (9)$$

The function $P(x,t|x_0,0)$ in this equation is not the standard propagator of a stochastic process following from the Fokker-Planck equation.[18] Instead, in involves the propagation of the classical trajectory $x(\tau)$ together with the off-diagonal component of the density matrix of the two-level system within the angular brackets in eq (1). The function $P(x,t|x_0,0)$ is therefore a solution of the stochastic Liouville equation,[3,4,7] instead of the Fokker-Planck equation.

The function $P(x,t|x_0,0)$ can be directly calculated by propagating the trajectory $x(\tau)$ as determined by the equations of motion of the bath, but modulating the propagation with the variable $\Omega(x(\tau))$. The corresponding path integral is taken with a complex Lagrangian according to the equation[16,19]

$$P(x,t|x_0,0) = \int_{\{x,x_0\}} \mathcal{D}x(\tau) \exp\left[i\int_0^t d\tau\delta\Omega(\tau) - \int_0^t L(x,\dot{x})d\tau\right] \quad (10)$$

The Lagrangian $L(x,\dot{x})$ in eq (10) describes the stochastic bath variable $x(t)$. For the Ornstein-Uhlenbeck process, it is given by the relation[16]

$$L(x,\dot{x}) = \frac{1}{4D}(\dot{x}+\gamma x)^2 - \gamma/2 \quad (11)$$

Here, $D = \sigma^2\gamma$ is the diffusion coefficient associated with the variable x and $\sigma^2 = \langle x^2\rangle$ is the variance of x. Finally, the path integral in eq (10) is taken over all trajectories satisfying the boundary conditions $x(0) = x_0$ and $x(t) = x$.

The evolution of trajectories is determined by the effective complex-valued Lagrangian

$$\tilde{L}(x,\dot{x}) = \frac{1}{4D}(\dot{x}+\gamma x)^2 - i\Omega(x) \quad (12)$$

The equation of motion for the trajectory minimizing the action along the path is found from the Euler-Lagrange equation[16]

$$\frac{d}{dt}\frac{\partial\tilde{L}}{\partial\dot{x}} - \frac{\partial\tilde{L}}{\partial x} = 0 \quad (13)$$

In order to simplify the notation, we will introduce the dimensionless time $\epsilon\gamma t \to t$, where ϵ is given by eq (7). The equation of motion, obtained by substituting eq (12) into (13), takes a relatively compact form

$$\ddot{x} - x = \kappa, \quad \kappa = -\frac{2ia\sigma^2}{\gamma\epsilon^2} \tag{14}$$

The solution of eq (14) with $x_0 = x(0)$ and $x = x(t)$ is

$$x(\tau) = x\frac{\sinh\tau}{\sinh t} + x_0\frac{\sinh(t-\tau)}{\sinh t} - 2\kappa\frac{\sinh(\tau/2)\sinh(t-\tau)/2}{\cosh(t/2)} \tag{15}$$

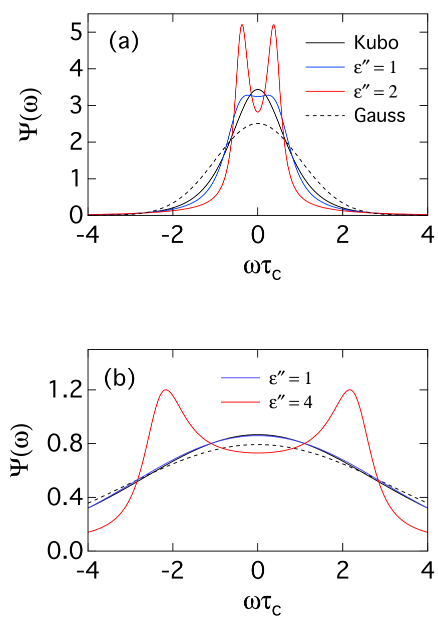

Figure 1: Spectral lineshape at $(\Delta\tau_c)^2 = 1$ (a) and 10 (b). The calculations are done by using eq (6) with the imaginary part ϵ'' of $\epsilon^2 = 1 - i\epsilon''$ indicated in the plot. The solid black lines refer to the Kubo lineshape and the dashed lines denote the Gaussian short-time limit, $g(t) = (\Delta t)^2/2$. The solid black and blue lines nearly coincide on the scale of the plot in (b).

According to the standard rules of performing Gaussian path integrals (with the Lagrangian of the second order in the path variable),[16] the result of integration can be obtained by calculating the action on the trajectory satisfying the equation of motion.[16] The propagator $P(x, t|x_0, 0)$ in eq (10) thus becomes

$$P(x, t|x_0, 0) = e^{S(x,t|x_0,0)} \tag{16}$$

with the corresponding action (neglecting a constant term affecting normalization)

$$-4\sigma^2 S(x, t|x_0, 0) = x^2 - x_0^2 + \epsilon x\dot{x}\big|_0^t + \epsilon\kappa\int_0^t x(\tau)d\tau \tag{17}$$

The substitution of eqs (16) and (17) into eq (9) results in the lineshape function in eq (6) with $\Delta = a\sigma$.

Dynamic lineshapes

Equation (6) presents a closed-form, exact solution for the lineshape function with a linear-quadratic dependence of the transition frequency on a classical, overdamped nuclear mode. The fact that the solution presents an infinite summation of the cumulant series is clearly seen from a non-trivial algebraic dependence of $g(t)$ on the complex-valued parameter ϵ. A cumulant expansion in eq (1) would have produced a series in powers of the quadratic term in eq (5) proportional to powers of the coefficient b.[15] In contrast, eq (6) sums up an infinite series in b through the parameter ϵ.

We now present the lineshapes given as Fourier transforms $\Psi(\omega)$ of $\Psi(t)$ in eq (1) under the condition $\Psi(-t) = \Psi(t)$. Those are shown in Figures 1a and 1b calculated for $(\Delta\tau_c)^2 = 1$ and 10, respectively. The results of these two calculations are qualitatively similar. As expected, the short-time approximation $g(t) \simeq (\Delta t)^2/2$ is progressively accurate with increasing $\Delta\tau_c$. The approach to this slow-modulation limit is, however, counterbalanced by the imaginary part ϵ'' in the parameter $\epsilon^2 = 1 - i\epsilon''$ in eq (7). The lineshape function increasingly deviates from both the short-time approximation and the Kubo lineshape with increasing ϵ''. Since non-zero ϵ'' produces an imaginary component in $g(t)$, a splitting of the spectral line around its center develops, which does not occur for the Kubo function. As a result, the line splits into two separate sub-bands, a situation somewhat similar to the well-studied model of two-state jump modulation.[2,4] For slower modulation (larger $\Delta\tau_c$), a larger ϵ'' is required for the double-band lineshape to appear.

The model discussed here is quite general and can be applied to either local or collective nuclear modes substituted for the coordinate $x(t)$. A potential application of the model is to the infra-red vibrational spectroscopy, where transition frequencies are often found to be linear-quadratic functions of the fluctuating electric field projected on a local bond.[20,21] For this application, the nuclear coordinate is the field projection $x(t) = E(t)$, the linear coefficient $a = \Delta m_0/\hbar$ comes from the alteration of the bond dipole m_0 caused by the transition, and $b = -\Delta\alpha_0/\hbar$ arises from the corresponding alteration of the bond polarizability.[21]

Conclusions

Quadratic term in the dependence of the transition frequency on the bath coordinates, $(1/2)bx^2$, results in an additional parameter controlling the dynamic modulation of the transition frequency. The fast modulation limit for the spectral lineshape is achieved not only by decreasing $\Delta\tau_c$, as in the Kubo's theory, but also by increasing $\Pi\tau_c$. The growth of the second modulation parameter leads to splitting of the spectrum into two Lorenzian lines. The slower dynamics of the bath, achieved by growing the relaxation time τ_c, causes the competition between the tendency to reach the Gaussian limit ($\Delta\tau_c \gg 1$) and to split the line into two sub-bands ($b\langle x^2\rangle\tau_c = \Pi\tau_c \gg 1$). The transition to the static limit, $\tau_c \to \infty$, leads to an overall non-Gaussian static lineshape.[13]

Acknowledgement This research was supported by the National Science Foundation (CHE-1213288).

References

(1) Kubo, R. Note on the Stochastic Theory of Resonance Absorption. *J. Phys. Soc. Jpn.* **1954**, *9*, 935–944.

(2) Anderson, P. W. A Mathematical Model for the Narrowing of Spectral Lines by Exchange or Motion. *J. Phys. Soc. Jpn.* **1954**, *9*, 316–339.

(3) Kubo, R. Stochastic Liouville Equations. *J. Math. Phys.* **1963**, *4*, 174–183.

(4) Kubo, R. In *Adv. Chem. Phys.*; Shuler, K., Ed.; Wiley Interscience: New York, 1969; Vol. 15; A Stochastic Theory of Line Shape, pp 101–127.

(5) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.

(6) Hamm, P.; Zanni, M. *Concepts and Methods of 2D Infrared Spectroscopy*; Cambridge University Press: Cambridge, UK, 2011.

(7) Tanimura, Y. Stochastic Liouville, Langevin, Fokker-Planck, and Master Equation Approaches to Quantum Dissipative Systems. *J. Phys. Soc. Jpn.* **2006**, *75*, 082001.

(8) Lax, M. The Frank-Condon Principle and Its Application to Crystals. *J. Chem. Phys.* **1952**, *20*, 1752–1760.

(9) Sillescu, H.; Kivelson, D. Theory of Spin–Lattice Relaxation in Classical Liquids. *J. Chem. Phys.* **1968**, *48*, 3493–3505.

(10) Hsu, D.; Skinner, J. L. On the Thermal Broadening of Zero-Phonon Impurity Lines in Absorption and Fluorescence Spectra. *J. Chem. Phys.* **1984**, *81*, 1604–1614.

(11) Yan, Y. J.; Mukamel, S. Eigenstate-Free, Green Function, Calculation of Molecular Absorption and Fluorescence Line Shapes. *J. Chem. Phys.* **1986**, *85*, 5908–5923.

(12) Matyushov, D. V.; Voth, G. A. A Theory of Electron Transfer and Steady-State Optical Spectra of Chromophores with Varying Electronic Polarizability. *J. Phys. Chem. A* **1999**, *103*, 10981–10992.

(13) Matyushov, D. V. Time-Resolved Spectroscopy of Polarizable Chromophores. *J. Chem. Phys.* **2001**, *115*, 8933.

(14) Chernyak, V.; Mukamel, S. Quadratic Brownian-Oscillator Model for Solvation Dynamics in Optical Response. *J. Chem. Phys.* **2001**, *114*, 10430.

(15) Mančal, T.; Valkunas, L.; Fleming, G. R. Theory of Exciton–Charge Transfer State Coupled Systems. *Chem. Phys. Lett.* **2006**, *432*, 301–305.

(16) Kleinert, H. *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*, 3rd ed.; World Scientific: New Jersey, 2004.

(17) Wang, M. C.; Uhlenbeck, G. E. On the Theory of the Brownian Motion II. *Rev. Mod. Phys.* **1945**, *17*, 323–342.

(18) Gardiner, C. W. *Handbook of Stochastic Methods*; Springer: Berlin, 1997.

(19) Onsager, L.; Machlup, S. Fluctuations and Irreversible Processes. *Phys. Rev.* **1953**, *91*, 1505–1512.

(20) Yang, M.; Skinner, J. L. Signatures of Coherent Vibrational Energy Transfer in IR and Raman Line Shapes for Liquid Water. *Phys. Chem. Chem. Phys.* **2010**, *12*, 982–991.

(21) Saggu, M.; Levinson, N. M.; Boxer, S. G. Experimental Quantification of Electrostatics in $X - H \ldots \pi$ Hydrogen Bonds. *J. Am. Chem. Soc.* **2012**, *134*, 18986–18997.

Graphical TOC Entry