Lineshape of a Stochastic Oscillator with Two State Frequency Modulations

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The transformations of the lineshape with a fluctuating frequency for the Kubo-Anderson oscillator are considered. Assuming that the frequency of the oscillator fluctuates between two values and the rate of this fluctuation is a stochastic function of the time the analytical expression of the lineshape is obtained. It is assumed that the stochastic fluctuations of the potential barrier for the Kubo-Anderson oscillator lead to the stochastic fluctuations of the frequency. The transformations of the lineshape are extremely sensitive to the function, which describes the distributions of the frequency fluctuations. The obtained expression is applied to the different distributions of the fluctuation frequency rate. It is shown that a unusual type of the motional narrowing phenomenon is observed for the log-normal and log-Lorentzian distribution.

Key words: Kubo-Anderson Oscillator; Lineshape; Molecular Motions.
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1. Introduction

The stochastic oscillator two state jump model with a stochastic fluctuating frequency has found wide applications in condensed phase physics ranging from magnetic resonance spectroscopy [1 – 12] and nonlinear optical spectroscopy [13 – 17] to problems of decoherence and dephasing in spin-based solid state quantum computers [18 – 20]. This model is described by the Kubo-Anderson master equation of the form [2, 3]

$$\dot{x} = \mathrm{i}\omega(t) \cdot x, \tag{1}$$

where the stochastic frequency $\omega(t)$ can take the value of either Δ or $-\Delta$.

The average solution of (1) has the form

$$\langle x(t)\rangle = \left\langle x(0) \cdot \exp\left(\mathrm{i}\int_0^t \omega(t')\mathrm{d}t'\right)\right\rangle, \tag{2}$$

where the symbol $\langle\cdots\rangle$ means an operation of averaging over all realizations of the random process. The function $\langle x(t)\rangle$ is the linear response function [21], and for a stationary stochastic process the Fourier transform of the correlation function (2) gives the lineshape of the stochastic Kubo-Anderson oscillator [13 – 21].

Assuming that $\omega(t)$ is a Poisson random variable with the exponential sojourn time probability density function (PDF)

$$\psi(t) = W \cdot \exp(-Wt), \tag{3}$$

it is easily to show that the oscillator dynamics is described by the stochastic Liouville equation (SLE) [21 – 23],

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = [\mathrm{i}\Delta \cdot \hat{A} + W \cdot \hat{B}] \cdot x(t), \tag{4}$$

where

$$\hat{A} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \hat{B} = \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}, \quad x = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}. \tag{5}$$

In this case

$$\langle x(t)\rangle = p_1 x_1(t) + p_2 x_2(t), \tag{6}$$

where the initial distribution of the state $\pm\Delta$ is described by $p_{1,2}$. The value W in (4) is an average rate of frequency jump from one to another state.

The solution of (2) [or (4)] is well-known and describes the well-known motional narrowing phenomenon [1].

Recently, using the continuous time random walks (CTRW) theory [23, 24], the solution of (2) for the arbitrary PDF $\psi(t)$ has been obtained [13]. It has been shown that in the case, when $\psi(t)$ decays as $t^{5/2}$ at long times, new types of the resonance peaks and narrowing behaviour have been observed [13 – 16]. However, the similar motional behaviour has been obtained in the case, when it was assumed that the mean sojourn time $\tau = W^{-1}$ fulfills the Arrhenius activation law

$$\tau = \tau_0 \exp(E_a/kT), \tag{7}$$

where the activation energy E_a is the stochastic variable, driven by a bistable process of telegraphic type [25].

In the present paper we consider the generalized Poisson process, for which the probability of the occurrence of N jumps of the frequency $\omega(t)$ in the time interval $(0,t)$ is defined by the distribution

$$P(N,t) = \exp\left(-\int_0^t W(t')\mathrm{d}t'\right)\frac{1}{N!}\left(\int_0^t W(t')\mathrm{d}t'\right)^N. \tag{8}$$

It is easy to show that in this case the dynamics of the Kubo-Anderson oscillator is described by the SLE (4), in which W is the stochastic function of the time. We assume that the stochastic fluctuations of the potential barrier for the Kubo-Anderson oscillator cause the stochastic fluctuations of the frequency W.

2. Lineshape Theory

We will assume that the value W in (4) is the stochastic function of the time. The distribution of all possible values $W(t)$ is described by the function $p(W)$ and the jumps from one value, W_k, to another, W_m, are independent and distributed uniformly over the time with the density ν_C (the value $\nu_C\mathrm{d}t$ determines the average jumps value in the time interval $\mathrm{d}t$) (Fig. 1).

The solution of (4) can be easily obtained using the method of the differentiation formulae [26]. Then we obtain

$$\frac{\mathrm{d}x_k}{\mathrm{d}t} = \mathrm{i}\Delta\cdot\hat{A}\cdot x_k + \hat{B}\cdot x_{k+1} - \nu_C x_k + \nu_C\cdot\langle W^k\rangle\cdot x_0, \tag{9}$$

where

$$x_k = \langle W^k(t)\cdot x(t)\rangle. \tag{10}$$

The Laplace transformation of (9) has the form

$$\bar{x}_k = \nu_C\hat{L}\cdot\overline{\langle x_0\rangle\cdot\langle W^k\rangle} + \hat{L}\langle x_0(0)\rangle + \hat{L}\cdot\hat{B}\cdot\bar{x}_{k+1}, \tag{11}$$

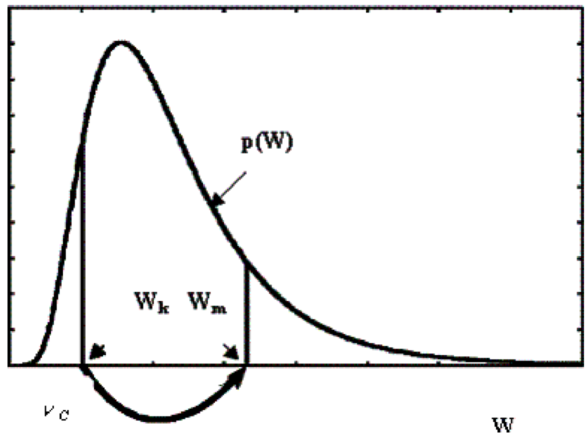

Fig. 1. Schematic presentation of the distribution function $p(W)$. The arrow designates the jump of the mean sojourn time $W(t)$ from the value W_k to the value W_m. The value ν_C determines the density of these jumps.

where $\hat{L} = [(z+\nu_C)\cdot\hat{E} - \mathrm{i}\Delta\cdot\hat{A}]^{-1}$, $\hat{E}$ is the unity matrix, and

$$\overline{\langle W^k\rangle\cdot\langle x_0\rangle} = \int_0^\infty \mathrm{e}^{-zt}\langle (W(t))^k\rangle\cdot\langle x_0\rangle\cdot\mathrm{d}t,$$

$$\overline{x_k} = \int_0^\infty \mathrm{e}^{-zt}\cdot x_k\mathrm{d}t.$$

Using (11) we obtain

$$\overline{x(z)} \equiv \overline{x_0(z)} = [\hat{E} - \nu_C\cdot\hat{M}]^{-1}\cdot\hat{M}\cdot x(0), \tag{12}$$

where

$$\hat{M} = \langle(\hat{E} - W\hat{L}\hat{B})^{-1}\rangle\cdot\hat{L} = \begin{bmatrix}(z+\nu_C+\mathrm{i}\Delta)r(z)+q(z) & q(z)\\ q(z) & (z+\nu_C-\mathrm{i}\Delta)r(z)+q(z)\end{bmatrix}, \tag{13}$$

and

$$[\hat{E}-\nu_C\cdot\hat{M}]^{-1} = \frac{1}{1-\nu_C[(2z+\nu_C)r(z)+2q(z)]}\left\{\hat{E}-\nu_C \cdot\begin{bmatrix}(z+\nu_C-\mathrm{i}\Delta)r(z)+q(z) & q(z)\\ q(z) & (z+\nu_C+\mathrm{i}\Delta)r(z)+q(z)\end{bmatrix}\right\}. \tag{14}$$

In (13) and (14)

$$r(z) \equiv \int_0^\infty \mathrm{d}W\cdot\frac{p(W)}{(z+\nu_C)(z+\nu_C+2W)+\Delta^2}, \tag{15}$$

$$q(z) \equiv \int_0^\infty \mathrm{d}W \cdot \frac{W \cdot p(W)}{(z+\nu_C)(z+\nu_C+2W)+\Delta^2}. \quad (16)$$

Assuming that $p_1 = p_2 = 1/2$ and with the help of (12)–(14) we obtain the final expression for the lineshape function of a stochastic oscillator with two state frequency modulations:

$$\overline{x(z)} = \frac{1}{z+\Delta^2 f(z)}, \quad (17)$$

where

$$f(z) = \frac{(z+\nu_C)\cdot r(z)}{1-[\nu_C(z+\nu_C)+\Delta^2]\cdot r(z)}. \quad (18)$$

3. Discussion

At first we shall note that, if $\nu_C = 0$ and $p(W) = \delta(W-W_0)$, from (17) it follows the well-known result [1, 7, 9, 10, 18]

$$\overline{x(z)} = \frac{z+2W_0}{z(z+2W_0)+\Delta^2}.$$

In the case, when the stochastic process is a bistable process of telegraphic type and $p(W) = \frac{1}{2}\delta(W-W_1) + \frac{1}{2}\delta(W-W_2)$, from (17) it also follows the known result [25]

$$\overline{x(z)} = \frac{1}{z+\Delta^2 f(z)}, \quad (19)$$

where

$$f(z) = \left\{(z+\nu_C)(z+\nu_C+2\bar{W})+\Delta^2\right\}\left\{(z+2\bar{W}) \cdot[(z+\nu_C)(z+\nu_C+2\bar{W})+\Delta^2]-4(z+\nu_C)\sigma^2\right\}^{-1}. \quad (20)$$

In (20)

$$\bar{W} = \frac{W_1+W_2}{2}, \quad \sigma = \frac{W_2-W_1}{2}. \quad (21)$$

In the next examples we will assume that the frequency W fulfills the Arrhenius activation law:

$$W(t) = W_0 \exp\left(-\frac{E(t)}{kT}\right), \quad (22)$$

in which the fluctuated activation energy E is described by the distribution function $g(E)$.

We will also assume that the frequency ν_C, describing the fluctuations of the potential barrier E and so the fluctuations of the frequency W, fulfills an Arrhenius activation law:

$$\nu_C = \nu_0 \exp\left(-\frac{E_b}{kT}\right). \quad (23)$$

Now we consider three examples of the distribution function $g(E)$:

1) the function $g(E)$ has an exponential form:

$$g(E) = \frac{1}{\sigma_E}\exp\left[-\frac{|E-\bar{E}|}{\sigma_E}\right]; \quad (24)$$

2) the function $g(E)$ has a normal (Gauss) shape:

$$g(E) = \frac{1}{\sigma_E\sqrt{2\pi}}\exp\left[-\frac{(E-\overline{E_a})^2}{2\sigma_E^2}\right]; \quad (25)$$

3) the function $g(E)$ has a Lorentz shape:

$$g(E) = \frac{\sigma_E}{\pi\cdot[(E-\bar{E})^2+\sigma_E^2]}. \quad (26)$$

If the distribution of the activation energy E has an exponential form, the distribution of all possible values $W(t)$ is described by the log-exponential function

$$p(W) = \frac{kT}{W\cdot\sigma_E}\exp\left[-\frac{\left|kT\cdot\ln\left(\frac{W}{W_0}\right)+\bar{E}\right|}{\sigma_E}\right]. \quad (27)$$

If the distribution of the activation energy E has a normal (Gauss) form, the distribution of all possible values $W(t)$ is described by the log-normal function

$$p(W) = \frac{kT}{\sigma_E\cdot W\sqrt{2\pi}}\exp\left[-\frac{\left(kT\cdot\ln\left(\frac{W}{W_0}\right)+\bar{E}\right)^2}{2\sigma_E^2}\right]. \quad (28)$$

If the distribution of the activation energy E has a Lorentz form, the distribution of all possible values $W(t)$ is described by the log-Lorentz function

$$p(W) = \frac{kT}{W\cdot\pi}\frac{\sigma_E}{\left(kT\cdot\ln\left(\frac{W}{W_0}\right)+\bar{E}\right)^2+\sigma_E^2}. \quad (29)$$

The results of our calculations are shown in Figure 2. From this figure it follows that the temperature transformations of the lineshape are extremely sensitive to the form of the distribution function of the frequency fluctuations. In the case, when the distribution of the

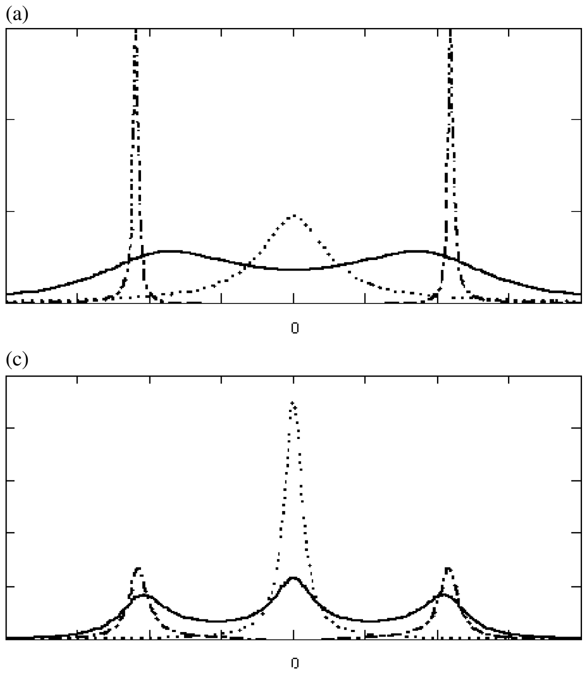

Fig. 2. The temperature transformations of the Kubo-Anderson oscillator lineshape; x-axis, frequency ω; y-axis, line amplitude; $\Delta = 21.7$ kHz, $\overline{E_a} = 73$ kJ/mol; $\sigma_E = 0.2 \cdot E_a$; $W_0 = \nu_0 = 1.2 \cdot 10^{12}$ s; $E_b = E_a$. (a) $p(W)$ is described by the function (27). (b) $p(W)$ is described by the function (28). (c) $p(W)$ is described by the function (29). The dot-dashed lines represent the line shapes at (a) $T = 455$ K and (b, c) $T = 420$ K, the continuous lines represent the lineshapes at (a) $T = 500$ K and (b, c) $T = 455$ K and the dotted lines represent the lineshape at $T = 550$ K.

activation energy E has the exponential form (24), the temperature transformations of the lineshape reflect the well-known phenomenon of motional narrowing (Fig. 2a) [1]. At the same time, in the cases, when the distribution of the activation energy E has the Gauss (25) or Lorentz (26) form, the temperature transformations of the lineshape have unusual behaviour: there are three peaks at $\omega = \pm\Delta$ and $\omega = 0$ in the slow modulation region ($\nu_C \approx \delta$). As was mentioned above in [13] this additional peak has been obtained assuming that the sojourn time probability density function $\psi(t)$ decays as $t^{5/2}$ at long times. For the fast modulation case we again observe only a single peak at $\omega = 0$.

4. Conclusion

We considered the temperature transformations of the lineshape for the Kubo-Anderson oscillator with a fluctuating frequency. In our considerations we assumed stochastic fluctuations of the frequency being the result of stochastic fluctuations of the potential barrier for the Kubo-Anderson oscillator. From the results obtained it follows that the temperature transformations of the lineshape are extremely sensitive to the distribution function of the frequency fluctuations. In the case, when the distribution of the activation energy E has the exponential form, the temperature transformations of the lineshape reflect the well-known phenomenon of motional narrowing. However, unusual temperature transformations of the lineshapes have been observed in the slow modulation region ($\nu_C \approx \delta$) for the cases, when the distribution of the activation energy E has the Gauss or Lorentz form. In these cases there are three peaks at $\omega = \pm\Delta$ and $\omega = 0$.

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