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# Quantum Theory of a Two-Dimensional Rotator in a Dissipative Environment: Application to Far-Infrared Spectroscopy

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Quantum coherence and its destruction by coupling to a dissipative environment play important roles in time-resolved optical response. We study a two-time correlation function of a two-dimensional rotator coupled to a harmonic-oscillator bath. Generating functionals of reduced density matrix elements for the rotator degrees of freedom are calculated by diagonalizing the total Hamiltonian with the use of unitary transformations and then performing path integrals. A closed-form expression of linear absorption spectrum for a dipole rotator, i.e., a Fourier transformation of the dipole two-time correlation function, is derived from the generating functionals characterized by the bath spectral density. Based on the theory, the spectra for a methyl rotation in a toluene are depicted for various damping constants and temperatures. Because of the cyclic boundary condition that is constrained to fit the rotator degree of freedom, the energy states of the rotator in the absence of damping are discrete: the spectra consist of rotational branches, which correspond to change of the angular momentum. Owing to damping, the spectra exhibit a continuous band which is broadened as temperatures increase.

KEYWORDS: two-dimensional rotator, dissipative system, path integral, correlation function

Rotational motion in general plays an important role in many fields such as physics, chemistry, and biology. Optical measurement can reveal information about molecular rotation and optical spectra are obtained from the two-time correlation function of the angle of the rotator $\theta$ as $\langle[\cos\theta(t), \cos\theta(0)]\rangle$.

For free rotators, transitions between their rotational energy levels are observed with spectrographs as a series of closely spaced lines. Such lines are due to the quantization of the rotational degrees of the freedom with a cyclic boundary condition and are given by $E_l = l^2\hbar^2/2\mu$ ($l = 0, \pm 1, \cdots$), where $\mu$ is the moment of inertia. This is a purely quantum effect that classical theory cannot explain. In this Letter, we are interested in the effects of a dissipative environment on the dynamics of a quantal rotator. In classical cases, the damped rotator system has been studied in terms of a phenomenological Langevin equation approach with various realistic conditions. In quantal cases, however, one needs a quantum mechanical treatment of the system and dissipative environment. For this purpose, one introduces a model Hamiltonian for the system and an environmental system represented by an ensemble of harmonic oscillators. This problem can be regarded as one of the central issues in statistical physics: similar problems are analytically solved for quantum Brownian motion[1)] and for a quantum damped free particle.[2)] Here we take the same approach to the two-dimensional rotator and introduce the Hamiltonian,

$$\hat{H} = \frac{L^2}{2\mu} + \sum_i \left[ \frac{\hat{p}_i^2}{2m_i} + \frac{m_i\omega_i^2}{2}\left(\hat{q}_i - \frac{c_i\theta}{m_i\omega_i^2}\right)^2 \right], \qquad (1)$$

which reduces to the Langevin equation for the rotational motion in the classical limit. Here, $L$ and $\theta$ are the angular momentum defined by $L \equiv (\hbar/\mathrm{i})\partial/\partial\theta$ and the angular coordinate, respectively. The bath operators $\hat{q}_i$ and $\hat{p}_i$ commutate with $\theta$ and $L$. Note that the original rotational symmetry of the rotator recovers and the angular coordinate is $-\pi \le \theta < \pi$ with $\theta = -\pi$ and $\theta = \pi$ identified after tracing out the bath degrees of freedom owing to the properties of the Gaussian integration. In order to calculate the two-time correlation function, we introduce the generating functional $Z[J]$ as follows:

$$Z[J] = \mathrm{Tr}\left(\hat{\rho}_I^{J_3}\hat{U}^\dagger_{J_2}(\infty, t_I)\hat{U}_{J_1}(\infty, t_I)\right), \qquad (2)$$

where

$$\hat{U}_{J_\alpha}(\infty, t_I) = \mathrm{T}_t\left(\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\int_{t_I}^{\infty}\mathrm{d}t\left(\hat{H} - J_\alpha(t)\theta\right)}\right) \qquad (3)$$

and

$$\hat{\rho}_I^{J_3} = \mathrm{T}_\tau\left(\mathrm{e}^{-\frac{1}{\hbar}\int_0^{\beta\hbar}\mathrm{d}\tau\left(\hat{H} - \frac{\mathrm{i}}{\hbar}J_3(\tau)\theta\right)}\right). \qquad (4)$$

Here, $\hat{\rho}_I{}^{J_3=0}$ gives an equilibrium distribution at the initial time $t_I$ and $\tau$ is the imaginary time parameter with $0 \le \tau \le \beta\hbar$ in which $\beta$ is the inverse temperature. The symbol $\mathrm{T}_{t(\tau)}$ stands for the real (imaginary) time ordering operator. We represent the function in the two real time path by the suffix $\alpha = 1, 2$ and the imaginary one by $\alpha = 3$.

We consider the optical response of the rigid rotator. The linear absorption spectrum is calculated from the Fourier transformation of the two-time correlation function of the dipole moment. Since the dipole moment is

expressed as $d = d_0 \cos\theta$, this is written as[3)]

$$\sigma(\omega) = \mathrm{Im}\left[\frac{\mathrm{i}}{\hbar} d_0^2 \int_0^\infty \mathrm{d}t \mathrm{e}^{\mathrm{i}\omega t} \langle [\cos\theta(t), \cos\theta(0)]\rangle\right]. \quad (5)$$

Note that eq. (5) corresponds to the third-order off-resonant Raman response by the replacement of $d$ with the polarizability $\alpha$. The two-time correlation function of $\cos\theta$ is evaluated from the generating functional as

$$\langle T_C \cos\theta(t_1)\cos\theta(t_2)\rangle = \sum_{a_1,a_2=\pm 1} \frac{Z[J]}{4Z[J=0]}\bigg|_{J(s)=\hbar(a_1\delta_C(s-t_1)+a_2\delta_C(s-t_2))}. \quad (6)$$

Here, the index $C$ implies the contour time path that starts from $t_I$ to $t_F$ along the real path ($C_1$), returns to $t_I$ ($C_2$) and goes to $t_I - \mathrm{i}\beta\hbar$ parallel to the imaginary axis ($C_3$).[4,5)] The operator $T_C$ and the function $\delta_C(t)$ are the time-ordering operator and the $\delta$-function on the contour time path, respectively.

In order to evaluate $Z[J]$, we consider the unitary transformation which was utilized in the study of a free particle coupled to a harmonic-oscillator bath.[2)] We set $y_i \equiv m_i\omega_i^2 q_i/c_i$, $p_{yi} \equiv c_i p_i/(m_i\omega_i^2)$, $\mu_i \equiv c_i^2/(m_i\omega_i^4)$ and $r_i \equiv \mu_i/\mu'$ with $\mu' \equiv \mu + \sum_j \mu_j$. Then the unitary operator is expressed as

$$\hat{X} = \exp\left(-\frac{\mathrm{i}}{\hbar}\theta\sum_i \hat{p}_{yi}\right)\exp\left(\frac{\mathrm{i}}{\hbar}\sum_i r_i L\hat{y}_i\right). \quad (7)$$

The model Hamiltonian is transformed as

$$\hat{\tilde{H}} \equiv \hat{X}^\dagger \hat{H}\hat{X} = \tilde{H}_S + \tilde{H}_B, \quad (8)$$

where

$$\tilde{H}_S = \frac{1}{2\mu'}L^2, \quad (9)$$

and

$$\tilde{H}_B = \frac{1}{2\mu}\left(\sum_i \hat{p}_{yi}\right)^2 + \sum_i\left(\frac{\hat{p}_{yi}{}^2}{2\mu_i} + \frac{1}{2}\mu_i\omega_i^2\hat{y}_i{}^2\right). \quad (10)$$

After the unitary transformation (7), the generating functional is rewritten as

$$Z[J] = \mathrm{Tr}\left(\hat{\tilde{\rho}}_I^{J_3}\hat{\tilde{U}}_{J_2}^\dagger(\infty,t_I)\hat{\tilde{U}}_{J_1}(\infty,t_I)\right), \quad (11)$$

where $\hat{\tilde{\rho}}_I^J$ and $\hat{\tilde{U}}_J^{(\dagger)}(\infty,t_I)$ are defined by $\hat{\tilde{\rho}}_I^J \equiv \mathrm{T}_\tau \exp\left(-(1/\hbar)\int_0^{\beta\hbar}\mathrm{d}\tau\tilde{H}_J\right)$ and $\hat{\tilde{U}}_J(\infty,t_I) \equiv \mathrm{T}_t \times \exp\left(-(\mathrm{i}/\hbar)\int_{t_I}^\infty \mathrm{d}t\tilde{H}_J\right)$, and $\tilde{H}_J$ is the transformed Hamiltonian expressed as $\tilde{H}_J \equiv \tilde{H} - J(t)(\theta - \sum_i r_i\hat{y}_i)$ with the aid of $\hat{X}^\dagger \mathrm{e}^{\pm\mathrm{i}\theta}\hat{X} = \mathrm{e}^{\pm\mathrm{i}(\theta-\sum_i r_i\hat{y}_i)}$.

Since the Hamiltonian is divided into the rotator part, $\tilde{H}_S - J(t)\theta$, and the bath coordinate part, $\tilde{H}_B + J(t)\sum_i r_i\hat{y}_i$, the generating functional is factorized as

$$Z[J] = Z_S[J]Z_B[J], \quad (12)$$

where $Z_S[J]$ and $Z_B[J]$ are defined by eq. (11) for the Hamiltonian $\tilde{H}_S$ and $\tilde{H}_B$, respectively. The calculation of $Z_B[J]$ is parallel to the Brownian free particle.[1)] It is given by

$$Z_B[J] = \mathrm{e}^{\Xi[J]}\mathrm{e}^{-\Upsilon[J]}Z_B[J=0]. \quad (13)$$

Here, $\Upsilon[J]$ is expressed as

$$\Upsilon[J] = \frac{\mathrm{i}}{2\hbar}\int_C \mathrm{d}t\int_C \mathrm{d}t' J(t)J(t')\left\{\lim_{\omega\to 0}\left[\frac{\mathrm{i}}{2\mu'\omega\sinh\frac{\omega\beta\hbar}{2}} \times\left(\theta_C(t-t')\cos\omega(t-t'+\frac{\mathrm{i}\beta\hbar}{2}) + (t\leftrightarrow t')\right)\right]\right\}. \quad (14)$$

The function $\theta_C(t)$ in eq. (14) is a step function on the contour time path. To characterize the bath we choose the spectral density defined formally by $I(\omega) \equiv \pi\sum_i c_i^2/(2m_i\omega_i)\delta(\omega-\omega_i)$ as the Ohmic dissipation $I(\omega) = \mu\omega\gamma$. Here, the constant $\gamma$ relates to the mass-independent damping kernel, $\gamma(t) \equiv \int_0^\infty \mathrm{d}\omega 2I(\omega)/(\pi\mu\omega)$, by $\gamma(t) = 2\gamma\delta(t)$. In this case, $\Xi[J]$ is expressed as[1)]

$$\Xi[J] \equiv \Xi^{-+}[J] + \Xi^{--}[J] + \Xi^{-3}[J] + \Xi^{33}[J], \quad (15)$$

where

$$\Xi^{-+}[J] = \int_{t_I}^\infty \mathrm{d}t\int_{t_I}^t \mathrm{d}t' J_-(t)\frac{\mathrm{i}(1-\mathrm{e}^{-\gamma(t-t')})}{\hbar\mu\gamma}J_+(t'), \quad (16)$$

$$\Xi^{--}[J] = -\frac{1}{2\beta\hbar^2}\int_{t_I}^\infty \mathrm{d}t\int_{t_I}^t \mathrm{d}t' J_-(t) \times\left(\sum_{l=1}^\infty \frac{2\gamma\mathrm{e}^{-\nu_l|t-t'|}}{\mu\nu_l(\gamma^2-\nu_l^2)} - \frac{\beta\hbar\mathrm{e}^{-\gamma|t-t'|}}{2\mu\gamma}\cot\left(\frac{\gamma\beta\hbar}{2}\right) + \lim_{l\to 0}\frac{1}{\mu\nu_l^2+\mu\gamma|\nu_l|} - \frac{|t-t'|}{\mu\gamma} + \frac{1}{\mu\gamma^2}\right)J_-(t'), \quad (17)$$

$$\Xi^{-3}[J] = \frac{\mathrm{i}}{\beta\hbar^2}\sum_l\int_0^\infty \mathrm{d}t\int_0^{\beta\hbar}\mathrm{d}\tau J_-(t+t_I)\mathrm{e}^{-\nu_l\tau} \times\left[\frac{\mathrm{e}^{-\nu_l t}}{\mu\nu_l^2+\mu\gamma|\nu_l|} - \frac{1}{\mu\gamma}\left(\frac{1-\mathrm{e}^{-\nu_l t}}{\nu_l} - \frac{\mathrm{e}^{-\gamma t}-\mathrm{e}^{-\nu_l t}}{\nu_l-\gamma}\right)\right]J_3(\tau), \quad (18)$$

and

$$\Xi^{33}[J] = \frac{1}{2\beta\hbar^2}\sum_l\int_0^{\beta\hbar}\mathrm{d}\tau\int_0^{\beta\hbar}\mathrm{d}\tau' J_3(\tau) \times\frac{\mathrm{e}^{-\mathrm{i}\nu_l(\tau-\tau')}}{\mu\nu_l^2+\mu\gamma|\nu_l|}J_3(\tau'). \quad (19)$$

Here, $J_+ \equiv (J_1+J_2)/2$, $J_- \equiv J_1 - J_2$, and $\nu_l \equiv 2\pi l/(\beta\hbar)$.

To evaluate the rotator part $Z_S[J]$, we introduce the

completeness relations

$$\sum_{l=-\infty}^{\infty} |l\rangle\langle l| = 1. \tag{20}$$

Here, $\{|l\rangle\}$ in eq. (20) is a set of eigenstates of $L$ defined by $L|l\rangle = \hbar l|l\rangle$ for an integer $l$, and the matrix element of the function $f(\theta)$ is given by $\langle l|f(\theta)|l'\rangle = \int_{-\pi}^{\pi} \mathrm{d}\theta \mathrm{e}^{-\mathrm{i}l\theta} f(\theta) \mathrm{e}^{\mathrm{i}l'\theta}$. The overlap of the eigenstates is given by $\langle l|l'\rangle = \delta_{l,l'}$. We divide the time interval on the contour path $C$ into $N+1$ pieces ($t_0 = t_I, t_1, \ldots, t_N$, and $t_{N+1} = t_I - \mathrm{i}\beta\hbar$) and insert the completeness relations (20). The functional $Z_S[J]$ is then given by

$$Z_S[J] = \lim_{N\to\infty} \left(\prod_{j=1}^{N+1} \int_{-\pi}^{\pi} \mathrm{d}\theta_j\right)\left(\prod_{j=1}^{N+1} \frac{1}{2\pi} \sum_{l_j=-\infty}^{\infty}\right) \times \exp\left\{\mathrm{i}\sum_{j=1}^{N+1}\left[l_j(\theta_j - \theta_{j-1}) - \frac{\Delta t_j}{\hbar}\left(\frac{\hbar^2 l_j^2}{2\mu'} - J(t_{j-1})\theta_j\right)\right]\right\}_{\theta_0=\theta_{N+1}}, \tag{21}$$

where $\Delta t_j = t_j - t_{j-1}$ ($j = 1, \ldots, N+1$). The periodic boundary condition $\theta_0 = \theta_{N+1}$ arises from the "trace" operation involved in defining the generating functional. After integrating over $\theta_1, \theta_2, \ldots$, and $\theta_{N+1}$, we get $\delta_{0,l_j - l_{j-1} + \Delta t_j J_{j-1}/\hbar}$ ($j = 1, 2, \ldots,$ and $N+1$) and $\delta_{0,l_{N+1} - l_1 + \Delta t_{N+1} J_N/\hbar}$, which allow us to sum up over $l_1, l_2, \ldots,$ and $l_N$. Note that $\Delta t_j J(t_{j-1})/\hbar = \int_{t_{j-1}}^{t_j} \mathrm{d}t J(t)/\hbar$ is 0 or 1 because $J(t)$ is set as in eq. (6). Rewriting the result with the aid of the relation, $\sum_k \exp[\mathrm{i}(Ak^2 + Bk)] = \sum_l \sqrt{\mathrm{i}\pi/A} \exp[-\mathrm{i}(B + 2\pi l)^2/(4A)]$, we obtain

$$Z_S[J] = \frac{1}{\delta(0)} \delta_{0,R_J} \mathrm{e}^{\Upsilon[J]} Z_0 \times \sum_l \mathrm{e}^{-\frac{1}{\beta\hbar^2}\left[-2\pi l \int_C \mathrm{d}s(t_I - \mathrm{i}\beta\hbar - s)J(s) + \frac{\mu'}{2}(2\pi l)^2\right]}, \tag{22}$$

where $R_J = \int_C \mathrm{d}s J(s)/\hbar$ and $Z_0 = \int_{-\infty}^{\infty} \mathrm{d}\theta \times \langle\theta|\hat{\rho}_I^S \hat{U}_S^\dagger(\infty, t_I)\hat{U}_S(\infty, t_I)|\theta\rangle$ in which $\hat{\rho}_I^S$ and $\hat{U}_S^{(\dagger)}$ are defined by $\hat{\rho}_I^S \equiv \mathrm{T}_\tau \exp\left(-(1/\hbar)\int_0^{\beta\hbar} \mathrm{d}\tau \tilde{H}_S\right)$ and $\hat{U}_J(\infty, t_I) \equiv \mathrm{T}_t \exp\left(-(\mathrm{i}/\hbar)\int_{t_I}^{\infty} \mathrm{d}t \tilde{H}_S\right)$. The condition $R_J = 0$ selects transitions induced by irradiated pulses, as shown later. From eqs. (12), (13) and (22) we have the generating functional in the form

$$Z[J] = \frac{1}{\delta(0)} Z_B[J=0] Z_0 \delta_{0,R_J} \mathrm{e}^{\Xi[J]} \times \sum_l \mathrm{e}^{-\frac{1}{\beta\hbar^2}\left[-2\pi l \int_C \mathrm{d}s(t_I - \mathrm{i}\beta\hbar - s)J(s) + \frac{\mu'}{2}(2\pi l)^2\right]}. \tag{23}$$

In consequence of eqs. (6) and (23), we arrive at an expression for a two-body correlation function

$$\langle[\cos\theta(t_1), \cos\theta(t_2)]\rangle = \frac{\sum_l \mathrm{e}^{-\frac{\mu'(2\pi l)^2}{2\beta\hbar^2}} \cosh\left(2\pi l \frac{t_1 - t_2}{\beta\hbar}\right)}{\sum_l \mathrm{e}^{-\frac{\mu'(2\pi l)^2}{2\beta\hbar^2}}} \times \mathrm{i}\mathrm{e}^{\tilde{S}_0(t_1 - t_2)} \sin\left(-\frac{\hbar(1 - \mathrm{e}^{-\gamma(t_1 - t_2)})}{2\mu\gamma}\right), \tag{24}$$

where

$$\tilde{S}_0(t_1 - t_2) = \frac{1}{\beta}\left[\sum_{l=1}^{\infty} \frac{2\gamma(\mathrm{e}^{-\nu_l(t_1 - t_2)} - 1)}{\mu\nu_l(\gamma^2 - \nu_l^2)} - \frac{\beta\hbar(\mathrm{e}^{-\gamma(t_1 - t_2)} - 1)}{2\mu\gamma} \cot\frac{\gamma\beta\hbar}{2} - \frac{t_1 - t_2}{\mu\gamma}\right]. \tag{25}$$

The above result reduces to the correlation function of a free rotator system without the bath for $\gamma \to 0$. Here, we note that $\sum_i \mu_i$ in $\mu'$ is diverged for the low frequency of $I(\omega)$ as $\sum_i \mu_i = \int_{\omega_c}^{\infty} \mathrm{d}\omega 2I(\omega)/\pi\omega^3 = 2\mu\gamma/\omega_c$, where $\omega_c$ is the low-frequency cutoff. The damping function $\gamma(t)$ is rewritten using $\omega_c$ as $\gamma(t) = \int_{\omega_c}^{\infty} \mathrm{d}\omega 2I(\omega)/(\pi\mu\omega)\cos(\omega t) = 2\gamma\delta(t) - 2\gamma\sin(\omega_c t)/(\pi t)$, and we find that $\gamma(t)$ has a long time tail. In the present study we focus on the motion of the rotator in a short time period so that the cutoff $\omega_c$ can be regarded as small.

We now numerically demonstrate our results by taking a parameter from a rotational motion of methyl group (-$CH_3$) in a toluene molecule. We set $\mu = 2.062$ [kg·m$^2$] and introduce a parameter, $\alpha = \hbar/(2\mu) = 2.547 \times 10^{12}$ [Hz] ($\hbar\alpha = 2.674 \times 10^{-22}$ [J] $= 1.666 \times 10^{-3}$ [eV]). We consider the case where the system is in a nonpolar solvent whose effects were commonly studied using the present model with the aid of the Langevin equation.

In Fig. 1, we plotted absorption spectra $\sigma(\omega)$ calculated from eq. (5) for different temperatures (a) $T = 1$ [K], (b) $T = 10$ [K], and (c) $T = 100$ [K], where frequency is normalized by $\alpha$. The free rotator ($\gamma = 0$ [Hz]) and the weakly damped rotator ($\gamma = 1.3 \times 10^6$ [Hz]) are depicted as a solid and a dashed line, respectively. For a free rotator ($\gamma \to 0$), eq. (24) reduces to $\sigma(\omega) = \{\pi/(4\hbar)\}\sum_l a_l\{\delta(\omega - (2l+1)\alpha) - \delta(\omega + (2l+1)\alpha)\}$, where $a_l \equiv (\mathrm{e}^{-\beta E_l} - \mathrm{e}^{-\beta E_{l+1}})$ and $E_l = \hbar^2 l^2/(2\mu)$. We denote this spectrum by the solid lines at the position $(2l+1)\alpha$ with the height $a_l$. The peak at $(2l+1)\alpha$ corresponds to the transition from $|l\rangle$ to $|l \pm 1\rangle$ and its intensity $a_l$ is determined by the difference of initial thermal distribution. The distribution of peak intensities therefore shifts to blue as temperature increases. For the damped rotator, we set the very weak damping constant $\gamma$ which is much smaller than the energy gap between neighboring peaks in the free rotator $2\alpha$. The spectrum for the weakly damped case, however, becomes a continuous broad band regardless of temperatures as shown in the dashed line in Figs. 1(a)–1(c). This can be understood from the following argument. The linear coupling between the heat bath and the system changes the momentum of inertia from $\mu$ to $\mu'$ so that the new rotational energy level is given by

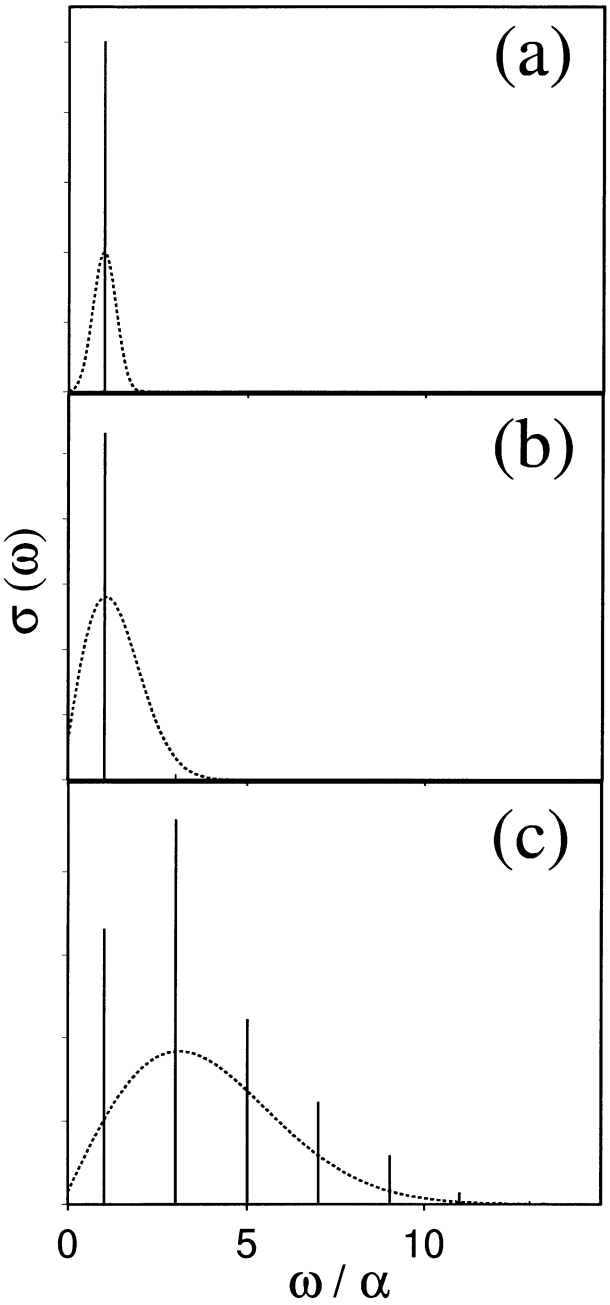


Fig. 1. Absorption spectra at different temperatures (a) $T = 1$ [K], (b) $T = 10$ [K], and (c) $T = 100$ [K]. Damping constant is set as $\gamma = 0.0$ [Hz] for a free rotator (solid line) and $\gamma = 1.3 \times 10^6$ [Hz] for a damped rotator (dashed line).

$E'_l = l^2\hbar^2/(2\mu')$. In the Ohmic dissipation, $\mu'$ becomes infinity if the cutoff $\omega_c$ goes to zero, which changes the rotational discrete energy levels into a continuous band. Notice that the line shape reflects the initial thermal distribution and we see that the peak shifts to higher frequency and the band broadens as the temperature increases. Using the same procedure, we find that the symmetric correlation function $\langle\{\cos\theta(t_1), \cos\theta(t_2)\}\rangle$ for $t_1 > t_2$ is given by replacing $\sin(\cdots)$ in eq. (24) with $-\mathrm{i}\cdot\cos(\cdots)$. In the classical limit ($\hbar \to 0$), this result reduces to eq. (3.23) in ref. 6, which is obtained from a classical stochastic approach.

In this Letter, we derived an analytical expression of the generating functional for a rotator system that is linearly coupled to a harmonic bath with the use of a unitary transformation and path integral method. The generating functional leads to the two-time correlation function which is related to the response functions of the dielectric relaxation, the infrared absorption, and the Raman scattering process spectrum. To demonstrate our result, we employed the parameter from the rotational motion of a methyl group and plotted absorption spectra for different temperatures and damping constants. In the absence of damping, the spectrum consists of the discrete lines corresponding to the rotational branches. On the other hand, a broad band peak appeared for the damped case due to the continuous energy band induced by the Ohmic dissipation.

In this study we assumed continuous Ohmic distribution for the spectral distribution of the heat bath. If we employ the discrete spectra distribution, such as $I(\omega) \propto \delta(\omega - \omega_B)$, then an absorption spectrum is no longer continuous and consists of the discrete energy levels. The effects of spectral distribution of the bath upon the absorption spectra and the detailed derivation of the present results will be presented in a separate paper. Generalization of the present study to the three- and four-time correlation functions aiming at the two-dimensional Raman and infrared spectroscopy[7] is under investigation.

In this study, we limited our analysis to the free rotator case. In many realistic problems, however, the rotators are confined by a potential. For instance, internal rotation of a molecule has rotational barriers which are expressed by a periodic potential $\sum_n V_n\{1-\cos(n\theta)\}/2$, where $V_n$ is a parameter of the barrier height. For small barriers, we can take into account such effects perturbatively by expanding the source terms of the generating functional. For large barriers where the perturbative theory breaks down, we can employ a variety of variational approaches, such as the optimized perturbation method using the generating functional.[8,9] We will leave them for future studies.

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1) H. Grabert, P. Schramm and G.-L. Ingold: Phys. Rep. **168** (1988) 115.
2) V. Hakim and V. Ambegaokar: Phys. Rev. A **32** (1985) 423.
3) S. Mukamel: *Principle of Nonlinear Optical Spectroscopy* (Oxford, New York, 1995).
4) R. Fukuda, M. Sumino and K. Nomoto: Phys. Rev. A **45** (1992) 3559.
5) R. Fukuda, M. Komachiya, Y. Yokojima, Y. Suzuki, K. Okumura and T. Inagaki: *Novel Use of Legendre Transformation in Field Theory and Many Particle Systems —On-shell Expansion and Inversion Method—* Prog. Theor. Phys. Suppl. **121** (1995).
6) C. Uchiyama and F. Shibata: Physica A **153** (1988) 469.
7) Y. Tanimura and S. Mukamel: J. Chem. Phys. **99** (1993) 9496.
8) P. M. Stevenson: Phys. Rev. D **23** (1981) 2916.
9) Y. Suzuki and Y. Tanimura: Phys. Rev. E **59** (1999) 1475.