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On the Temperature Dependence of Molecular Line Shapes Due to Linearly Coupled Phonon Bands†

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Simple closed-form expressions of line-shape functions are derived for models of a two-level chromophore linearly coupled to harmonic oscillator baths on the basis of an accurate approximation for the coth(x/2) function. The expressions are valid for arbitrary temperature and can be extended to a general spectral density given by a sum of algebraic terms with exponential damping factors. Detailed analyses for three typical spectral densities reveal, in the strong-coupling limit, general temperature dependences of the line widths, and in the weak coupling limit, important features of temperature dependence.

The spectral line shape of a collection of molecules reflects the dynamical and statistical nature of the transitions being probed and thus is an important frequency domain probe of the microscopic details of the molecules and their interactions with the environment. For simple molecules in the gas phase[1] or perfect crystalline media,[2−4] well-established theoretical results exist, providing satisfactory explanations for important characteristics of line shapes. For large macromolecules or in more complex condensed media,[4−7] the microscopic implications of the spectral line shapes remain unknown in many cases.

One of the main issues of molecular spectroscopy in general condensed media[4−7] is how to characterize and quantify different line-broadening mechanisms that are not known a priori. Nonlinear spectroscopies[6−16] such as hole burning[8−10] and photon echo[11−16] are major experimental approaches that can address this issue to provide important information on the dynamics of chromophores in molecular solids[11,12] and liquids.[6,13−16] However, in general, only partially complete information can be obtained from these experiments, and the assumptions involved in the interpretations are not always simple to confirm. Recent advances in single-molecule spectroscopy[17] complement these subensemble methods and in principle allow direct experimental study of individual relaxation dynamics. However, limitations in the time resolution and selectivity of the present level of experiments pose difficulties in the full realization of its potential. Temperature-dependence studies[18−23] and comparisons with ensemble experiments[18,22,24] have important implications in this regard. The former can assess the contributions of different line-broadening mechanisms indirectly, and the latter can confirm whether the small samples of single-molecule spectroscopy are representative of the ensemble.

In light of recent progress in single-molecule spectroscopy, detailed accounts of the line shape of a molecule in a condensed medium and its temperature dependence have direct experimental relevance and are thus a meaningful issues. The present article provides expressions that are useful in such analyses of the models of a two-level chromophore coupled to harmonic oscillator baths. Numerous studies have been conducted on these prototypical models,[3,6,25−35] but the issues being addressed here are relatively new. For many spectral densities of the bath, the form of the line shape in the very low or the very high temperature limit is fairly well-known, but the crossover between the two asymptotic regions is less well characterized. Without definite information on the values of parameters that determine the spectral density, it is not always clear whether the experimental condition belongs to either of the asymptotic regions. Therefore, knowing the general line shape over the entire range of temperature has practical importance regarding the proper analysis of the line shape without unfounded assumptions. Even for the simplest models with linear chromophore−bath coupling, our knowledge of the general temperature dependence is incomplete. On the basis of a simple and accurate approximation, we derive general expressions that enable us to obtain a more concrete understanding of how the spectral line shape varies with temperature for a class of spectral densities with exponential damping factors.

Consider a chromophore embedded in a bath of harmonic oscillators. The total Hamiltonian in the absence of radiation is assumed to be

$$H = E_{\mathrm{g}}|\mathrm{g}\rangle\langle\mathrm{g}| + (E_{\mathrm{e}} + \delta H_{\mathrm{b}})|\mathrm{e}\rangle\langle\mathrm{e}| + H_{\mathrm{b}} \qquad (1)$$

where $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$ are respectively the ground and the excited states of the chromophore, and E_{g} and E_{e} are their energies. H_{b} is the Hamiltonian of the bath for the ground-state chromophore, and δH_{b} is the change of the bath Hamiltonian upon excitation of the chromophore. It is assumed that $H_{\mathrm{b}} = \sum_n \hbar\omega_n(b_n^* b_n + {}^1/_2)$, and $\delta H_{\mathrm{b}} = \sum_n \hbar c_n(b_n + b_n^*)/\sqrt{2\omega_n}$, where ω_n is the frequency of the nth bath mode and $b_n^*(b_n)$ is the creation (annihilation) operator of the corresponding phonon. The spectral density of the bath is defined as

$$J(\omega) \equiv \sum_n \frac{c_n^2}{2\omega_n}\delta(\omega_n - \omega) \qquad (2)$$

In the presence of radiation, $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$ are coupled via a transition dipole, and the absorption line shape is given by

$$I(\Omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t \exp\{\mathrm{i}\Omega t - g_{\mathrm{r}}(t) - \mathrm{i}g_{\mathrm{i}}(t)\} \qquad (3)$$

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where Ω is the photon frequency relative to $(E_e - E_g)/\hbar$ and

$$g_r(t) \equiv \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \coth\left(\frac{\beta\hbar\omega}{2}\right)(1 - \cos(\omega t)) \tag{4}$$

$$g_i(t) \equiv \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} (\sin(\omega t) - \omega t) \tag{5}$$

We consider the following class of spectral densities

$$J_n(\omega) = \frac{\alpha_n}{n!} \frac{\omega^n}{\omega_c^{n-1}} e^{-\omega/\omega_c} \tag{6}$$

where α_n is a dimensionless constant determining the strength of the coupling, and ω_c is the cutoff frequency dictating the spectral width of the bath. Results for three cases ($n = 1, 2, 3$) in eq 6 are presented in detail; these can be related to different spatial dimensions in the deformation potential model.[9] The corresponding expressions for $g_r(t)$ and $g_i(t)$ are denoted as $g_r^{(n)}(t)$ and $g_i^{(n)}(t)$. For the spectral density given by eq 6, explicit expression for eq 5 can easily be obtained, but this is not the case for eq 4 because of the presence of $\coth(\beta\hbar\omega/2)$. Series expansions of this function can be used, but instead of using the full series, we suggest the following interpolation

$$\coth\left(\frac{x}{2}\right) \approx 1 + 2e^{-x} + 2e^{-2x} + \frac{2}{x}e^{-5x/2} \tag{7}$$

where $x = \beta\hbar\omega$. This approximation is obtained by the following two steps: (i) expansion of $\coth(^x/_2)$ with respect to e^{-x} up to the second order and (ii) supplementing this expansion with an additional term that decays faster than e^{-2x} while reproducing the small x expansion of $\coth(^x/_2)$ up to the order of x^0. Figure 1 compares eq 7 with the exact value. The agreement is remarkably good. Also shown are the small e^{-x} and small x expansions up to the first three terms. The inset in Figure 1 shows that the approximation, eq 7, is always better than these two expansions in the crossover region. This is interesting considering that the small x expansion of eq 7, $^2/_x + {^x/_4}$, is in error[36] with the correct expansion, $^2/_x + {^x/_6}$, by $^x/_{12}$.

Using eq 7, one can perform the explicit integration of eq 4 for the class of spectral densities given by eq 6. Before presenting the results, we first define

$$\theta \equiv \beta\hbar\omega_c \tag{8}$$

$$\tau_s \equiv \frac{\omega_c t}{1 + s\theta} \tag{9}$$

Then, for $n = 1$,

$$g_r^{(1)}(t) \approx \frac{\alpha_1}{2}\left\{\ln(1 + \tau_0^2) + 2\ln(1 + \tau_1^2) + 2\ln(1 + \tau_2^2) + 4\frac{(1 + 5\theta/2)}{\theta}\int_0^{\tau_{5/2}} d\tau' \tan^{-1}(\tau')\right\} \tag{10}$$

$$g_i^{(1)}(t) = \alpha_1(\tan^{-1}(\tau_0) - \tau_0) \tag{11}$$

For $n = 2$,

$$g_r^{(2)}(t) \approx \frac{\alpha_2}{2}\left\{\frac{\tau_0^2}{1 + \tau_0^2} + \frac{2}{(1 + \theta)}\frac{\tau_1^2}{(1 + \tau_1^2)} + \frac{2}{(1 + 2\theta)}\frac{\tau_2^2}{(1 + \tau_2^2)} + \frac{1}{\theta}\ln(1 + \tau_{5/2}^2)\right\} \tag{12}$$

$$g_i^{(2)}(t) = \frac{\alpha_2}{2}\left(\frac{\tau_0}{1 + \tau_0^2} - \tau_0\right) \tag{13}$$

Finally, for $n = 3$,

$$g_r^{(3)}(t) \approx \frac{\alpha_3}{3}\left\{\frac{\tau_0^4 + 3\tau_0^2}{(1 + \tau_0^2)^2} + \frac{2}{(1 + \theta)^2}\frac{\tau_1^4 + 3\tau_1^2}{(1 + \tau_1^2)^2} + \frac{2}{(1 + 2\theta)^2}\frac{\tau_2^4 + 3\tau_2^2}{(1 + \tau_2^2)^2} + \frac{2}{\theta(1 + 5\theta/2)}\frac{\tau_{5/2}^2}{(1 + \tau_{5/2}^2)}\right\} \tag{14}$$

$$g_i^{(3)}(t) = \frac{\alpha_3}{3}\left(\frac{2\tau_0}{(1 + \tau_0^2)^2} - \tau_0\right) \tag{15}$$

Although not shown here, explicit expressions can also be obtained for $n > 3$. The above expressions are valid for arbitrary values of temperature and ω_c. Because these expressions do not involve an infinite series, possible singularities are naturally avoided. Because the explicit functional forms in the time domain are available, a clear analysis of the integration in eq 3 can be made for various limits. Furthermore, these expressions are advantageous for more general situations where the spectral densities are given by a sum of functions of the type of eq 6. In the present work, we consider only the three model spectral densities listed above and analyze the features of the line shape in the limits of strong and weak coupling.

A. Strong-Coupling Limit ($\alpha_n \gg 1$)

The strong-coupling limit is defined as the limit of large enough α_n such that quadratic expansions of $g_r^{(n)}(t)$ and $g_i^{(n)}(t)$ in eq 3 result in a sufficiently good overall approximation of the line shape. The necessary condition for this approximation is $\alpha_n \gg 1$, but sufficient conditions differ depending on n and temperature. Given that these conditions are fulfilled, expansions of eqs 10−15 up to the second order of t lead to the following Gaussian forms of the line shape functions:

$$I_n(\Omega) \approx \frac{1}{\sqrt{2\pi\alpha_n\omega_c^2 D_n(\theta)^2}} \exp\left(-\frac{\Omega^2}{2\alpha_n\omega_c^2 D_n(\theta)^2}\right) \tag{16}$$

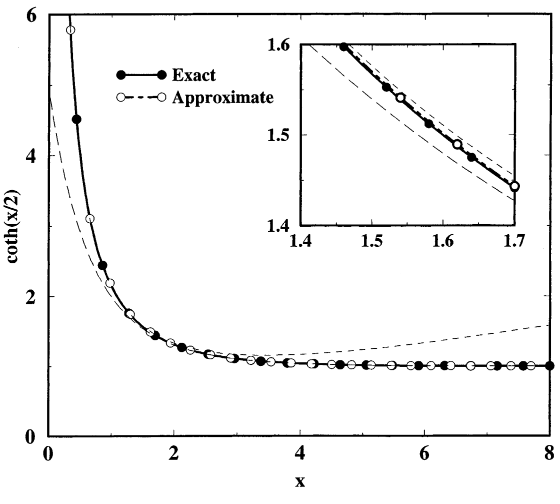

Figure 1. Comparison of the approximation, eq 7, with the exact value of $\coth(^x/_2)$. The short-dashed line corresponds to $^2/_x + {^x/_6}$, and the long-dashed line corresponds to $1 + 2e^{-x} + 2e^{-2x}$. The inset shows the crossover region between these two expansions.

where

$$D_n(\theta)^2 = 1 + \frac{2}{(1+\theta)^{n+1}} + \frac{2}{(1+2\theta)^{n+1}} + \frac{2}{n\theta(1+5\theta/2)^n} \tag{17}$$

Figure 2 shows the scaled line width $D_n(\theta)$ for each n as a function of the scaled temperature $1/\theta = k_BT/\hbar\omega_c$. In all cases, the widths show monotonic crossover from the finite zero-temperature limit to high-temperature asymptotic behavior, $\sqrt{2k_BT/(n\hbar)}$. Temperature dependences in crossover regions seem almost linear. The approach to the high-temperature limit is faster for smaller n.

The expressions presented above are valid only in the sufficiently strong coupling limit such that the line shape has a Gaussian form over the entire range of temperature. Equations 16 and 17 indicate how the line width in that limit varies with temperature for the class of spectral densities given by eq 2. These results can be generalized to the cases where the spectral density is given by a sum of algebraic functions with exponential damping factors. Given that the assumption of strong coupling can be confirmed either directly or indirectly, our expressions can help to obtain microscopic parameters from the temperature variation of experimental line width and also can be used to understand ensemble line shape for general cases where there exist inhomogeneity in α_n and ω_c as well as in the transition frequency.

B. Weak-Coupling Limit ($\alpha_n \ll 1$)

The weak-coupling limit is defined as the limit where α_n is small enough such that all the exponentials in eq 3 with bounded exponents can be expanded up to the first order of α_n. The necessary condition for this limit is $\alpha_n \ll 1$, but again, sufficient conditions depend on n and temperature.

For $n = 1$, all of the exponents are unbounded except for $\tan^{-1}(\tau_0)$ in $g_i^{(1)}(t)$ given by eq 11. The weak-coupling limit brings no substantial simplification for this case. In the zero-temperature limit, $\theta = \infty$, the line-shape function can be approximated as

$$I_1(\Omega, T=0) \approx \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Omega+\alpha_1\omega_c)t}(1+\tau_0^2)^{-\alpha_1/2} \times (1 - \mathrm{i}\alpha_1 \tan^{-1}(\tau_0)) \tag{18}$$

where $-\,\mathrm{i}\alpha_1 \tan^{-1}(\tau_0)$ causes the above line-shape function to be asymmetric with respect to $(\Omega + \alpha_1\omega_c)$ by contributing an antisymmetric function. For a qualitative understanding of the line shape near the peak maximum, disregarding the asymmetry, this antisymmetric contribution can be neglected. Thus, for $|\Omega + \alpha_1\omega_c| \ll \omega_c$,

$$I_1(\Omega, T=0) \approx \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Omega+\alpha_1\omega_c)t}(1+\tau_0^2)^{-\alpha_1/2} \propto |\Omega + \alpha_1\omega_c|^{\alpha_1-1}, \quad \alpha_1 < 1 \tag{19}$$

This type of power-law divergence is well-known[31,33] and has been considered to be the signature of the Ohmic behavior of the spectral density.[9] How this singular behavior changes at finite temperature is important in various contexts and has been addressed before.[33] Equation 10 gives a more quantitative analysis of the transition. At finite temperature, because of the second and third terms in eq 10, the effective value of the power becomes less negative. In addition, at finite temperature, the last term in eq 10 is unbounded and becomes proportional to $|t|$, thus dominating other logarithmic terms. The line shape near the peak maximum is determined by the long-time asymptotic behavior of this integrand. That is, for $|\Omega + \alpha_1\omega_c| \ll \omega_c/(1 + 5\theta/2)$,

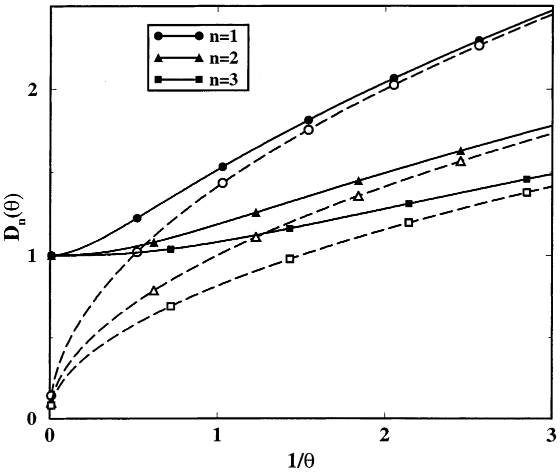

Figure 2. $D_n(\theta)$, eq 17, as a function of scaled temperature, $^1/_\theta = k_BT/\hbar\omega_c$. The long-dashed lines with open symbols correspond to the high-temperature asymptotics.

$$I_1(\Omega) \approx \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Omega+\alpha_1\omega_c)t - \pi\alpha_1|t|/(\beta\hbar)} = \frac{\pi\alpha_1 k_BT/\hbar}{(\Omega+\alpha_1\omega_c)^2 + (\pi\alpha_1 k_BT/\hbar)^2} \tag{20}$$

Thus, the zero-temperature divergence is replaced by a finite Lorentzian peak with a width proportional to temperature. This result is consistent with the observation that the pure dephasing rate is proportional to temperature[25,32,33] for an Ohmic bath at finite temperature. The present analysis clarifies that this behavior is limited to a frequency range smaller than $\omega_c/(1 + 5\theta/2)$, beyond which the power-law behavior persists.

For the case of $n = 2$, $g_r^{(2)}(t)$ consists of both bounded and unbounded terms, except for the zero-temperature limit, where all of the terms of $g_r^{(2)}(t)$ are bounded and the line shape can be approximated as

$$\begin{aligned} I_2(\Omega, T=0) &\approx \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\Omega+\alpha_2\omega_c/2)t} \times \left\{1 - \frac{\alpha_2}{2}\frac{\tau_0^2}{1+\tau_0^2} - \mathrm{i}\frac{\alpha_2}{2}\frac{\tau_0}{1+\tau_0^2}\right\} \\ &= \left(1 - \frac{\alpha_2}{2}\right)\delta\left(\Omega + \frac{\alpha_2\omega_c}{2}\right) + \frac{\alpha_2}{2\omega_c}H\left(\Omega + \frac{\alpha_2\omega_c}{2}\right)\mathrm{e}^{-|\Omega/\omega_c + \alpha_2/2|} \end{aligned} \tag{21}$$

where H is the Heavyside function. Thus, for $n = 2$, a well-resolved zero phonon line (ZPL) and a phonon sideband (PSB) exist in the zero-temperature limit. This feature changes at finite temperature. Using the full expression (eq 12) and expanding the exponentials with bounded exponents up to the first order of α_2, one can show that the weak-coupling limit of finite-temperature line shape can be approximated as

$$
\begin{aligned}
I_2(\Omega) \approx & \left\{1 - \frac{\alpha_2}{2}\left(1 + \frac{2}{(1+\theta)} + \frac{2}{(1+2\theta)}\right)\right\} \\
& \times \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}(\Omega+\alpha_2\omega_c/2)t}(1+\tau_{5/2}^2)^{-\alpha_2/(2\theta)} \\
& + \frac{\alpha_2}{4\pi}\int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{e}^{\mathrm{i}(\Omega+\alpha_2\omega_c/2)t}(1+\tau_{5/2}^2)^{-\alpha_2/(2\theta)} \\
& \times \left(\frac{1}{1+\tau_0^2} + \frac{2}{(1+\theta)(1+\tau_1^2)}\right. \\
& \left. + \frac{2}{(1+2\theta)(1+\tau_2^2)} - \mathrm{i}\frac{\tau_0}{(1+\tau_0^2)}\right)
\end{aligned} \tag{22}
$$

where the first term corresponds to the finite-temperature correction of the ZPL and the second term corresponds to that of the PSB. An important fact is that in the low-temperature region the first term of eq 22 shows a power-law divergence, as in the case of the zero-temperature limit of $n = 1$. That is, for $0 < T < \hbar\omega_c/(k_B\alpha_2)$,

$$
I_2(\Omega)_{\mathrm{ZPL}} \propto |\Omega + \alpha_2\omega_c/2|^{\alpha_2 k_B T/(\hbar\omega_c)-1} \tag{23}
$$

Thus, the ZPL is smeared out and shows power-law behavior with an exponent that is linearly dependent on temperature. This type of power-law dependence has already been recognized by Reichman et. al.,[33] but only in the context of the high-temperature limit.

For the case of $n = 3$, all terms of $g_r^{(3)}(t)$ are bounded, and the following approximation becomes valid:

$$
\begin{aligned}
& \mathrm{e}^{-g_r^{(3)}(t)-\mathrm{i}g_i^{(3)}(t)} \approx \\
& \quad \mathrm{e}^{\mathrm{i}\alpha_3\tau_0/3}\left(1 - g_r^{(3)}(\infty) + g_r^{(3)}(\infty) - g_r^{(3)}(t) - \mathrm{i}\frac{\alpha_3\tau_0}{3(1+\tau_0^2)^2}\right)
\end{aligned} \tag{24}
$$

where

$$
\begin{aligned}
& g_r^{(3)}(\infty) = \\
& \quad \frac{\alpha_3}{3}\left\{1 + \frac{2}{(1+\theta)^2} + \frac{2}{(1+2\theta)^2} + \frac{2}{\theta(1+5\theta/2)}\right\}
\end{aligned} \tag{25}
$$

Explicit contour integrations of eq 3 with the approximation of eq 24 can be made. The resulting line shape is

$$
\begin{aligned}
& I_3(\Omega) \approx (1 - g_r^{(3)}(\infty))\,\delta\left(\Omega + \frac{\alpha_3\omega_c}{3}\right) + \\
& \frac{\alpha_3}{3\omega_c}\left|\frac{\Omega}{\omega_c} + \frac{\alpha_3}{3}\right|\left\{H\left(\frac{\Omega}{\omega_c} + \frac{\alpha_3}{3}\right)\mathrm{e}^{-|\Omega/\omega_c+\alpha_3/3|} + \mathrm{e}^{-(1+\theta)|\Omega/\omega_c+\alpha_3/3|} + \right. \\
& \qquad \left. \mathrm{e}^{-(1+2\theta)|\Omega/\omega_c+\alpha_3/3|}\right\} + \frac{\alpha_3}{6\theta\omega_c}\mathrm{e}^{-(1+5\theta/2)|\Omega/\omega_c+\alpha/3|}
\end{aligned} \tag{26}
$$

where the first term corresponds to the ZPL and the remaining terms form the PSB. The fact that the ZPL has a delta function form implies that, for the present model, the width of the ZPL does not depend on temperature, in contrast to its intensity, which decreases with temperature. However, the PSB exhibits an interesting temperature dependence. Figure 3 shows the PSB at three different values of temperature. In the zero-temperature limit, the PSB is confined only to the positive side of the ZPL. Raising the temperature causes the PSB to be more symmetric, but the positive-side width remains almost invariant. In the very high temperature limit, the PSB becomes virtually symmetric and peaked at the position of the ZPL.

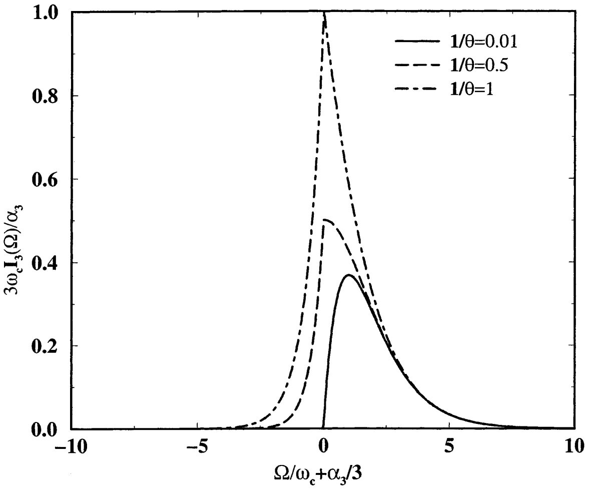

Figure 3. Phonon sidebands for three temperatures for the line-shape function $I_3(\Omega)$ given by eq 26.

It is well-known that the spectral features in the weak-coupling limit depend critically on the dimensionality of the spectral density. The analyses here substantiate this fact and provide a more quantitative basis for the understanding of their temperature dependences. Experimental confirmation of these aspects may be possible, given that other line-broadening mechanisms can be well identified.

In the present work, we disregarded line broadening due to lifetime decay, nonlinear system−bath couplings, and anharmonic bath modes. Our analyses are meaningful, given that these other mechanisms are negligible or can be incorporated independently. Another important issue is the form of the spectral density. Equation 6 represents those forms that are widely used in theoretical treatments of dissipative quantum dynamics,[34] but the actual spectral density in real systems can be different in a number of ways. The power-law behavior of the spectral density in the small ω region is quite general and reflects the effective dimensions of the bath, but the high-frequency tail can be more complicated than the exponential form. If the maximum and the range of the spectral density can be well fitted by eq 6, with a suitable choice of n, then it is expected that the deviation from the present result is small and is limited to a narrow range of temperature. Substantial differences can occur if the spectral density consists of multiple bands with well-separated frequency ranges. The best approach for these cases, within the present model, is to include the high-frequency portions (much larger than room temperature) as a renormalization of the system Hamiltonian and to model the low-frequency portions (smaller or comparable to room temperature) by a linear combinations of functions of the type of eq 6. The general form of $g_r(t)$ can be obtained for this model spectral density also. Many examples of complicated spectral densities including the cases with additional vibronic couplings can be addressed in this way, but the nature of the temperature dependence and the adequacy of our approach depend on specfic details of the system, which are beyond the scope of the present work.

Summarizing the main results of the present article, under the assumption that the spectral density of the bath can be modeled by eq 2, we have (i) derived closed-form expressions for $g_r(t)$ (eqs 10, 12, and 14); (ii) derived line-width expressions in the strong-coupling limit; and (iii) analyzed important characteristics of temperature dependences in the weak-coupling limit. Results (i) and (ii) are valid over the entire range of temperature. The crucial step in attaining these results has been the use of the simple approximation for $\coth(^x/_2)$ given in eq 7. In fact, this approximation is not limited to the line-shape theory but can also be applied to other areas of dissipative quantum dynamics[6,34] including surface scattering[37] and excitation energy-transfer reactions.[38] It will be interesting to discover whether these applications can also produce new and useful results.

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