Time-dependent optical linewidth in fluctuating environments: Stochastic models *

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Time-resolved optical lineshapes are calculated using a second-order inhomogeneous cumulant expansion. The calculation shows that in the inhomogeneous limit the optical spectra are determined solely by two-time correlation functions. Therefore, measurements of the Stokes-shift correlation function and the inhomogeneous linewidth cannot provide information about the heterogeneity lifetime for systems exhibiting dynamic heterogeneities. The theoretical results are illustrated using a stochastic model for the optical transition frequencies. The model rests on the assumption that the transition frequencies are coupled to the environmental relaxation of the system. The latter is chosen according to a free-energy landscape model for dynamically heterogeneous dynamics. The model calculations show that the available experimental data are fully compatible with a heterogeneity lifetime on the order of the primary relaxation time.

I. Introduction

The non-exponential response of supercooled liquids and other systems exhibiting slow relaxation has been a topic of many investigations, cf.[1, 2]. At present, there seems to be consensus about the fact that the primary or \( \alpha \)-relaxation in supercooled liquids near the calorimetric glass transition temperature \( T_g \) is of a heterogeneous nature[3, 4]. Several experimental techniques have been invented in order to monitor various aspects of these dynamic heterogeneities[3]. A supercooled liquid above \( T_g \) represents an ergodic system on long time scales. Therefore, the lifetime of the dynamic heterogeneities is finite. Up to now a couple of experimental methods exist that are able to detect these lifetimes. All of them are based on the idea of selecting a sub-ensemble of slowly relaxing entities and monitor its re-equilibration afterwards. The development of such techniques started with the invention of reduced four-dimensional (4d) NMR[7], which subsequently has been applied to a number of glass-forming systems[7, 8, 9, 10]. Other relevant techniques are the deep-bleach experiment designed by Cicerone and Ediger[11] and the atomic force microscopy method used by Russell and Israeloff[12].

A different experimental technique to monitor the dynamical behavior of liquids is provided by time-resolved fluorescence and phosphorescence spectroscopy, for a recent review see[13]. After an initial optical excitation with a laser-pulse, the time-dependent emission spectra are observed, cf. Fig.1. Most theoretical investigations of time-resolved fluorescence have concentrated on the Stokes-shift correlation function, which is related to the

* dedicated to Prof. Hans Sillescu on occasion of his 65th birthday
time-dependent mean $\langle \omega(t) \rangle$ of the emission spectrum:

$$C(t) = \frac{\langle \omega(t) \rangle - \langle \omega(\infty) \rangle}{\langle \omega(0) \rangle - \langle \omega(\infty) \rangle}$$

In particular, the dependence of $C(t)$ on molecular variables of the solvent have been investigated for both, polar and nonpolar solvation, see also the list of references in ref. [13].

In the field of supercooled liquids, triplet state solvation experiments have been applied. The observed behavior of the time-resolved inhomogeneous broadening of the optical lines has been interpreted in terms of dynamic heterogeneities. For one well studied system, quinoxaline (QX) in supercooled 2-methyltetrahydrofuran (MTHF), it has been concluded that the lifetime of the dynamic heterogeneities or the ’re-equilibration time’, $\langle \tau_{req} \rangle$, exceeds the mean time scale of the $\alpha$-relaxation, $\langle \tau_{\alpha} \rangle$, considerably. This is a somewhat surprising result for the following reasons. In all 4d-NMR experiments, performed on a variety of glassformers, ranging from polymers to simple molecular liquids, $\langle \tau_{req} \rangle \simeq \langle \tau_{\alpha} \rangle$ has been found. Furthermore, a strong temperature dependence of $\langle \tau_{req} \rangle$ has been observed in the deep-bleach experiments. These techniques cover the temperature range in which the solvation experiments have been performed. Therefore, MTHF is assumed to behave different from all systems studied so far. In addition, the finding of a long $\langle \tau_{req} \rangle$ relies on a purely phenomenological interpretation of the data in terms of a very special model.

It is the purpose of the present paper to present a sound theoretical description of time-dependent optical line shapes in complex systems. The actual calculation is based on a so-called inhomogeneous cumulant expansion. The results obtained bear a formal similarity to those of ref. [23], thus partly validating the phenomenological approach used there. In order to illustrate the general results, I then treat the optical transition frequencies as a non-Markovian stochastic process and calculate the relevant quantities in terms of a free-energy landscape model for the primary relaxation. The outline of the paper is as follows. In the next section I will give a theoretical description of optical lineshapes in the inhomogeneous limit in terms of an inhomogeneous cumulant expansion. Some formal aspects of the derivation are treated in Appendix A. Sect. III gives a brief description of the free-energy landscape model which then is used to calculate the relevant quantities. The results are discussed in Sect. IV and the paper closes with some conclusions.

II. Theory of time-dependent optical lineshapes

In this section the theory of time-dependent optical lineshapes in the inhomogeneous cumulant expansion will be presented. Throughout the discussion the inhomogeneous limit will be considered exclusively and vibronic regressions and also the finite lifetime of the excited state will be neglected. This means, I focus on the time evolution of the (slow, $\langle \tau_{\alpha} \rangle$ longer than roughly $10^{-8}$s) solvent relaxation. To this end, the following simplified Hamiltonian of a two-state electronic system is considered:

$$H = |g\rangle[H_0 + W_g]\langle g| + |e\rangle[H_0 + W_e + \hbar\omega_{eg}]\langle e|$$

Here, the electronic ground and excited state are denoted by $|g\rangle$ and $|e\rangle$, respectively. $H_0$ is the solvent Hamiltonian in the absence of the solute, $W_g$ and $W_e$ denote the solute-solvent
interactions in the respective electronic states of the solute and \( h\omega_{eg} \) is the 0–0 transition frequency of the solvated solute. In the following, \( h \) will be set to unity. In Appendix A the time-dependent optical lineshape is calculated from the third order (in the electric field) response \([17, 18]\) in the rotating wave approximation. In the inhomogeneous limit both, time-dependent fluorescence (\( |e⟩ = |S₁⟩ \)) and phosphorescence (\( |e⟩ = |T₁⟩ \)) can be treated on the same footing. In the latter case it has to be assumed additionally that intersystem crossing and internal conversion are much faster than any other relevant time scale. For systems with slow environmental relaxation with typical relaxation times in the \( ms \) regime this provides no severe restriction.

In this section the optical emission lineshape will be calculated within the framework of an inhomogeneous cumulant expansion \([26]\) starting from

\[
I(ω, t) = \int_{-∞}^{∞} dω₀ P(ω, t|ω₀)S_0(ω₀)
\]

where \( S_0(ω) \) denotes the initial absorption spectrum, usually approximated by the initial (non-equilibrium) emission spectrum. Additionally, \( P(ω, t|ω₀) \) is the conditional probability for finding the transition frequency \( ω \) at time \( t \) given it had the value \( ω₀ \) at time \( t = 0 \). \( P(ω, t|ω₀) \) can be cast in the form

\[
P(ω, t|ω₀) = \frac{1}{4π²S₀(ω₀)} \int_{-∞}^{∞} dτ₁ \int_{-∞}^{∞} dτ₂ e^{−iω₀τ₁} e^{iωτ₂} \langle e^{iω₀(0)τ₁} e^{−iω(t)τ₂} \rangle_e
\]

which follows immediately from the definition of the joint probability, \( P(ω, t|ω₀)S₀(ω₀) = \langle δ(ω − ω(t))δ(ω₀ − ω(0)) \rangle_e \) with \( \langle A \rangle_e = Tr[Aρ_e] \), cf. Appendix A and ref. \([20]\). In Appendix A, Eq.\( (3) \) is derived from the general expression for the third order response and the inhomogeneous cumulant expansion is performed in detail, yielding Eqns.\( (A.5, A.7) \) for the lineshape.

Eq.\( (1) \) allows to discuss the formal connection to observables of other experimental techniques such as 2d-NMR. In this case, the conditional probability \( P(ωₗ, t|ω₀) \) with \( ωₗ \) denoting the Larmor frequency is observed directly \([21]\). In contrast to the optical case in NMR the dependence of \( ωₗ \) on molecular orientation is known explicitly and equilibrium correlation functions of the form \( \langle e^{iω₀(0)τ₁} e^{−iω(t)τ₂} \rangle_e \) are accessible directly. As is well known \([21]\), 2d-NMR spectra are not able to provide information about dynamic heterogeneities let alone their lifetimes. This is because in order to address this question one has to probe the system at four points in time at least \([22]\). It was this knowledge that led to the invention of higher-dimensional NMR techniques \([9]\). It is important to note that according to Eqns.\( (3,4) \) \( I(ω, t) \) does not contain any information about molecular motions beyond the two-time correlation functions \( \langle e^{iω(0)τ₁} e^{−iω(t)τ₂} \rangle_e \) and therefore cannot provide further insight into the issue concerning the lifetime of dynamic heterogeneities. Furthermore, due to the complex dependence of \( ω(t) \) on all relative distances and orientations of the solute relative to the solvent molecules, the optical lineshapes can be interpreted in terms of molecular quantities in a simple way only in favourable cases. An example is the relation between the solvation coordinate and the dielectric properties of the solvent in case of polar solvation \([13, 14, 15, 16, 17]\).

Now, I proceed to perform an inhomogeneous cumulant expansion of Eq.\( (1) \). For this purpose the Taylor expansion of the phase correlation function \( \langle e^{iω(0)τ₁} e^{−iω(t)τ₂} \rangle_e \) is considered. Setting \( \langle ω \rangle_e = 0 \) and \( σ^2 = \langle ω^2 \rangle_e \) without loss of generality, one has in a first order
relaxation rates and processes has to be incorporated in the definition of these rates. Thus, in exchange models that account for a more complex behavior. In particular, the decomposition of $\lambda$ variable $\Gamma$, which in Eq.(8) corresponds to $\lambda$ and a distribution function $p(\lambda)$. One then has, using $\int d\lambda p(\lambda) = 1$, $\langle e^{i\omega(0)\tau_1} e^{-i\omega(t)\tau_2} \rangle_e \simeq \int d\lambda p(\lambda) \{1 - (\sigma_e^2/2)(\tau_1^2 + \tau_2^2) + \sigma_e^2 e^{-\lambda \tau_1 \tau_2}\}$. Exponentiating the expression in the curly brackets gives:

$$\langle e^{i\omega(0)\tau_1} e^{-i\omega(t)\tau_2} \rangle_e \simeq \int d\lambda p(\lambda) \exp \left\{ -\frac{\sigma_e^2}{2} [\tau_1^2 + \tau_2^2 - 2e^{-\lambda \tau_1 \tau_2}] \right\}$$

(7)

It is illustrative to compare this result with the corresponding one of an ordinary cumulant expansion. In this case one finds, without using Eq.(8)

$$\langle e^{i\omega(0)\tau_1} e^{-i\omega(t)\tau_2} \rangle_e \simeq e^{-(\sigma_e^2/2)\beta [\tau_1^2 + \tau_2^2 - 2\tau_1 \tau_2]}$$

(9)

Therefore, this expansion does not take into account the inhomogeneities reflected in Eq.(8). In the same way as an expansion of the form $C(t) \simeq \int d\lambda p(\lambda) (1 - \lambda t) \simeq \exp [-(\int d\lambda p(\lambda) \lambda) t]$ only yields an exponential decay the ordinary cumulant expansion can only produce Gaussian probability distributions. The inhomogeneous cumulant expansion instead allows one to account for a more complex behavior.

Performing the Fourier transform in Eq.(8), using Eq.(7), yields for the conditional probability:

$$P(\omega, t | \omega_0) = \int d\lambda p(\lambda) P(\lambda)(\omega, t | \omega_0)$$

$$P(\lambda)(\omega, t | \omega_0) = \frac{1}{\sqrt{2\pi \sigma_e^2(1 - e^{-2\lambda t})}} \exp \left( -\frac{[\omega - \omega_0 e^{-\lambda t}]^2}{2\sigma_e^2(1 - e^{-2\lambda t})} \right)$$

(8)

Note that Eq.(8) is the same as Eq.(A.8) for $\sigma_e^2(\Gamma) = \sigma_e^2$ independent of the environmental variable $\Gamma$, which in Eq.(8) corresponds to $\lambda$. It is important to notice that both, the distribution $p(\lambda)$ and the decay rates $\lambda$ are determined via the Stokes correlation function $C(t)$. In particular, the decomposition of $P(\omega, t | \omega_0)$ into the functions $P(\lambda)(\omega, t | \omega_0)$ is meaningful only if the $\lambda$ are static quantities. This means that the influence of possible exchange processes has to be incorporated in the definition of these rates. Thus, in exchange models that start from bare relaxation rates which are modified due to exchange, the $\lambda$ are the effective relaxation rates and $p(\lambda)$ the effective distribution. This will be further discussed below. Finally, the time independent absorption and emission spectra are given by:

$$S_g(\omega) = \frac{1}{\sqrt{2\pi \sigma_g^2}} e^{-(\omega - \Delta)^2/(2\sigma_g^2)}$$

and

$$S_e(\omega) = p^{eq}(\omega) = \frac{1}{\sqrt{2\pi \sigma_e^2}} e^{-\omega^2/(2\sigma_e^2)}$$

(9)
where $\Delta = \langle \omega \rangle_g$ denoted the overall red-shift. Additionally, $\sigma_g^2 = \langle (\omega - \Delta)^2 \rangle_g$, $\sigma_e^2 = \langle \omega^2 \rangle_e$ and $\langle \omega \rangle_e = 0$ has been used without loss of generality. In Eq.(9) the spectrum $S_e(\omega)$ is determined by ensemble averages with respect to the excited-state Hamiltonian, because the system occupies this state before photon-emission.

Using the result of the inhomogeneous cumulant expansion, Eq.(8), in Eq.(3) gives a superposition of Gaussians for the optical lineshape $I(\omega, t)$. The expectation value of any dynamical variable $A$ can then be calculated according to

$$
\langle A(t) \rangle = \int d\omega A(\omega)I(\omega, t) = \int d\omega \int d\omega_0 A(\omega)P(\omega, t|\omega_0)S_g(\omega_0)
$$

(10)

From this one finds the $n^{th}$ frequency moment using $A = \omega^n$. The time-dependent mean is directly related to the Stokes-shift correlation function,

$$
\langle \omega(t) \rangle = \Delta \times C(t) = \Delta \times \int d\lambda p(\lambda)e^{-\lambda t}
$$

(11)

and the second moment to $C(2t)$:

$$
\langle \omega^2(t) \rangle = \sigma_e^2 + (\Delta^2 + \sigma_g^2 - \sigma_e^2)C(2t) \quad \text{where} \quad C(2t) = \int d\lambda p(\lambda)e^{-2\lambda t}
$$

(12)

Therefore, the time-dependent variance is given by:

$$
\sigma^2(t) = \sigma_e^2 + (\sigma_g^2 - \sigma_e^2)C(t)^2 + \Delta^2 \left[ C(2t) - C(t)^2 \right]
$$

(13)

This expression was found to give excellent agreement with the experimentally observed linewidth in the triplet state solvation studies on supercooled liquids\cite{13,21,24}.

The results for the optical lineshape and the frequency moments obtained above and in Appendix A can be reduced to expressions given earlier in the literature. If there is only one value for the environmental variable $\Gamma$ (or $\lambda$) Eq.(A.5) reduces to the expression already given above\cite{20,33}. Note that $C(t)$ does not necessarily decay exponentially in this case. This result is obtained by performing an ordinary cumulant expansion, cf. the discussion above. In that case the variance is given by $\sigma^2(t) = \sigma_e^2 + (\sigma_g^2 - \sigma_e^2)C(t)^2$ and changes monotonously from $\sigma^2(0) = \sigma_g^2$ to $\sigma^2(\infty) = \sigma_e^2$ because of $C(0) = 1$ and $C(\infty) = 0$.

The result for the $P(\lambda)(\omega, t|\omega_0)$ derived above, Eq.(5), can be mapped onto an expression given by Richert\cite{23} if his loosely defined 'local response functions' $\chi(t, \tau)$ are replaced by $e^{-\lambda \tau}$. This point will be discussed further below. Of course, in any theoretical calculation of a conditional probability one can only obtain approximations to the two-time correlation function $\langle e^{i\omega(0)\tau_1}e^{-i\omega(t)\tau_2} \rangle$. In a second order cumulant expansion the information is further reduced to the autocorrelation function $\langle \omega(t)\omega(0) \rangle$. As mentioned already above, no two-time correlation function is able to provide any information about the lifetime of dynamic heterogeneity.

### III. A free-energy landscape model for the optical lineshape

In order to illustrate the results derived above in this section the transition frequencies $\omega(t)$ are treated as a non-Markovian stochastic process. For this purpose I consider the description of $\omega(t)$ in terms of a free-energy landscape model. This approach has been used previously to
describe several aspects of the $\alpha$-relaxation in supercooled liquids\cite{27,28}. The basic idea is the following. The $\alpha$-relaxation is assumed to be associated with activated transitions among an extensive number of metastable glassy states or valleys in the free-energy landscape\cite{34}. This activated dynamics is described as a stochastic process $\epsilon(t)$. For simplicity, $\epsilon(t)$ is modeled as a stationary Markov process. The corresponding master equation (ME) for the conditional probability (Green’s function) $G(\epsilon, t|\epsilon_0) \equiv P_{1|1}(\epsilon; t|\epsilon_0)$ then reads\cite{33}:

$$\frac{\partial}{\partial t} G(\epsilon, t|\epsilon_0) = \int d\epsilon' \kappa(\epsilon|\epsilon')G(\epsilon', t|\epsilon_0) - \kappa(\epsilon)G(\epsilon, t|\epsilon_0) \quad \text{with} \quad \kappa(\epsilon) = \int d\epsilon' \kappa(\epsilon'|\epsilon)$$  \hspace{1cm} (14)

Here, $\kappa(\epsilon|\epsilon')$ denotes the rate for a $\epsilon' \rightarrow \epsilon$-transition. The dynamics described by Eq.(14) is supposed to be relevant for the environmental relaxation of the system. Of course, such a model can be applied to any system exhibiting activated dynamics, e.g. proteins, if the $\kappa(\epsilon|\epsilon')$ are chosen appropriately. In the following calculations I choose a simple globally connected model\cite{27} for the kinetics. After an escape out of valley (initial state $\epsilon'$) with an activation energy ($E_A - \epsilon'$) any other valley (final state $\epsilon$) can be reached with a probability given by its density of states, $\eta(\epsilon) \propto e^{-\epsilon^2/2\sigma(\epsilon)^2}$:

$$\kappa(\epsilon|\epsilon') = k_{\infty} \eta(\epsilon)e^{\beta\epsilon'}$$ \hspace{1cm} (15)

Here, $k_{\infty}$ is a prefactor and $\beta = (k_{\text{Boltzmann}}T)^{-1}$. In ref.\cite{27} other models have been considered also.

The main assumption of the model is that if $x(t)$ is a process observed experimentally, then $x(t)$ is allowed to change its value solely due to the $\epsilon' \rightarrow \epsilon$ transitions. Therefore, $x(t)$ can be considered as a \textquote[\textit{slave process}] of $\epsilon(t)$\cite{36}. In particular, $x(t)$ is not Markovian. In this context it is to be mentioned that in terms of Heuer’s $Q$ parameter\cite{32}, which is a measure of how long a relaxation rate remains correlated to earlier values, this model corresponds to $Q = 1$ by definition, i.e. $\langle \tau_{\text{req}} \rangle = \langle \tau_{\alpha} \rangle$. Previously, mainly the orientation of tagged particles, $x(t) = \Omega(t)$, and the position, $x(t) = \vec{r}(t)$, have been considered\cite{27,28}. In the present paper, $x(t)$ is identified with the optical transition frequencies, $x(t) = \omega(t)$. In order to describe the dynamics of $\omega(t)$, different approaches can be used.

A. Langevin equations

A simple approach is to assign a value $\omega_x(t)$ to each of the valleys $\epsilon$ and consider the coupled Langevin equations:

$$\dot{\omega}_x(t) = -\kappa(\epsilon)\omega_x(t) + \int d\epsilon' \kappa(\epsilon|\epsilon')\omega_{\epsilon'}(t) + L_x(t)$$\hspace{1cm} (16)

where $L_x(t)$ is a delta-correlated white noise, $\langle L_x(t) \rangle = 0$, $\langle L_x(t)L_x'(t') \rangle = \Gamma_{\epsilon,\epsilon'}\delta(t-t')$. For a finite number of valleys, the integral in Eq.(16) is to be replaced by a sum. After diagonalization of the matrix defined in Eq.(16) one has the decoupled Langevin equations

$$\dot{\omega}_{\lambda}(t) = -\lambda\omega_{\lambda}(t) + L_{\lambda}(t)$$ \hspace{1cm} (17)

where $\lambda$ are the eigenvalues. These equations are directly related to Gaussian conditional probabilities\cite{35,37}, determined by the correlation functions $\langle \omega_{\lambda}(t)\omega_{\lambda}(0) \rangle = \sigma^2 e^{-\lambda t}$. Therefore, these Langevin equations yield Eq.(8) without further approximations. Due to the
in contrast to the Langevin equations considered above, in such an approach non-Markovian Gaussian is a structure of Eq. (16) the products, another approach allowing for a richer dynamics is to consider the ME for the composite Markov process \{\omega(t), \epsilon(t)\} as has been done previously. In the ME, the transition rates \( \kappa(\omega, \epsilon|\omega', \epsilon') \) are chosen as simple products, \( \kappa(\omega, \epsilon|\omega', \epsilon') = \kappa(\epsilon|\epsilon') \Lambda(\omega|\omega') \). Here, the dimensionless functions \( \Lambda(\omega|\omega') \) determine the magnitude of changes in \( \omega \) associated with a \( \epsilon' \rightarrow \epsilon \)-transition. Allowing only for very small frequency changes, \( \omega \rightarrow \omega' = \omega + \delta, \delta \ll 1 \), one can use a Kramers-Moyal expansion of the ME as described in Appendix B. As a result, the following equation for the conditional probability is obtained:

\[
\dot{P}_{1|1}(\omega, \epsilon; t|\omega_0, \epsilon_0) = -\kappa(\epsilon)P_{1|1}(\omega, \epsilon; t|\omega_0, \epsilon_0) + [1 + \rho \Lambda^{FP}(\omega)] \int d\epsilon' \kappa(\epsilon|\epsilon') P_{1|1}(\omega, \epsilon'; t|\omega_0, \epsilon_0) \tag{18}
\]

where the Fokker Planck (FP)-operator \( \Lambda^{FP}(\omega) \) is defined by:

\[
\Lambda^{FP}(\omega) = \frac{\partial}{\partial \omega} \omega + \frac{\sigma^2}{2} \frac{\partial^2}{\partial \omega^2}
\]

and

\[
\rho = \frac{\delta^2}{2 \sigma^2}\tag{20}
\]

The 'fluctuation parameter' \( \rho \ll 1 \) measures the scale of the \( \omega \)-fluctuations relative to the width of the equilibrium distribution. An analytic solution of Eq. (18) is not feasible in general. However, one can perform an expansion in terms of the eigenfunctions of \( \Lambda^{FP}(\omega) \) which are Hermite polynomials \( H_n(z) \):

\[
P_{1|1}(\omega, \epsilon; t|\omega_0, \epsilon_0) = e^{-\bar{\omega}^2} \sum_{n=0}^{\infty} \frac{H_n(\bar{\omega})}{2^n n! \sqrt{2\pi \sigma^2}} G_n(\epsilon, t|\epsilon_0) \quad \text{where} \quad \bar{\omega}^2 = \omega^2/2\sigma^2
\]

The Green’s functions \( G_n(\epsilon, t|\epsilon_0) \) are the solutions of the rate equations:

\[
\dot{G}_n(\epsilon, t|\epsilon_0) = -\kappa(\epsilon)G_n(\epsilon, t|\epsilon_0) + [1 - n\rho] \int d\epsilon' \kappa(\epsilon|\epsilon') G_n(\epsilon', t|\epsilon_0) \tag{22}
\]

Note that \( G_0(\epsilon, t|\epsilon_0) = G(\epsilon, t|\epsilon_0) \) according to Eq. (14). A comparison of these rate equations with those occurring in the treatment of molecular reorientations shows that the term \( n\rho \)
corresponds to $P(\cos \theta)$, the $l$th order Legendre polynomial of the jump angle $\theta$. A full solution of the problem requires the calculation of all $G_n(\epsilon, t|\epsilon_0)$, $n = 0, 1, \cdots, \infty$. From this solution the stochastic process $\omega(t)$ can be defined as a projection of the composite Markov process $\{\omega(t), \epsilon(t)\}$. For this purpose one has to integrate the joint probabilities over the variables $\epsilon$. In the special case of uncorrelated equilibrium probabilities, $p^{eq}(\omega, \epsilon) = p^{eq}(\omega)p^{eq}(\epsilon)$, this yields the marginal distributions\[27\]

$$P(\omega, t|\omega_0) = \int d\epsilon_0 p^{eq}(\epsilon_0) \int d\epsilon P_{1|1}(\omega, \epsilon; t|\omega_0, \epsilon_0)$$

(23)

From this expression and Eqns.\{21, 22\} it becomes clear that $P(\omega, t|\omega_0)$ can not be written as a superposition of Gaussians. This shows that even though Eq.(18) resembles a Fokker-Planck equation, $\omega(t)$ is not only non-Markovian but also non-Gaussian in general.

**Inhomogeneous cumulant expansion**

The non-Gaussian nature of the stochastic process $\omega(t)$ in the approach starting from a ME allows to discuss the inhomogeneous cumulant expansion in detail. For this purpose I proceed in exactly the same manner as in Sect.II. There, it became clear that the only relevant quantity determining the conditional probability is the frequency autocorrelation function. Using the properties of the Hermite polynomials, this function can be calculated from Eq.(21):

$$\langle \omega(t)\omega(0) \rangle = \int d\omega_0 p^{eq}(\omega_0) \omega_0 \int d\omega \omega P(\omega, t|\omega_0) = \sigma_\epsilon^2 \int d\epsilon_0 p^{eq}(\epsilon_0) \int d\epsilon G_1(\epsilon, t|\epsilon_0)$$

$$= \sigma_\epsilon^2 \int d\epsilon_0 p^{eq}(\epsilon_0) \int d\epsilon \int d\lambda(1) \Phi_{(1)}(\epsilon, \lambda(1)) \Psi_{(1)}(\epsilon_0, \lambda(1)) e^{-\lambda(1)t}$$

(24)

Here, $\Phi_{(1)}(\epsilon, \lambda(1))$ and $\Psi_{(1)}(\epsilon_0, \lambda(1))$ are the right and left eigenvectors of the matrix defined in Eq.(22) for $n = 1$. The $\lambda(1)$ are the corresponding eigenvalues. Performing the same calculation as in Sect.II, one recovers Eq.(8) for the conditional probability, $P(\omega, t|\omega_0)$, with

$$p(\lambda(1)) = \int d\epsilon_0 p^{eq}(\epsilon_0) \int d\Phi_{(1)}(\epsilon, \lambda(1)) \Psi_{(1)}(\epsilon_0, \lambda(1))$$

(25)

Thus, the inhomogeneous cumulant expansion provides an explicit expression for the ‘distribution of relaxation rates’, $p(\lambda)$.

Note, that a Gaussian approximation is equivalent to approximating the Green’s functions $G_n(\epsilon, t|\epsilon_0)$, $n > 1$, by $G_n(\epsilon, t|\epsilon_0) \simeq f d\lambda_1 \Phi_{(1)}(\epsilon, \lambda(1)) \Psi_{(1)}(\epsilon_0, \lambda(1)) e^{-n\lambda(1)t}$. Inserting this expression into Eq.(21) allows one to compute the sum over $n$ resulting in a Gaussian\[37\]. Using Eq.(23) yields Eq.(8) with $p(\lambda)$ given by Eq.(23). It is important to point out that the frequency autocorrelation function, Eq.(24), also determines the conditional probability in an ordinary cumulant expansion, cf. the discussion in Sect.II. Therefore, in the present context Eq.(8) is the result of an *inhomogeneous Gaussian approximation*.

In general the assumption of Gaussian fluctuations presents an approximation, only. There are, however, two limits in which $\omega(t)$ becomes a Gaussian stochastic process. As shown in Appendix C a perturbation expansion of Eq.(22) yields a Gaussian probability distribution in the limits of short and long times, respectively.

In the short time limit, one has to replace the rates $\lambda$ in Eq.(8) by $\rho\kappa(\epsilon)$ and to set $p(\lambda) = p^{eq}(\epsilon)$. The relaxation rates are therefore determined by the escape rates $\kappa(\epsilon)$. This means
that any single $\epsilon \rightarrow \epsilon'$ transition is effective for the relaxation of the transition frequencies $\omega(t)$. This limit therefore corresponds to a situation in which the $\omega(t)$ fluctuate in a quasi-static environment.

In the long time limit, only the average relaxation rate, $\rho\langle \kappa \rangle = \int d\kappa \kappa / f(\kappa)$, determines the temporal behavior of $P(\omega, t|\omega_0)$ and one has to set $\rho(\lambda) = \delta(\lambda - \rho(\kappa))$ in Eq.(8). Therefore, in this limit $\omega(t)$ is an Ornstein-Uhlenbeck process which means that $\omega(t)$ is Markovian and Gaussian in this limit. Only the time scale for relaxation is set by the mean environmental relaxation rate $\langle \kappa \rangle$.

The inhomogeneous Gaussian approximation discussed above smoothly interpolates between these two limits, if $\rho \ll 1$. Here, the difference between an inhomogeneous cumulant expansion and an ordinary one can be seen most clearly. In both cases the correct long time limit is approached, as is well known from the theory of random walks. The correct short time limit, however, is only reached if the inhomogeneous cumulant expansion is performed.

Model calculations

In Fig.2 the Stokes-shift correlation function $C(t)$, calculated according to Eq.(24), and the time-dependent part of the variance, Eq.(13), are shown for $\rho = 0.1$ and $\sigma_g = \sigma_g'$. The parameters, $\kappa_0$ and $\sigma(\epsilon)$, cf. Eq.(14), are chosen in such a way that $C(t)$ is well parametrized by a Kohlrausch function, $C(t) = \exp \left[-(t/\tau_K)^\beta \kappa\right]$. For the curves with $\beta_K = 0.5$, the choice was guided by the experimental results of Wendt and Richert on triplet state solvation in MTHF. As already mentioned in the last section, the shown behavior for $C(2t) - C(t)^2 = [\sigma^2(t) - \sigma^2]\Delta^2$ is in excellent agreement with the experimental data. Comparing the different curves in Fig.2, it is seen that for more stretched $C(t)$ the range of positive $C(2t) - C(t)^2$ is increased. Also the absolute value increases with decreasing $\beta_K$. Without showing the results of calculations for other choices of the fluctuation parameter $\rho$ here I just mention that this has only a small effect on the overall behavior if $\rho$ is not chosen too large. In this latter case, however, the Kramers-Moyal expansion is no longer meaningful and Eq.(13) ceases to be valid.

As has been pointed out, the solution of Eq.(13) results in a stochastic process $\omega(t)$ that is not only non-Markovian, but also non-Gaussian. A detailed study of the deviations from Gaussian behavior of the exact solution of Eq.(18) is difficult in general. However, one can compare the low-order moments calculated in the inhomogeneous Gaussian approximation, Eqns.(8,24), with those obtained using the exact Eqns.(21,22). In a way similar to the calculation of $\langle \omega(t)\omega(0) \rangle$ one finds for $\sigma_e = \sigma_g$

$$\langle \omega(t) \rangle_{NG} = \Delta \times C(t) \quad \text{and} \quad \langle \omega^2(t) \rangle_{NG} = \sigma^2_e + \Delta^2 \int d\epsilon \rho^e(\epsilon) \int d\epsilon_0 G_2(\epsilon, t|\epsilon_0)$$

The first moment of course coincides with the Gaussian approximation, Eq.(11), $\langle \omega(t) \rangle_{NG} \equiv \langle \omega(t) \rangle$. For the second moment and the variance, $\sigma^2(t)$, this is not true. Here, Eq.(13) has to be compared to

$$\sigma^2(t)_{NG} = \sigma^2_e + \Delta^2 \xi(t) \quad \text{where} \quad \xi(t) = \int d\epsilon \rho^e(\epsilon) \int d\epsilon_0 G_2(\epsilon, t|\epsilon_0) - C(t)^2$$

This quantity is plotted in Fig.3(a) for the same parameters as used in Fig.2 for $\beta_K = 0.5$ along with $C(2t) - C(t)^2$ for comparison. It is clearly seen that $\xi(t)$ exceeds $C(2t) - C(t)^2$
in the whole range where both functions are nonzero. In order to qualitatively discuss higher order moments \( \langle \omega^n(t) \rangle_{(NG)} \) it is sufficient to notice that these are determined by \( \int d\epsilon \rho(\alpha) \int d\epsilon_0 G_n(\epsilon, t|\epsilon_0) \), as can be seen from Eq.(21). Therefore, the functions

\[
\zeta_n(t) = \int d\epsilon \rho(\alpha) \int d\epsilon_0 G_n(\epsilon, t|\epsilon_0) - C(nt)
\] (28)

give a qualitative measure for the deviations of \( \langle \omega^n(t) \rangle_{(NG)} \) from a Gaussian behavior. This is because in the Gaussian approximation the \( \zeta_n(t) \) vanish identically, \( \zeta_n(t) \equiv 0 \). The \( \zeta_n(t) \) are plotted in Fig.3(b) for \( n = 2, 4, 6, 8 \). From this plot it is evident that the deviations from Gaussian behavior even increase with \( n \). Thus, if one wants to go beyond the Gaussian approximation, it is not sufficient to consider only the first few moments. In particular, the second moment gives only a poor approximation to the inhomogeneous linewidth. Additionally, the Stokes-shift correlation function is no longer determined by the first moment but also higher moments become important. However, it should be kept in mind that if higher order terms are kept in the cumulant expansion of \( P(\omega, t|\omega_0) \), these terms also have to be taken into account for the static spectra \( S_e(\omega) \) for reasons of internal consistency, cf. the discussion in Appendix A. As will be discussed further below, it is the identification of \( \sigma^2(t)_{(NG)} \) with the inhomogeneous linewidth for one special exchange model that let Richert\[25\] to the incorrect conclusion that models with \( \langle \tau_{req} \rangle \approx \langle \tau_\alpha \rangle \) are incompatible with the experimental data obtained for QX in MTHF\[24\].

**IV. Discussion**

In Sect.II and Appendix A an inhomogeneous cumulant expansion has been performed to calculate the time-dependent optical linewidths in complex systems like supercooled liquids or proteins. Because the expansion has been truncated at second order, the transition frequencies \( \omega(t) \) constitute a stochastic process that is Gaussian but non-Markovian in this approximation. In Sect.III the theoretical results have been illustrated by a specific stochastic model for \( \omega(t) \). The coupling of these frequencies to the environmental fluctuations, treated in terms of the free-energy landscape model, renders \( \omega(t) \) non-Markovian. The same is true if exchange models are considered instead\[39\].

In theoretical treatments of polar solvation\[15, 16, 17\] a simple interpretation of the time-dependent Stokes shift \( C(t) \) and accordingly the solvation coordinate is given in terms of the dielectric properties of the solvent. If the solvation coordinate can be modeled as a Gaussian Markov process, also the interpretation in terms of solvation free energies is straightforward\[15, 17\]. This, however, usually leads to exponential relaxation. If instead the Stokes-shift correlation function decays non-exponentially, such a simple relation is no longer obvious as in this case the solvation coordinate does not constitute a Markov process. Rewriting the non-exponentially decaying Stokes-shift correlation function as in Eq.(3) still allows to relate \( C(t) \) to the dielectric response via an expression of the form \( C(t) \sim \int d\lambda \rho(\lambda) \exp(-t/\tau_{\text{die}}(\lambda)) \). Here, \( \tau_{\text{die}}(\lambda) \) denote dielectric relaxation times, the values of which depend on the model considered\[13\]. Thus, the treatment of \( \omega(t) \) as a projection from a higher-dimensional Markov process along with the inhomogeneous cumulant expansion might be helpful in the interpretation of the solvation coordinate in more complex situations.
The free-energy landscape model for the dynamics used in the last section to treat the spectral diffusion process is of a phenomenological nature and specific assumptions about the dynamical evolution of the 'order parameter' \( \epsilon(t) \) and the coupling between the different processes have to be made in order to obtain a tractable model. One of the main features of this model lies in the fact that there is no difference between 'relaxation rates' and 'exchange rates' as in typical exchange models\(^1\). Additionally, as mentioned above, the choice of the \( \kappa(\epsilon|\epsilon') \) according to Eq.(15) corresponds to a minimum rate memory, \( Q \equiv 1 \)\(^2\). This means that the lifetime of the dynamic heterogeneities is the same as the time scale of the \( \alpha \)-relaxation.

The treatment of the spectral diffusion process in terms of coupled Langevin equations, Eq.(16), immediately gives the result of the inhomogeneous cumulant expansion, Eq.(8), for the conditional probability. Consequently, the first moment is given by Eq.(11) and the time-dependent variance by Eq.(13). The reason for this behavior is given by the fact that in such a Langevin equation model one starts from Gaussian fluctuations from the outset. Therefore, \( \omega(t) \) represents a non-Markovian Gaussian process. According to ref.\(^24\) this means that this model gives excellent agreement with the experimental data on QX in MTHF if the transition rates are chosen in such a way that the Stokes-shift correlation is well parameterized by a Kohlrausch function with \( \beta_K = 0.5 \). Therefore, the experimental data are fully compatible with \( Q \equiv 1 \).

A richer dynamical behavior of \( \omega(t) \) can be studied by considering the more general case of a ME for the composite Markov process \{\( \omega(t), \epsilon(t) \)\}. The Kramers-Moyal expansion of this ME has led to the introduction of the parameter \( \rho = (\delta^2/2\sigma^2) \) that measures the fluctuations in transition frequency relative to width of the equilibrium steady state emission spectrum. It has already been mentioned in the context of Eq.(22) that the fluctuation parameter \( \rho \) plays a role very similar to the jump angle in models for the reorientational motion. 2d-NMR experiments performed in the time domain allow to extract these jump angles, roughly on the order of \( 10^\circ \) in supercooled liquids\(^8, 9, 41\). As it is the reorientational and translational motion of the solvent molecules that is responsible for the \( \omega \)-fluctuations, one expects that \( \rho \) also takes on finite values. Note that such finite fluctuations cannot be treated in terms of Langevin equations.

In general, the process \( \omega(t) \) is neither Markovian nor Gaussian in the treatment using the ME. Only in two limiting situations the result of the inhomogeneous cumulant expansion, Eq.(8), is found for the conditional probability for small \( \rho \). At short times the transition frequencies fluctuate in a quasi-static environment and every \( \epsilon \rightarrow \epsilon' \) transition gives rise to relaxation. Therefore, in this limit the relevant rates are just the 'escape rates' \( \kappa(\epsilon) = \int d\epsilon' \kappa(\epsilon'|\epsilon) \). Conversely, at long times the environmental relaxation appears to be fast compared to the changes in \( \omega(t) \). Thus, only the average rate \( \langle \kappa \rangle \) is relevant for the time scale of the \( \omega \)-fluctuations, rendering \( \omega(t) \) an Ornstein-Uhlenbeck process. Note that these two limits can be compared to the so-called short-time approximation and long-time approximation in stochastic lineshape theory\(^42\). Apart from these limits, \( \omega(t) \) is not a Gaussian process and the deviations from Gaussian behavior have been discussed in context of Fig.3. Furthermore, I have discussed an inhomogeneous Gaussian approximation for the conditional probability which allows to smoothly interpolate between the limits of short and long times, where it becomes exact. For this approximation, the result of the inhomogeneous cumulant expansion, Eq.(8), is recovered. In contrast, an ordinary cumulant expansion fails to reproduce the exact behavior at short times.
It has been mentioned already that the expression for the $P(\lambda)(\omega, t|\omega_0)$, Eq.(8), can be compared to a corresponding one given by Richert[23], if his $\chi(t, \tau)$ are replaced by $\exp(-\lambda t)$. However, in ref.[23] these functions were denoted as conditional probabilities and an expression similar to Eq.(8) was postulated to hold rather than derived from a theoretical treatment. Additionally, the meaning of the 'local response function' $\chi(t, \tau)$ remains unclear. Unfortunately, no definition for these objects was given apart from the fact that they are related to the Stokes-shift correlation function via $C(t) = \langle \chi(t, \tau) \rangle$ which contradicts the term 'response function'. Thus, it appears that a meaningful interpretation of the $\chi(t, \tau)$ can be given only if these functions are identified with $\exp(-\lambda t)$. Surprisingly, this apparently is not Richert’s interpretation because he concludes that the time-dependent variance is determined by the 'spatially distributed local solvent responses' $\chi(t, \tau)$ in case of a static heterogeneity. Additionally, in ref.[25] he considers exchange models in which the 'time constants $\tau$ of the local responses' fluctuate in time. He furthermore claims that the experimental results are only compatible with slow rate exchange. Of course, in an inhomogeneous cumulant expansion the rates $\lambda$ (or corresponding time constants $\tau$) have to be static quantities. As I have shown in the last section, stochastic models which do not distinguish at all between 'relaxation' and 'exchange' give results compatible with the available experimental data[24]. The same holds for exchange models[39]. The confusion seems to have its origin in the fact that the exchange models studied in ref.[27] are not Gaussian. Therefore, a Gaussian approximation has to be applied to the models in order to be able to compare the results to an inhomogeneous cumulant expansion truncated at the second order. Otherwise, $C(t)$ is not determined by the first moment and the linewidth is not given by $\sigma^2(t)$. As noted above, including higher order terms is non-trivial, as this should also be done for the static spectra. These difficulties can be avoided if one considers models which are Gaussian intrinsically, like Langevin equation models.

IV. Conclusions

In the present paper I have derived an expression for the time-dependent optical linewidths in the inhomogeneous limit for systems exhibiting slow relaxation. For this purpose, an inhomogeneous cumulant expansion has been performed, utilizing the fact that a non-exponentially decaying Stokes-shift correlation function can be represented as a weighted sum of exponentially decaying functions.

In a free-energy landscape model developed to model the primary relaxation in supercooled liquids, the optical transition frequencies were treated as a stochastic process $\omega(t)$, which is not Markovian in general. Two variants of this model have been considered, a Langevin approach and a treatment in terms of a master equation. In the former case the model is solved exactly by the inhomogeneous cumulant expansion as the fluctuations truly are Gaussian. Therefore, in this case $\omega(t)$ is a non-Markovian Gaussian process. This does not hold for the more general ME approach. Here, the conditional probabilities are Gaussians only in the short time and the long times limits. I have additionally considered an inhomogeneous Gaussian approximation that interpolates between these limits. In general, however, in such more complex models $\omega(t)$ is not only non-Markovian but additionally non-Gaussian.

Due to the fact that the system is probed at two times only in the optical experiments under consideration, one cannot obtain any information about the lifetime of dynamic het-
erogeneities from these experiments alone[32]. This is in contrast to recent claims where it was concluded on the existence of long lived heterogeneities within a special model scenario that was assumed to apply[23]. The model calculations performed in the present paper clearly show that the experimental data are also fully compatible with the assumption that the lifetime of the dynamic heterogeneities is on the same order as the $\alpha$-relaxation time.

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Appendix A: Nonlinear response theory of optical lineshapes

In this Appendix the result for the time-dependent optical lineshapes will be derived from an inhomogeneous cumulant expansion of the corresponding third order optical response.

The starting point is the Hamiltonian, Eq. (2), to which the radiation-matter interaction responsible for the electronic transitions is added. In the Condon approximation the latter is simply given by $H_{\text{int}} = |g\rangle \langle e| + |e\rangle \langle g|$. Treating the excitation pulse classically and the emitted radiation quantum mechanically, the following expression for the time-resolved lineshape is obtained in the rotating wave approximation, see eg. [17, 18]:

$$ S(\omega_S, \omega_L, t) \propto \text{Re} \int_{-\infty}^{\infty} d\tau_3 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_1 e^{i(\omega_L \tau_1 + \omega_S \tau_3)} E_L(t - \tau_1 - \tau_2 - \tau_3) E_\gamma^*(t - \tau_2 - \tau_3) R(t_1, t_2, t_3) $$

(A.1)

where $E_L(t)$ denotes the time-dependent amplitude of the incoming field and $R(t_1, t_2, t_3)$ is a third order response function which in the inhomogeneous limit is given by [17]:

$$ R(t_1, t_2, t_3) = \text{Tr} \left[ e^{-iU_{t_3} t_2} e^{-iL_e t_2} e^{iU_{t_1} t_2} \varrho_g \right] $$

(A.2)

In this expression, $U = W_e - W_g$ and $\varrho_g$ denotes the canonical ground state density operator, $\varrho_g = \exp\left(-\beta H_g\right)/\text{Tr}\left[\exp\left(-\beta H_g\right)\right]$ with $H_g = \langle g|H|g\rangle$ and $\beta = (k_B T)^{-1}$. Furthermore, $L_e$ denotes the Liouville operator corresponding to $H_e$ [26].

Eq. (A.1) describes the processes visualized in the double-sided Feynman diagram [26] in Fig. 4. It is to be noted that a term corresponding to a resonant Raman process has been neglected completely in Eq. (A.1).

Following ref. [17], in a next step it is assumed that the solvation coordinate $U$ is the only relevant quantity determining the solvent relaxation. After a projection onto the operator $U$ and a second order cumulant expansion, one gets a simple expression for the response function $R(t_1, t_2, t_3)$, which is determined solely by the Stokes-shift correlation function $\text{Tr} \left[ \{ e^{iH_{t_3} U} e^{-iH_{t_2} t_2} \} U_e(0) \varrho_e \right]$ and some static quantities. Therefore, in the inhomogeneous limit the optical lineshape is completely determined by a two-time correlation function.

In order to perform an inhomogeneous cumulant expansion [26], it is assumed that all quantities depend on a configurational variable $\Gamma$ chosen from some distribution $p(\Gamma)$. One then calculates $R(t_1, t_2, t_3) = \int d\Gamma p(\Gamma) R(t_1, t_2, t_3; \Gamma)$, cf. [26], with a result analogously to that obtained in ref. [17]:

$$ R(t_1, t_2, t_3) = \int d\Gamma p(\Gamma) \exp \left( im_e(\Gamma) t_1 \right) \exp \left( it_3 \left[ m_e(\Gamma) + (m_g(\Gamma) - m_e(\Gamma)) C(t_2; \Gamma) \right] \right) \times $$

$$ \times \exp \left( -t_1^2/2 \sigma_e^2(\Gamma) + (\sigma_g^2(\Gamma) - \sigma_e^2(\Gamma)) C^2(t_2; \Gamma) \right) \times $$

$$ \times \exp \left( -t_1^2/2 \sigma_g^2(\Gamma) - t_1 t_3 \sigma_g^2(\Gamma) C^2(t_2; \Gamma) \right) $$

(A.3)

where

$$ m_\alpha(\Gamma) = \langle \omega(0; \Gamma) \rangle_\alpha, \quad \sigma_\alpha^2(\Gamma) = \langle (\omega^2(0; \Gamma))_\alpha \rangle - m_\alpha^2(\Gamma) $$

$$ C(t; \Gamma) = \left( \langle \omega(t; \Gamma) \omega(0; \Gamma) \rangle_e - m_e^2(\Gamma) \right)/\sigma_e^2(\Gamma) $$

(A.4)

Here, $\langle A(t; \Gamma) \rangle_\alpha = \text{Tr} \left[ A(t; \Gamma) \varrho_\alpha \right]$, $\alpha \in \{ e, g \}$ and $\omega(t; \Gamma)$ is the classical analogue of $(\omega_{eg}(\Gamma) + U(t; \Gamma))$. As in Eq. (A.3) one has $\langle A(t) \rangle_\alpha = \int d\Gamma p(\Gamma) \langle A(t; \Gamma) \rangle_\alpha$. 


A simple expression for \( S(\omega_S, \omega_L, t) \) is obtained by assuming that \( t_1 \) is very short and additionally neglecting the optical coherence during \( t_3 \). In this case \( t_2 \) can be replaced with the observation time \( t \), cf. Fig.4. Formally, these approximations amount to replace \( E_L(t - t_1 - t_2 - t_3)E_L^*(t - t_2 - t_3) \) in Eq.(A.1) by \( |E_L|^2 \delta(t_2 - t)\delta(t_1) \). The remaining \( t_3 \)-integration can be performed and one finds for the \( \omega_L \)-independent normalized lineshape:

\[
I(\omega_S, t) = \int d\Gamma \rho(\Gamma) \frac{1}{\sqrt{2\pi \Sigma^2(t; \Gamma)}} \exp \left( -\frac{\{\omega_S - [m_e(\Gamma) + m_g(\Gamma) - m_e(\Gamma)]C(t; \Gamma)]^2}{2\Sigma^2(t; \Gamma)} \right)
\]

with

\[
\Sigma^2(t; \Gamma) = \sigma^2_e(\Gamma) + (\sigma^2_e(\Gamma) - \sigma^2_e(\Gamma))C^2(t; \Gamma)
\]

Alternatively, Eq.(A.5) can be cast in the form

\[
I(\omega, t) = \int d\Gamma \rho(\Gamma) \int d\omega' P(\Gamma)(\omega, t|\omega') S_\alpha(\omega'; \Gamma)
\]

where \( S_\alpha(\omega; \Gamma) = [2\pi \sigma^2_\alpha(\Gamma)]^{-1/2} \exp \left[ -\frac{(\omega - m_\alpha(\Gamma))^2}{2 \sigma^2_\alpha(\Gamma)} \right] \). \( P(\Gamma)(\omega, t|\omega') \) is the conditional probability to find the emission frequency \( \omega \) at time \( t \), given that it had the value \( \omega' \) at time \( t = 0 \),

\[
P(\Gamma)(\omega, t|\omega_0) = \frac{1}{\sqrt{2\pi \sigma^2_\alpha(\Gamma)(1 - C^2(t; \Gamma))}} \exp \left( -\frac{[\omega - \omega_0 C(t; \Gamma)]^2}{2 \sigma^2_\alpha(\Gamma)(1 - C^2(t; \Gamma))} \right)
\]

From the properties of the conditional probability\[33\] one has

\[
I(\omega, 0) = \int d\Gamma \rho(\Gamma) S_\alpha(\omega; \Gamma) \quad \text{and} \quad I(\omega, \infty) = \int d\Gamma \rho(\Gamma) S_e(\omega; \Gamma)
\]

One might argue that the derivation given here is rather formal, especially as the result again can be cast into a form that resembles ordinary linear response theory, Eq.(A.7). The reason for the formal treatment is twofold. From the inhomogeneous cumulant expansion for the response function, Eq.(A.3), it becomes clear that the 'ingredients' in Eq.(A.7) are not independent. This does not become clear from Eq.(A.4) alone. If only this expression would be given, there would be no reason for restricting the cumulant expansions for \( S_g(\omega'; \Gamma) \) and the conditional probability to the same order. Also, a generalization of the expression \( I(\omega, t) = \int_{-\infty}^{\infty} d\omega_0 P(\omega, t|\omega_0) S_g(\omega_0) \), cf. ref.\[20\] is not straightforward in general. In particular it is not clear how to perform the inhomogeneous cumulant expansion. Only in the limit of \( \Gamma \)-independent static quantities, it suffices to consider \( P(\omega, t|\omega_0) \).

In the text, only the case of \( \Gamma \)-independent static quantities \( m_\alpha \) and \( \sigma_\alpha \) is considered for simplicity. This means that one has \( S_\alpha(\omega) = S_\alpha(\omega; \Gamma) \) independent of \( \Gamma \). Additionally, this allows to rewrite Eq.(A.7) as \( I(\omega, t) = \int_{-\infty}^{\infty} d\omega_0 P(\omega, t|\omega_0) S_\alpha(\omega_0) \). In the text I choose \( m_e = 0 \) and additionally rename \( m_g = \Delta \) denoting the overall red-shift.

**Appendix B: Kramers Moyal expansion**

In this appendix the derivation of Eq.(18) is outlined. The starting point is the ME

\[
\frac{\partial}{\partial t} P_{11}(\omega, \epsilon; t|\omega_0, \epsilon_0) = \int d\omega' \Lambda(\omega|\omega') \int d\epsilon' \kappa(\epsilon|\epsilon') P_{11}(\omega', \epsilon'; t|\omega_0, \epsilon_0) - \int d\omega' \Lambda(\omega'|\omega) \int d\epsilon' \kappa(\epsilon'|\epsilon) P_{11}(\omega, \epsilon; t|\omega_0, \epsilon_0)
\]

(B.1)
As noted in the text, the \( \Lambda(\omega|\omega') \) are assumed to be finite for small jump-lengths only. This means, that \( \omega(t) \) is modelled as a so-called one-step process\[35, 43\] with a jump length \( \delta \) \( (\delta^2 = 2\sigma^2_\epsilon \rho) \), cf. Eq.(20)). Furthermore, it is assumed that spectral diffusion in the limit of vanishing \( \delta \) can be viewed as a diffusion in a potential of the form \( U(\omega) = (4\beta \sigma^2_\omega)^{-1}\omega^2 \) with \( \beta = (k_B T)^{-1} \). (The factor 1/4 is introduced here for convenience only.) The force originating from this potential ensures that the time-dependent distribution approaches the equilibrium distribution \( p^{eq}(\omega) \), Eq.(9), in the long time limit. With the functions \( A(\omega) = -\rho \omega \) and \( B(\omega) = 2\rho \sigma^2_\epsilon \) the \( \Lambda(\omega|\omega') \) can be written in the form

\[
\Lambda(\omega|\omega') = \left[ \frac{A(\omega)}{2\delta} + \frac{B(\omega)}{2\delta^2} \right] \delta(\omega' - [\omega + \delta]) + \left[ -\frac{A(\omega)}{2\delta} + \frac{B(\omega)}{2\delta^2} \right] \delta(\omega' - [\omega - \delta]) \quad \text{(B.2)}
\]

The occurrence of the inverse powers of \( \delta \) has its origin in the scaling properties of the \( \Lambda(\omega|\omega') \). In the limit of small \( \delta \) a Kramers-Moyal (KM) expansion (or equivalently in this case van Kampen’s system size expansion\[35\]) can be performed. With the definition of the jump moments \( \alpha_n(\omega) = \int d\omega'(\omega' - \omega)^n \Lambda(\omega'|\omega) \)\[35\] and the relations

\[
\int d\omega' \Lambda(\omega|\omega') f(\omega') = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left( \frac{\partial}{\partial \omega} \right)^n \alpha_n(\omega) f(\omega) \quad \text{and} \quad \int d\omega' \Lambda(\omega|\omega') f(\omega) = \alpha_0(\omega) f(\omega)
\]

holding for an arbitrary function \( f(\omega) \) one finds

\[
\frac{\partial}{\partial t} P_{11}(\omega, \epsilon; t|\omega_0, \epsilon_0) = -\alpha_0(\omega) \kappa(\epsilon) P_{11}(\omega, \epsilon; t|\omega_0, \epsilon_0) + \left[ \alpha_0(\omega) + \Lambda^{KM}(\omega) \right] \int d\epsilon' \kappa(\epsilon') P_{11}(\omega, \epsilon'; t|\omega_0, \epsilon_0) \quad \text{(B.3)}
\]

with \( \Lambda^{KM}(\omega) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \left( \frac{\partial}{\partial \omega} \right)^n \alpha_n(\omega) \). Using \( \alpha_0(\omega) = 1 \), \( \alpha_1(\omega) = -\rho \omega \) and \( \alpha_2(\omega) = \rho 2\sigma^2_\epsilon \) in Eq.(B.3) and truncating the expansion at the second order directly yields Eq.(18) in the text. The validity of the truncation is controlled by the smallness of the jump moments \( \alpha_3(\omega) = -2\rho^2\sigma^2_\epsilon \omega \) and \( \alpha_4(\omega) = 4\sigma^4_\epsilon \rho^2 \).

**Appendix C: Perturbation theory for \( \rho \ll 1 \)**

This Appendix gives a brief summary of the perturbation expansion of Eq.(22). For small values of the fluctuation parameter \( \rho = \delta^2/(2\sigma^2_\epsilon) \) a first-order expansion yields

\[
G_n(\epsilon, t|\epsilon_0) \approx G(\epsilon, t|\epsilon_0) - n\rho \int_0^t d\tau \int d\epsilon' \int d\epsilon'' G(\epsilon, t-\tau|\epsilon') \kappa(\epsilon') \epsilon' G(\epsilon'', \tau|\epsilon_0) \quad \text{(C.1)}
\]

and thus, using \( \int d\epsilon G(\epsilon, t|\epsilon_0) = 1 \)

\[
\int d\epsilon G_n(\epsilon, t|\epsilon_0) \approx \exp \left[ -n\rho \int_0^t d\tau \int d\epsilon' \kappa(\epsilon') G(\epsilon', \tau|\epsilon_0) \right] \quad \text{(C.2)}
\]

Here, \( \exp(-x) \approx (1-x) \) and the definition of \( \kappa(\epsilon) \), cf. Eq.(14), has been used. Inserting Eq.(C.2) in Eq.(23) and using Eq.(21) shows that the resulting sum over \( n \) can be evaluated\[37\].

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In the short time limit, one can replace $G(\epsilon', \tau|\epsilon_0)$ by its initial value, $G(\epsilon', \tau = 0|\epsilon_0) = \delta(\epsilon' - \epsilon_0)$, yielding $\int d\epsilon G_n(\epsilon, t|\epsilon_0) \simeq \exp \left[ -n\rho\kappa(\epsilon_0)t \right]$. Thus, one finds Eq.(8) with $\lambda = \rho\kappa(\epsilon)$ and $p(\lambda) = p^\text{eq}(\epsilon)$.

In the long time limit, on the other hand, one can write $G(\epsilon', \tau = \infty|\epsilon_0) = p^\text{eq}(\epsilon')$ in Eq.(C.2). This gives $\int d\epsilon G_n(\epsilon, t|\epsilon_0) \simeq \exp \left[ -n\rho\kappa(t) \right]$, where the mean relaxation rate is defined as $\langle \kappa \rangle = \int d\epsilon \kappa(\epsilon)$. Again, one recovers Eq.(8) with $p(\lambda) = \delta(\lambda - \rho(\kappa))$.

Figure captions

Fig.1 : Sketch of the evolution of the optical emission spectrum. The environmental relaxation gives rise to the Stokes shift of the observed time-resolved emission spectra. Here $|g\rangle$ and $|e\rangle$ denote the ground and excited electronic state, respectively. $I(\omega, t)$ is the time-dependent optical lineshape evolving from the initial absorption spectrum $S_g(\omega)$ at $t=0$ to the steady state emission spectrum $S_e(\omega)$ at long times.

Fig.2 : $C(t)$ (upper panel) and $C(2t) - C(t)^2$ (lower panel) versus scaled time $t/\tau_K$ for $\rho = 0.1$. The parameters are chosen such that the $C(t)$ are well fitted to $C(t) = \exp \left( -t/\tau_K \right)$. Dashed lines: $\beta_K = 0.65$, $\kappa = 2.3 \times 10^3 \text{s}^{-1}$, $\sigma(\epsilon) = 3.055$; full lines: $\beta_K = 0.50$, $\kappa = 7.2 \times 10^4 \text{s}^{-1}$, $\sigma(\epsilon) = 3.65$; dotted lines: $\beta_K = 0.35$, $\kappa = 5.83 \times 10^9 \text{s}^{-1}$, $\sigma(\epsilon) = 5.03$. Here, $\sigma(\epsilon)$ is given in temperature units ($\langle \beta = 1 \rangle$. Additionally, the values of $\epsilon$ are restricted to the interval $\epsilon \in \{-\sigma(\epsilon)^2, \sigma(\epsilon)^2\}$, giving equilibrium probabilities $p^\text{eq}(\epsilon) \propto \eta(\epsilon)e^{-\beta\epsilon}$ that are truncated Gaussians. Note, that the prefactors include a factor $\exp(-\beta E_A)$ and therefore are only related in an indirect way to the attempt frequencies, typically on the order of $10^{15} \text{s}^{-1}$.

Fig.3 : (a): $\xi(t)$ as defined in Eq.(27) and $C(2t) - C(t)^2$ versus scaled time for the same parameters as in Fig.2 for $\beta_K = 0.5$. The difference between $\xi(t)$ and $C(2t) - C(t)^2$ shows the deviations from the Gaussian approximation, Eq.(27), for the conditional probability.

(b): The quantities $\zeta_n(t)$, defined in Eq.(28), versus scaled time. In the Gaussian approximation the $\zeta_n(t)$ vanish identically, $\zeta_n(t) = 0$.

Fig.4 : Double-sided Feynman diagram for the excitation and for the emission of an electronic two-level system, cf. Eq.(A.11). The solute-system initially is in thermal equilibrium in the ground state ($\rho \propto |g\rangle\langle g|$). The interaction with the incoming radiation, the wavy lines, produces an optical coherence ($|e\rangle\langle g|$), which then is converted into an excited state population ($|e\rangle\langle e|$). After photon emission, which again is accompanied with a coherence, the system is again in a ground state population ($|g\rangle\langle g|$).
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\[ I(\omega, t) \]

G. Diezemann, Fig. 1
\[ \beta_K = 0.65 \]

\[ \beta_K = 0.5 \]

\[ \beta_K = 0.35 \]

G. Diezemann, Fig. 2
\begin{align*}
\xi(t) &= \zeta_n(t) \\
&= C(2t) - C(t)^2,
\end{align*}

G. Diezemann, Fig. 3
G. Diezemann, Fig. 4