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We study the relaxation dynamics of photoexcited Fe-II complexes dissolved in water and identify the relaxation pathway which the molecular complex follows in presence of a hydration shell of bound water at the interface between the complex and the solvent. Starting from a low-spin state, the photoexcited complex can reach the high-spin state via a cascade of different possible transitions involving electronic as well as vibrational relaxation processes. By numerically exact path integral calculations for the relaxation dynamics of a continuous solvent model, we find that the vibrational life times of the intermittent states are of the order of a few ps. Since the electronic rearrangement in the complex occurs on the time scale of about 100 fs, we find that the complex first rearranges itself in a high-spin and highly excited vibrational state, before it relaxes its energy to the solvent via vibrational relaxation transitions. By this, the relaxation pathway can be clearly identified. We find that the lifetime of the vibrational states increases with the size of the complex (within a spherical model), but decreases with the thickness of the hydration shell, indicating that the hydration shell acts as an additional source of fluctuations.

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I. INTRODUCTION

When a photoexcited molecule is placed in a polarizable solvent, it will relax its energy in presence of potentially strong interactions with its bath, i.e., its nearest neighbor solvent molecules. This interplay manifests itself already in the properties of the steady state by the observed Stokes shift between the absorption and emission energies of the solute, which typically reflect the rearrangement of the caging solvent around the excited solute.1–3 A pioneering femtosecond transient absorption laser study of photoexcited NO in solid Ne and Ar rare gas matrices was capable of extracting mechanistic movements of the caging rare gas atoms in combination with model calculations,4, 5 but in liquid media this connection to the actual solvent movements in response to the creation of an excited state dipole moment is inherently difficult to observe experimentally. Quantum chemical calculations have meanwhile advanced and now permit simulating the dynamic response inside a box containing the excited molecule itself and a certain number of moving solvent molecules. In this way, simple ions,6 but also more complex molecules, such as aqueous [Fe(bpy)3]2+ could be treated.7 In a recent experiment, Haldrup et al.8 have attempted to tackle this phenomenon exploiting combined x-ray spectroscopies and scattering tools. This picosecond time-resolved experiment used x-ray absorption spectroscopy to unravel the electronic changes visible around the Fe K absorption edge. They occur concomitant to the geometric structural changes already extracted from the extended x-ray absorption fine structure (EXAFS) region.9 The latter monitors the molecular changes around the central Fe atom. While these studies only shed light on the excited molecular dynamics (MD) within itself, the recent study combined x-ray emission spectroscopy (XES) with x-ray diffuse scattering (XDS) to obtain a picture of the internal electronic and structural dynamics (via XES) simultaneously with the geometric structural changes in the caging solvent shell. One surprising result from this experimental campaign has yielded information about a density increase right after photoexcitation (i.e., within the 100 ps time resolution of that study), which was fully in line with the MD simulations of Ref. 7. They calculated a change in the solvation shell between the low spin (LS) ground and high spin (HS) excited state, which resulted in the expulsion of, on average, two water molecules from the solvation shell into the bulk solvent. This showed up in the XDS data as a density increase in the transient XDS pattern, and even the quantitative analysis extracted an average density increase due to about two water molecules expelled into the bulk solvent per photoexcited [Fe(bpy)3]2+. This success has triggered the current theoretical study: If it is becoming possible to experimentally gain new insight into guest-host interactions in disordered systems like aqueous solutions, would it be possible to eventually understand the influence of guest-host interactions on the dynamic processes occurring within the solute? Indeed, aqueous [Fe(bpy)3]2+ is an ideal model system for several reasons. Internally, it undergoes several ultrafast transition processes involving correlations within the 3d orbitals: after photoexcitation from the 1A1 ground state into its singlet excited metal-to-ligand charge transfer state (1MLCT), it rapidly undergoes an intersystem crossing into the triplet manifold (3MLCT)
within about 30 fs,\textsuperscript{10,12} and leaves the MLCT manifold in 120 fs.\textsuperscript{11} Fluorescence up-conversion experiments on Fe(bpy)$_3^2^+$ have determined a mirror-like emission spectrum compared to the absorption at quasi-zero time delay and have quantified the ultrafast initial intersystem crossing time at different excitation energies to be <30 fs.\textsuperscript{12} Femtosecond XAS studies observed the appearance of the finally accessed HS $^5T_2$ state in less than 250 fs,\textsuperscript{13,14} which was also confirmed by an ultrafast optical-UV transient absorption study.\textsuperscript{15} A very recent femtosecond XES study revealed the existence of a metal-centered intermediate electronic state on the fly before the system settles into the HS state.\textsuperscript{16}

This electronic and spin-switching process sequence starts from the LS ground state which is formed by six paired electrons in the lower $t_{2g}$ level. Then, the cascade proceeds to the HS excited state. There, the six electrons are distributed via $t_{2g}^6e_g^2$ and both $e_g^2$ electrons with parallel spins to two of the four $t_{2g}$ electrons. Overall, $S = 2$ in the HS state (against $S = 0$ in the ground state) results. Such a transition is very common in Fe-II based spin crossover (SCO) compounds, but little is understood about both the internal dynamic processes involved as well as about the possible influence of the solvent on this rapid spin-switching scheme. Indeed, the initially excited MLCT manifold should interact with the caging solvent molecules, but currently little is known about the actual dynamic processes. This mystery motivates the calculations performed in this work.

Here we investigate the energy relaxation dynamics in photoexcited aqueous [Fe(bpy)$_3$]$^{2^+}$ theoretically in order to provide a new view of the short-time guest-host interactions in this complex sequence of relaxation. The water molecules close to the compound are polarized and a hydration shell of bound water is formed. On the one hand, this hydration shell may shield the compound from polarization fluctuations provided by the bulk water. On the other hand, it may also act as an additional source of polarization fluctuations and thus enhance the relaxation process. To be specific here, we consider the case of [Fe(bpy)$_3$]$^{2^+}$ in water.\textsuperscript{7,8,14}

The set of states which are involved in the cascade of transitions from the LS to the HS state is schematically shown in Fig. 1. Also, several intermediate vibrionic states of the complex are relevant.\textsuperscript{17} An initial photoexcitation (green solid arrow) brings the Fe-II complex from the ground state of the LS configuration into an excited vibronic state of a configuration of the MLCT state. The photoexcitation at 400 nm provides an energy of about 3.1 eV or $\sim 25$ 000 cm$^{-1}$. More precisely, a state on the $^1$MLCT manifold is initially excited, but rapidly undergoes an intersystem crossing into the triplet manifold ($^3$MLCT) within about 30 fs.\textsuperscript{11,12}

The two manifolds are similar in their vibrational frequencies and correspond to the skeleton mode of bpy in the MLCT configuration. This mode has a rather high vibrational frequency of $\Omega_{MLCT} \sim 1607$ cm$^{-1}$ and its vibrational ground state has an energy of about 18 000 cm$^{-1}$. Hence, the photoexcitation populates mostly the vibrational state $|4\rangle_{MLCT}$ with a quantum number $v_{MLCT} = 4$.

The relaxation out of this state can now occur via two alternative relaxation pathways. Elements of these pathways are known, but the path which is eventually chosen by the system is not fully understood in detail up to present. On the one hand, the relaxation can proceed via energetically lowering vibrational states on the MLCT manifold, i.e., following $|4\rangle_{MLCT} \rightarrow |3\rangle_{MLCT} \rightarrow \ldots$ (the blue path, see the sequence of blue arrows in Fig. 1). In fact, the available MLCT states form a broad manifold of metal-centered states.\textsuperscript{14} From the MLCT ground state, the energy could be transferred to a vibrationally excited state of one of the metal-centered triplet states ($^1$3T). In the T state, the Fe–N bond length increases, such that the Fe-II complex expands by about 0.1 Å. This molecular configuration has a vibrational energy gap\textsuperscript{17} of $\Omega_T \sim 250$ cm$^{-1}$ which corresponds to a vibrational mode of the Fe–N bond. It is experimentally well-established that the transfer from the MLCT manifold to the intermediate T states occurs in about 120 fs. The system would reach the vibrational ground state of the T configuration via a sequence of vibrational relaxation steps. From the T-vibrational ground state, the energy would be transferred to a vibrational excited state of the HS configuration. Its HS vibrational ground state has an energy of $\sim 4000$ cm$^{-1}$. The vibrational energy gap is again determined by a vibrational mode of the Fe–N bond and is estimated\textsuperscript{17} as $\Omega_{HS} \sim 150$ cm$^{-1}$. It is established that the transfer from the T to the HS state occurs within 70 fs.\textsuperscript{14,16} Along with this occurs another rearrangement of the compound which results in an effective growth of the molecule (and thus somewhat the caging cluster) of 0.2 Å. After vibrational relaxation in the HS state, the system would reach its HS ground state configuration within 1–3 ps.\textsuperscript{11,15}

The second possible pathway (the red path, see the sequence of red arrows in Fig. 1) would start in a highly excited vibrational state on the MLCT manifold as before. Without performing a vibrational relaxation transition within the MLCT manifold, it directly yields to a highly excited vibrational state on the T manifold within 120 fs and continues again without a vibrational relaxation transition to another highly excited vibrational state of the HS...
configuration within 70 fs. From there, the complex relaxes into the HS ground state via vibrational transitions and removal of the corresponding energy into the hydration shell and bulk water on a 1 ps time scale.\textsuperscript{11, 15}

The final HS to LS relaxation occurs in 665 ps.\textsuperscript{11}

Both scenarios would allow the system to reach the HS electronic manifold within roughly 200 fs via several intermediate states. The initial energy is intermittently stored within molecular vibrations but finally transferred out of the complex into the solvent environment. The Fe-II complex expands, since the Fe–N bond lengths increase, when the compound is excited from the LS to HS state. Here, we assume that Fe–N stretching and bending modes are dominant.

What is unknown from the experimental perspective, is the vibrational life times of the intermediate vibrational electronic states (blue and red question marks in Fig. 1). For instance, if the highly excited vibrational states on the MLCT manifold live long enough such that the transfer to the T-manifold can occur within 120 fs, the system would most likely choose the red pathway. On the other hand, if the highly excited vibrational states on the MLCT manifold rapidly relax within 120 fs to the MLCT ground state, the system would prefer to follow the blue relaxation pathway.

To decide this question from a theoretical point of view, we follow a simplified model description which is accurate enough such that a clear qualitative answer follows. For this, we establish a model of a quantum mechanical two-state system which describes a bath-induced vibrational relaxation from an excited vibrational state to the ground state on a generic manifold. We thereby model the environmental polarization fluctuations including the effects of a hydration shell in terms of a refined Onsager model combined with a Debye relaxation picture.\textsuperscript{18, 19} A crucial aspect here is that we include the bulk solvent and the hydration shell on the same footing in terms of a continuum description of environmental Gaussian modes. This model allows us easily to modify the radius of the solvated complex (taken as a sphere in this work) and the thickness of the surrounding hydration shell. Within this simplified model, we determine the energy relaxation rate for several representative vibrational modes including the Fe–N stretching and bending modes in dependence of the Fe–N bond length and the hydration shell thickness. Technically, we use numerically exact real-time path integral simulations on the basis of a fluctuational spectrum which is highly structured and far from being Ohmic. Such a “slow” bath reflects the similar physical time scales on which the vibrational relaxation transitions within a vibrational manifold and the polarization fluctuations of the surrounding water occur. The highly non-Ohmic form (see below) of the bath spectral densities a priori calls for the use of an advanced theoretical method beyond the standard Markov-approximated dynamical Redfield equations.

We find vibrational energy relaxation times on generic manifolds in the range of 2–8 ps depending on the Fe–N bond lengths and the hydration shell thickness. For this, we tune the vibrational frequencies which are determined by the curvature of the manifolds over a relevant parameter range. We can determine the modes with fastest energy relaxation which dominates the energy relaxation dynamics of the Fe-II complex since internal energy redistribution is likely much faster. Most importantly, we observe that the vibrational relaxation times within a manifold are much longer than the typical time scales of a few hundred fs during which the HS state is formed. Two effects are competing here. A complex with a smaller radius of the solvation sphere brings the environmental fluctuations spatially closer to the complex and thus results in a faster decay. However, in turn, the stronger Fe–N bond results in larger mode frequencies. Overall, the calculated life times of the vibrationally excited states in the ps regime clearly show that the vibrational life times are much longer than the complex overall needs to reach the HS state, which are less than 200 fs. Thus, we can conclude that the energy relaxation basically occurs via the “red pathway,” i.e., the compound vibrationally relaxes into the ground state after it has reached the HS state.

Our findings for the vibrational energy relaxation times of the order of a few ps are consistent with those relaxation times known from standard vibrational wave packet dynamics. Wave packets composed of quantum states with energy differences corresponding to 200 fs or less will perform an excited state dynamics on this time scale and thus follow the “red pathway.”

II. MODEL

To determine the life time of the excited vibrational states, we formulate a minimal model in form of a quantum two-level system which is immersed in its solvent environment (model 1) and is, in addition, surrounded by a hydration shell (model 2). After expansion of the Fe-II complex, the stretching and bending modes involving the Fe–N bond change their respective vibrational frequency. We investigate their relaxation dynamics independently and use the spin-boson Hamiltonian as a minimal model, i.e.,

\begin{equation}
H = \frac{\hbar \Omega}{2} \sigma_z + \hbar \sigma_x \sum_j c_j (b_j + b_j^\dagger) + \sum_j \hbar \omega_j b_j^\dagger b_j. \tag{1}
\end{equation}

Here, the Pauli matrix \(\sigma_z\) contains the ground state \(|g\rangle\) and the excited state \(|e\rangle\) between which we investigate the relaxation transitions. The two states are separated in energy by the vibrational frequency \(\Omega\). The bath modes produce Gaussian fluctuations stemming from harmonic oscillators with frequencies \(\omega_j\), the corresponding creation and destruction operators of the bath modes are denoted as \(b_j^\dagger\) and \(b_j\). The fluctuations induce transitions in the system via the Pauli matrix \(\sigma_x\).

They can be characterized by a single function,\textsuperscript{21} the spectral density

\begin{equation}
J(\omega) = 2\pi \sum_j c_j^2 \delta(\omega - \omega_j). \tag{2}
\end{equation}

It provides the spectral weight contained in the fluctuations at frequency \(\omega\) which are provided by a Gaussian bath at thermal equilibrium at a given fixed temperature \(T = 1/(k_B\beta)\). The correlation function of the quantum bath fluctuations \(\xi(t)\) is...
This quantity determines the relaxation and dephasing rates. In this work, we consider several representative Fe–N stretching and bending modes with the frequencies Ω = 60, 120, 150, and 250 cm$^{-1}$. Moreover, we use a continuum description of the solvent (bulk) water and the hydration shell. The key quantity to characterize the environment, i.e., the spectral distribution $J(\omega)$ of the fluctuations, is determined in terms of the standard Onsager model of polarization fluctuations of the solvent water molecules. Their relaxation properties are described within a Debye relaxation picture. In this approach, the spectral density is related to the continuum dielectric function $\varepsilon(\omega)$ of the host material.

To be more specific, we consider two different situations, see Fig. 2: In model 1, we assume that the complex with its vibrational mode is placed inside a vacuum spherical cavity of radius $r_a$ with a dielectric constant $\varepsilon_s = 1$. This is situated in a continuum of bulk water modes with a frequency-dependent complex dielectric function $\varepsilon_b(\omega)$. In model 2, we add to model 1 an outer sphere with radius $r_b > r_a$. The shell formed by the two spheres describes the bound water or hydration shell in terms of a second frequency-dependent complex dielectric function $\varepsilon_{bw}(\omega)$. This model allows us to determine the relaxation rates also for varying the radii $r_a$ and $r_b$ independently. Throughout this work, we set $T = 300$ K.

### A. Model 1: Bulk water

Following Refs. 18, 22, and 23, one can calculate the reaction field by solving Maxwell’s equation for the particular geometry shown in Fig. 2. This yields the spectral density

$$J_1(\omega) = \frac{(\Delta \mu)^2}{2 \pi \varepsilon_0 \varepsilon_r a^3} \text{Im} \frac{\varepsilon_b(\omega) - 1}{2 \varepsilon_b(\omega) + 1} \omega \tau_s$$

with the respective transition dipole moment $\Delta \mu$ of the vibration, $\varepsilon_{s,0}$ being the static dielectric constant of the bulk solvent, and $\varepsilon_{s,\infty}$ the high-frequency dielectric constant of the bulk solvent, and

$$\tau_s = \frac{2 \varepsilon_{s,\infty} + 1}{2 \varepsilon_{s,0} + 1} \tau_{D,s}$$

and $\tau_{D,s}$ is the Debye relaxation time of the solvent. For water, we have $\varepsilon_{s,0} = 78.3$, $\varepsilon_{s,\infty} = 4.2$, and $\tau_{D,s} = 8.2$ ps.

Here, we are interested in the dependence of the spectral density on the cavity volume determined by its radius $a$ and we thus collect all constants in a prefactor. We arrive at

$$J_1(\omega) = \frac{\alpha_1}{a^3} \frac{\omega}{\omega^2 \tau_s^2 + 1},$$

with

$$\alpha_1 = \frac{1}{2 \pi \hbar} \frac{(\Delta \mu)^2}{2 \pi \varepsilon_0 \varepsilon_r a^3} \frac{6(\varepsilon_{s,0} - \varepsilon_{s,\infty})}{(2 \varepsilon_{s,0} + 1)(2 \varepsilon_{s,\infty} + 1) \omega^2 \tau_s^2 + 1} \tau_s,$$

where $\alpha_0$ is the typical length scale of the problem and where the now dimensionless radius $a = r/a_0$ is measured in units of $a_0$. We fix this to $a_0 = 1$ Å throughout this work. The spectrum is purely Ohmic with a cut-off frequency given by $\omega_{c,s} = 1/\tau_s$. For our considerations, we fix the dipole moment to a typical value of $\Delta \mu = 1$ D = $3 \times 10^{-30}$ cm. Collecting all parameters yields $\alpha_1 \approx 5$ for bulk water. Fig. 3 shows $J_1(\omega)$ of model 1 for the case $a = 6$ (corresponding to $r_a = 6$ Å). Maximal spectral weight is observed at roughly 70 cm$^{-1}$. Hence, it is clear that the resulting bath correlation times are comparable to or exceed internal system periods. This also prevents us from using a standard Markov approximation a priori, since a correlated and non-Markovian dynamics can in principle be expected (see below).

### B. Model 2: Bulk water plus hydration shell

We also include the hydration shell of bound water and do this by a second sphere with outer radius $r_b = ba_0$ with $b$ being the corresponding dimensionless number. We assume that the hydration shell is thin relative to the radius of the inner sphere and may then perform a Taylor expansion in the relative shell thickness $(b - a)/a$. The resulting spectral density is

$$J_2(\omega) = J_1(\omega) + J_{bw}(\omega),$$
with

$$J_{bw}(\omega) = \frac{(\Delta \mu)^2}{2\pi \varepsilon_0 c_0^2 (2\varepsilon(\omega) + 1)^2} \left(1 + \frac{2\varepsilon_{e,0}}{|J_{bw}(\omega)|^2}\right) \text{Im} \varepsilon_{bw}(\omega),$$

(9)

where $\varepsilon_{bw}(\omega)$ is the complex dielectric function of the bound water layer. Within the Debye relaxation model, we find

$$J_{bw}(\omega) = \frac{\varepsilon_{bw} b - a}{a^2} \omega^2 t_{bw}^2 + 1$$

(10)

with

$$\alpha_{bw} = \frac{1}{2\pi \hbar} \frac{3(\Delta \mu)^2}{2\pi \varepsilon_0 c_0^2} \frac{(\varepsilon_{bw,0} + \varepsilon_{e,0})(\varepsilon_{bw,0} - \varepsilon_{bw,\infty})}{\varepsilon_{bw,0}(2\varepsilon_{e,0} + 1)^2} t_{bw}.$$ 

(11)

Here, we have the static dielectric constant $\varepsilon_{bw,0}$ and the high-frequency dielectric constant $\varepsilon_{bw,\infty}$ of the bound water layer. From generic considerations,\textsuperscript{25} one may infer that the relaxation time of the bound water shell is one order of magnitude larger than the solvent relaxation time, i.e., we set $\tau_{bw} = 10\tau_v$. Likewise, we know\textsuperscript{25} that $\varepsilon_{s,0} \gg \varepsilon_{s,\infty}$. Moreover, $\varepsilon_{bw,0} \gg \varepsilon_{bw,\infty}$ and $\varepsilon_{s,0} \gg \varepsilon_{bw,0}$. Hence, we may use this and set $\varepsilon_{bw,0} = 1$ to obtain

$$\alpha_{bw} = \frac{1}{2\pi \hbar} \frac{3(\Delta \mu)^2}{2\pi \varepsilon_0 c_0^2} \frac{1}{4} t_{bw}.$$ 

(12)

For the parameters mentioned, we find $\alpha_{bw} \approx 118$.

Fig. 3 shows $J_2(\omega)$ for these parameters and for $a = 6$ and $(b - a)/a = 0.15$. Again, maximal spectral weight is observed at roughly 70 cm$^{-1}$. In general, the spectral weight of model 2 is higher than of model 1. This already indicates that within the continuum approach, the bound water shell acts as an additional source of fluctuations and not as a spectral filter for the continuous bulk modes. Hence, the calculated relaxation times for model 2 will be shorter than for model 1.

Moreover, it is clear that the vibrational life times on the MLCT manifold are much larger since there the spectral weight of the solvent environmental modes around the frequency of $\varepsilon_{MLCT} = 1607$ cm$^{-1}$ is strongly suppressed (in fact, we do not consider the vibrational relaxation around this frequency in this work).

### III. REAL-TIME DYNAMICS OF THE RELAXATION TRANSITIONS

To investigate the quantum relaxation dynamics of the two vibrational states under the influence of environmental fluctuations, we employ the numerically exact quasiadiabatic propagator path-integral (QUAPI)\textsuperscript{25} scheme which we have extended to allow the treatment of multiple baths.\textsuperscript{26} Specifically, QUAPI is able to treat highly structured and non-Markovian baths efficiently.\textsuperscript{27-29} It determines the time dependent statistical operator $\rho(t)$ which is obtained after the harmonic bath modes have been integrated over. We briefly summarize here the main ideas of this well-established method and refer to the literature for further details. The algorithm is based on a symmetric Trotter splitting of the short-time propagator $K(t_{k+1} - t_k)$ for the full Hamiltonian equation (1) into a part depending on the system Hamiltonian alone and a part involving the bath and the coupling term. The short-time propagator gives the time evolution over a Trotter time slice $\delta t$. This splitting in discrete time steps is exact in the limit $\delta t \to 0$, i.e., when the discrete time evolution approaches the limit of a continuous evolution. For any finite time slicing, it introduces a finite Trotter error which has to be eliminated by choosing $\delta t$ small enough such that convergence is achieved. On the other side, the environmental degrees of freedom generate correlations being non-local in time. We want to avoid any Markovian approximation at this point and take these correlations into account on an exact footing. We may, however, use the fact that for any finite temperature, these correlations decay exponentially quickly on a time scale denoted as the memory time scale. The QUAPI scheme now defines an object called the reduced density tensor. It corresponds to an extended quantum statistical operator of the system which is nonlocal in time since it lives on this memory time window. By this, one can establish an iteration scheme by disentangling the dynamics in order to extract the time evolution of this object. All correlations are fully included over the finite memory time $\tau_{mem} = K\delta t$, but are neglected for times beyond $\tau_{mem}$. To obtain numerically exact results, we have to increase accordingly the memory parameter $K$ until convergence is found. The two strategies to achieve convergence, i.e., minimize $\delta t$ but maximize $\tau_{mem} = K\delta t$, are naturally counter-current, but nevertheless convergent results can be obtained in a wide range of parameters, including the cases presented in this work.

### IV. RESULTS AND DISCUSSION

At first, we consider modes with a vibrational frequency of $\Omega = 150$ cm$^{-1}$. We determine the difference $P(t) = \langle \sigma_z \rangle_0 = \text{tr} \{\rho(t)\sigma_z\}$ of the populations of the ground and the excited states. We start out from the initial preparation of the excited state, i.e., $\rho(0) = |e\rangle\langle e|$. Fig. 4 shows examples of the relaxation dynamics for the environmental models 1 and 2 for different values of the shell thickness $(b - a)/a$. We mainly observe exponential relaxation on a time scale of a few picoseconds. For an increasing shell thickness, a tendency towards a decaying oscillatory dynamics appears. A pronounced oscillation with a period of $\sim 250$ fs develops for the largest thickness considered.

![FIG. 4. Time evolution of the population difference $P(t)$ for $\Omega = 150$ cm$^{-1}$ for $T = 300$ K for different values $(b - a)/a$ of the shell thickness.](image-url)
To quantify the decay in terms of life times of the excited state, we extract from the time evolution the corresponding rate by a fit to an exponential. Fig. 5 shows the relaxation time in ps (colour scale) as a function of the radius $a$ of the complex varying it between 5 to 7 Å and the relative shell thickness $(b - a)/a$ varying it between 0% to 30%, which is consistent with the numerical findings of Ref. 7. The plot shows results of both, models 1 and 2 (model 1 corresponds to the line with $(b - a)/a = 0$). The data for $(b - a)/a = 0$, 0.1, 0.2, and 0.3 are shown again in Fig. 6 for better readability. The calculated relaxation times or life times of the excited state vary from 2 to 8 ps. For a larger complex radius, the life time increases as expected since the prefactor of the spectral density decreases proportional to $1/r^6$. This reflects the assumption that the effective transition dipole sits in the center of the sphere and an increasing complex pushes the solvent fluctuations further away. This reduces their strength due to the distance dependence of the dipolar coupling. Moreover, the life times decrease with increasing hydration shell thickness. Thus, the hydration shell does not act as a shield from bulk solvent fluctuations but acts as an additional source of fluctuations instead.

Fig. 6 also shows the results of the vibrational life times calculated within a Born-Markov approximation. The inverse life time or the relaxation rate can be obtained after expanding the transition rates in a master equation approach up to lowest order in the system-bath interaction, together with a Markovian approximation of the bath-induced correlations. This corresponds effectively to only including single-phonon transitions in the bath. The inverse vibrational life time then follows as

$$
\tau^{-1} = J(\Omega) \coth \frac{\hbar \Omega \beta}{2}.
$$

As is shown by the dashed lines in Fig. 6, significant deviations from the exact life times occur and the approximated life times are somewhat overestimated.

Next, we show the results for the calculated life times for other vibrational frequencies, i.e., for $\Omega = 60, 120, 150,$ and $250$ cm$^{-1}$ in Fig. 7. These values span the regime of the vibrational frequencies for the Fe–N stretching and bending modes in the LS and HS state. Note that the frequencies are comparable to or larger than the frequency for which the maximal spectral weight in the environmental fluctuation spectrum occurs. Hence, the energy relaxation dynamics occurs in the regime in which non-Markovian multi-phonon transitions already are noticeable. We note that for larger values of $\Omega$, no convergent results have been achieved, which is a further strong indication of non-Markovian behavior.

Finally, a discussion of the validity of the modeling of the vibrational life times via a simple quantum two-level system in is in order. Certainly, the true vibrational relaxation dynamics of the entire compound involves a complex coupled electron-vibrational motion. However, the photoexcited Fe–II is at present by far too complex to model its dynamics with all the intermediate nonadiabatic quantum states microscopically in the presence of the solvent and the hydration shell. Hence, our modeling provides only the proper time scale on which the relaxation in presence of a solvent and a hydration shell occurs. Nevertheless, a simple model allows to understand the role of the hydration shell on the relaxation rate between two quantum states. If more than the ground state and the first excited states are involved, an improved estimate of the total relaxation rate will be obtained by incoherently adding the relaxation rates generated in a sequence of single-phonon relaxational steps. In this simplistic way, also the complex role of vibronic states is not included. Nevertheless, the similar order of magnitude of the relaxation time scale will arise.

Moreover, we point out that the spectral density of the fluctuations is not structure-less as assumed in a pure Ohmic spectral density. Instead, it is non-monotonous in a relevant frequency range of the electronic dynamics. Hence, the validity of the often used Markovian approximation is a priori not clear. Only in the hindsight and after a comparison with a Born-Markov relaxation rate, we can confirm that the deviations between the weak-coupling analytical rate and the exact one are of the order of 20%.

We also note that the interaction of the compound with the bulk water is the same also in presence of a hydration shell as compared to without the shell. The interaction in both cases is treated within the Onsager model of solvation. The key quantity is the time-dependent reaction field at the location of the central dipole. The dipole polarizes the solvent which generates, in turn, a reaction field for the dipole. The reaction field is determined by solving the classical Maxwell equations with the corresponding boundary conditions which is appropriate in the low-energy or long-wave-length sector. This is reflected in a Debye-like spectral density which depends

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**FIG. 5.** Relaxation time (color scale in ps) of the excited vibrational state for varying radius $r_a = \alpha a_0$ with $\alpha_0 = 1$ Å and for varying relative shell thickness $(b - a)/a$ for $\Omega = 150$ cm$^{-1}$. Model 1 with no hydration shell is contained via the cut along the line $(b - a)/a = 0$.

**FIG. 6.** Solid lines: Cut through the 2D plot of Fig. 5 along the lines $(b - a)/a = 0, 0.1, 0.2, \text{and } 0.3$. The dashed lines indicate the results of the vibrational life times calculated within a Born-Markov approximation (see text).
linearly on the frequency for small frequencies, but which might acquire a structure at frequencies comparable to the Debye frequency. These two features are the prevailing ones which will survive also in a more detailed treatment, for instance, by including more vibrational molecular modes. Those are typically located at larger frequencies. Hence, the modeling within the conventional Onsager-Debye theory of solvation applies to both situations with and without the hydration shell in the continuum approach. In general, the Onsager continuum model certainly has its limitations, e.g., when the hydration shell consists of a few water molecules only. Further work will be necessary to understand the details much better. Nevertheless, our modeling constitutes the low-energy, long-wave-length limit of more refined models.

V. CONCLUSIONS

We observe that under the assumption of equal strengths of the coupling to the environmental fluctuations, all Fe–N stretching and bending modes in the LS and HS state exhibit quite similar vibrational life times on the order of 5 ps. The vibrational energy gap has been modified from 60 to 250 cm$^{-1}$ and all cases show similar results. An increased radius of the complex results in a larger life time since the fluctuating solvent molecules are moved further outside. A finite hydration shell thickness reduces the vibrational life times noticeably.

Our results indicate that all vibrational modes contribute similarly to the energy relaxation after initial photoexcitation. At the same time, all vibrational modes live too long in order to relax the energy already in the MLCT or the T state (assuming here the vibrational modes being identical to the modes in the LS state). Hence, the energy after the photoexcitation is first rapidly transferred from a highly excited vibrational MLCT state to a highly excited vibrational T state and then further to a highly excited vibrational HS state within about less than 200 fs. Only then, the full excess energy is dissipated while the electronic subsystem is in the HS state. Hence, the system follows the “red relaxation pathway” sketched in Fig. 1.

Energy redistribution within more molecular vibrational states is not included in our simplified model. Assuming the excess energy initially equally distributed among the Fe–N stretching and bending modes, each mode gets roughly an excitation energy of 440 cm$^{-1}$. This implies that roughly two excitations of the mode $\Omega = 250$ cm$^{-1}$ and up to three or four excitations of the mode with $\Omega = 120$ cm$^{-1}$ and $\Omega = 150$ cm$^{-1}$ occur. Thus, the total equilibration time of the complex after photoexcitation roughly follows as three times 5 ps which yields a value of 15 ps. These results could be experimentally verified by ultrafast spectroscopy of the intermediate MLCT and T states.

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