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A Spin-Boson Screening approach for unraveling dominant vibrational energy transfer pathways in molecular materials

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ABSTRACT

Vibrational energy transfer driven by anharmonicity is the major mechanism of energy dissipation in polyatomic molecules and in molecules embedded in condensed phase environment. Energy transfer pathways are sensitive to the particular intra-molecular structure as well as to specific interactions between the molecule and its environment, and their identification is a challenging many-body problem. This work introduces a theoretical approach which enables to identify the dominant pathways for specified initial excitations, by screening the different possible relaxation channels. For each channel, the many-body Hamiltonian is mapped onto a respective all-vibrational Spin-Boson Hamiltonian, expressed in terms of the harmonic frequencies and the anharmonic coupling parameters obtained from the electronic structure of the molecule in its environment. A focus is given on the formulation of the relaxation rates when different limits of perturbation theory apply. In these cases the proposed Spin-Boson Screening approach becomes especially powerful.

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1. Introduction

Vibrational energy transfer is a prominent dissipation mechanism in molecular systems. It is the most important mechanism for heat production and transport in the context of natural as well as synthetic molecular devices [1,2]. Overcoming spontaneous vibrational energy redistribution in molecules is the major challenge for mode-selective chemistry [3–8], and for controlling chemical reactions in condensed phases. Recent advances of ultrafast vibrational spectroscopy led to observations of novel intriguing phenomena including ballistic transport of vibrational energy along molecular wires and strong dependence of the transport pathways on the molecular structure [9,10]. Energy transfer between molecular high frequency modes is associated also with quantum mechanical coherence transfer, with relevance to the role of quantum mechanics in the control of biological processes [11].

A convenient framework for characterization of the initial steps of vibrational energy transfer following (electronically adiabatic) vibrational excitation is based on the normal mode analysis of the abundant geometries of the molecule within its environment (typically the equilibrium geometry or the distribution of molecular geometries around equilibrium). Within this framework, the interactions which drive energy transfer between specific normal modes are attributed to the anharmonic terms of the multi-dimensional potential energy surface of the molecule and its environment at the ground electronic state. Normal mode frequencies and anharmonic coupling constants are expressed in terms of energy derivatives with respect to the coordinates, and are routinely calculated in standard electronic structure codes [12].

Formally, the flow of energy from an initially excited normal mode (or a superposition of normal modes) is a dynamical process associated with an interacting many-body Hamiltonian. In a complete and rigorous treatment, the many-body dynamics should be followed. Considering the large dimensions of the vibrational Fock space in poly-atomics, statistical approaches based on random matrix theory were insightful for a qualitative analysis of the vibrational energy flow in large molecules. The diagonal Hamiltonian corresponding to the uncoupled modes (within a relevant energy interval) was augmented by off-diagonal anharmonic coupling matrix elements, which enabled to map vibrational relaxation onto a quantum diffusion process in a disordered lattice [13,14], characterized by a transition between quantum ergodicity to localization. The statistical approach to vibrational energy flow in the vibrational state space has been generalized in order to account for local

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effects and bottlenecks below as well as above the transition to quantum ergodicity [15,16]. In small molecules the diffusion was found to be highly anisotropic, and computational approaches were introduced in order to locate specific energy flow pathways [17–19]. Pointing out the dominant energy transfer pathways (or "relaxation channels") for a specified initial excitation in a specific system is the prime goal of many theoretical studies of vibrational relaxation in molecules, and of this work in particular. Since high-frequency modes are typically involved (in the sense that the vibration quantum of the excited mode is larger than the thermal energy, $\hbar\omega > K_B T$), a quantum mechanical treatment of the dynamics is necessary.

Powerful methods, such as the Multi-Configuration Time-Dependent Hartree (MCTDH) of the Heidelberg group [20,21] enable to study the combined quantum dynamics of strongly coupled modes in a numerically exact fashion [22]. However, for molecules in a detailed condensed phase environment the number of coupled modes and therefore the computational task of a full treatment become formidable. Other methods are aimed for direct simulations of the many-body dynamics invoking different approximations, such as the Vibrational Configuration Interaction (VCI) method [23], or purely classical Molecular Dynamics (MD) simulation [24,25], which limited in applications to processes involving only low frequency modes.

The most common approaches to the dynamics of vibrational relaxation are based on the assumption that the (anharmonic) coupling between the initially excited mode and the other modes is weak. In this case the other modes can be regarded as a bath, and the dynamics can be followed within time-dependent perturbation theory, to the second order in the system-bath coupling. When the vibrational energy relaxation is much slower than the bath response time, and when the coupling between energy transfer and coherence transfer can be neglected, vibrational energy relaxation is well described by a rate constant according to Fermi's golden rule. For linear coupling in the relaxing mode coordinate [26], this leads to the Landau-Teller formula [27–33], i.e. the rate is formulated as a Fourier transform of the autocorrelation function of the force exerted by the bath modes on the relaxing mode. For bi-linear coupling to a harmonic bath this correlation function is directly related to the dissipative friction kernel exerted by the bath in a framework of a generalized Langevin equation [34,35], and the quantum mechanical Landau-Teller rate can be calculated exactly using classical mechanics in this case [36–38]. This motivated calculations of fast-decaying force correlation functions using classical mechanics also for other (more realistic) models, using equilibrium properties [39], or classical MD simulations [40–42]. The quantum nature of the vibrations is accounted for in these calculations in terms of quantum correction factors [36,43–51]. Generalizations of the Landau-Teller formula were also introduced in order to account for non-linear (quadratic) coupling to the bath, in the relaxing mode coordinate (explicit fluctuations in the frequency of the relaxing mode) [52–55], and for non-Markovian effects [54,55]. A full quantum calculation of the correlation function for realistic models is still formidable, but semi-classical alternatives were introduced [56–64], by linearizing the forward-backward action in the quantum mechanical path integral formulation. Correlation functions obtained with this approach are accurate as long as the relaxation is fast, and they become exact for harmonic systems and/or time zero.

Several studies considered vibrational relaxation rates beyond the weak coupling limit. The flux-flux correlation function formulation enables to calculate the relaxation rate transiently, irrespective of the coupling strength [65]. In situations where the vibrational relaxation is driven by strong rather than weak coupling to the bath [66], the problem of vibrational energy transfer between two modes becomes analogous to the problem of non-adiabatic electron transfer in a polar environment, and a perturbative (Fermi's golden-rule based) rate expression for vibrational energy transfer was derived in the spirit of the classical Marcus theory [67].

In this work we introduce a new Spin-Boson Screening (SBS) approach for unravelling dominant vibrational relaxation pathways in polyatomic molecular materials (molecules in their environment). As mentioned above, we restrict the discussion to cases where the identification of an energy transfer "pathway" from an initially excited vibrational state into specific mode(s) is meaningful (in the sense that the ergodicity in the vibrational state space breaks down [14]). This usually implies that the respective mode frequencies are high, and distinctive from the continuum of low frequency modes. Therefore, we focus on assessing and comparing the rates of energy transfer between specified initially excited state and final states involving high frequency modes (or a superposition of modes, when relevant). As shown below, this amounts to the solution of an "all-vibrational" Spin-Boson model problem for each final state, where the initial and final states are presented as the "spin" degree of freedom, while all the unspecified modes (intra as well as inter molecular) are regarded as a bosonic bath.

Since high-frequency modes are involved both in the system and in the bath, a full quantum mechanical estimation of the relaxation rate is necessary, yet highly challenging with the methods available today, vide supra. To this end, our method allows for two major advantages: First, it provides a unified approach to the problem in both regimes of weak and strong coupling to the bath modes [66]. Second, since the exact calculations of the rate constants are impractical (because of the complexity of each single rate calculation, and the multiplicity of possible pathways to be tested for a given excitation), we employ time-dependent perturbation theories. The choice of the proper perturbative limit (weak or strong dissipation) depends on the particular Spin-Boson model parameters, namely the respective harmonic frequencies and anharmonic coupling constants. Thus, the SBS approach provides a convenient and economic quantum mechanical platform to estimate the different vibrational relaxation rates, and enables to effectively screen the different relaxation channels and to unravel the most efficient ones.

The rest of the paper is organized as follows: In Section 2 the interacting normal modes Hamiltonian is outlined. In Section 3 we introduce the projection of the full Hamiltonian onto Spin-Boson models. Energy transfer rates are formulated analytically in terms of anharmonic coupling constants in Sections 4 and 5, for limiting cases of strong or weak dissipation to the boson field, respectively. Conclusions and perspectives are given in Section 6.

2. The interacting normal modes Hamiltonian

The nuclear Hamiltonian of a polyatomic molecule in its environment, at the ground electronic state takes the generic form,

$$\begin{aligned}
\hat{H} &= \hat{H}^{(0)} + \sum_{k=3}^{\infty} \hat{V}^{(k)} \\
\hat{H}^{(0)} &= \sum_{j} \hbar\omega_j \, \hat{a}_j^{\dagger} \hat{a}_j \\
\hat{V}^{(k)} &= \sum_{j_k} \sum_{j_{k-1}} \cdots \sum_{j_2} \sum_{j_1} \lambda_{j_k, j_{k-1}, \ldots, j_2, j_1} (\hat{a}_{j_k}^{\dagger} + \hat{a}_{j_k})(\hat{a}_{j_{k-1}}^{\dagger} + \hat{a}_{j_{k-1}}) \cdots (\hat{a}_{j_2}^{\dagger} + \hat{a}_{j_2})(\hat{a}_{j_1}^{\dagger} + \hat{a}_{j_1}).
\end{aligned} \tag{1}$$

In Eq. (1) $\hat{a}_j^{\dagger}$ and $\hat{a}_j$ are the harmonic oscillator ladder operators of the jth normal mode, $\hat{q}_j = \frac{1}{\sqrt{2}}(\hat{a}_j^{\dagger} + \hat{a}_j)$ is the respective position

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