Relationship between Quantum Decoherence Times and Solvation Dynamics in Condensed Phase Chemical Systems

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A relationship between the time scales of quantum coherence loss and short-time solvent response for a solute/bath system is derived for a Gaussian wave packet approximation for the bath. Decoherence and solvent response times are shown to be directly proportional to each other, with the proportionality coefficient given by the ratio of the thermal energy fluctuations to the fluctuations in the system-bath coupling. The relationship allows the prediction of decoherence times for condensed phase chemical systems from well-developed experimental methods. [S0031-9007(98)07929-0]

Quantum processes in condensed phases are often studied by focusing on a small subset of degrees of freedom and treating the rest as a bath. The subsystem of interest may comprise a single molecule, a molecule plus its nearest surroundings, or even a single vibrational mode within a molecule. The remaining degrees of freedom form the bath. In the presence of system-bath interactions, the subsystem's wave function evolves into a superposition of quantum states. Because of an enormous density of states in a macroscopic environment, small differences in the system-bath coupling lead to rapid divergence between bath evolutions corresponding to different states of the subsystem. The reduced density matrix of the microscopic subsystem, obtained from the total density matrix by integrating over bath degrees of freedom, soon becomes diagonal [1]. Quantum states decohere [1–4]. The decoherence rate is determined by the sensitivity of bath evolutions to the quantum state of the subsystem. Notably, this sensitivity also determines bath response to a perturbation within the subsystem. In the context of the condensed phase chemical physics, the rate of the solvent bath rearrangements following a perturbation of the solute subsystem is described by a well-developed solvent response theory [5–7]. In this Letter, we establish for the first time a quantitative relationship between quantum coherence loss and the short-time solvent response.

The new relationship is important because a link between solvation dynamics and decoherence is capable of providing valuable insights into both phenomena. Modern techniques of the solvent response theory employing the concepts of dielectric and mechanical relaxation [8,9], and instantaneous normal modes [7] then become transferable to the description of decoherence. The theory of short-time solvation can benefit from the recent theoretical ideas on quantum Brownian motion [10,11] and quantum measurement [1,3,4]. Most importantly, currently available experimental means to measure quantum coherence loss [12–14] and short-time solvent response

[5,8,15] in a nonequilibrium system can be combined. A relationship between decoherence and solvation time scales further provides a tool to deconvolute the contribution of each effect on observed dynamics. The results presented below form a basis for evaluation of quantum decoherence times in various solute-solvent systems based on the extensive solvent response data accessible from both experimental measurements and adiabatic molecular dynamics simulations.

Following Ref. [16], we consider the direct product of the system S and bath B Hilbert spaces. For simplicity, the system space is assumed to be two dimensional. We consider two orthogonal states ϕ_1^S and ϕ_2^S of the system and a system-bath interaction that induces quantum transitions in the combined system, with the bath state responding to that of the system:

$$\phi_\alpha^S \otimes \phi_0^B \rightarrow \phi_\alpha^S \otimes \phi_\alpha^B, \qquad \alpha = 1, 2, \qquad (1)$$

where ϕ_0^B is the initial state of the bath. Transitions from an arbitrary initial system state $c_1\phi_1^S + c_2\phi_2^S$ are then described in terms of the reduced density matrix

$$\begin{pmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{pmatrix} \rightarrow \begin{pmatrix} |c_1|^2 & c_1 c_2^* (\phi_2^B | \phi_1^B) \\ c_1^* c_2 (\phi_1^B | \phi_2^B) & |c_2|^2 \end{pmatrix}. \qquad (2)$$

Decoherence is defined [1,2] as decay of the nondiagonal matrix elements, which, for the reduced density matrix of Eq. (2), is clearly determined by the decay of the inner product of the bath states $(\phi_1^B | \phi_2^B)$. Initially, the bath wave functions coincide: $\phi_1^B = \phi_2^B = \phi_0^B$. Later on, the bath wave functions correlated with the different states of the system diverge, and the overlap integral decreases. It is not the decay of the nondiagonal matrix elements *per se* that is most important from the practical point of view, but rather it is the associated slowing down of quantum transitions [16–18], known as the quantum Zeno effect in the limit of infinitely fast decoherence [18]. The lifetime of the quantum state in the presence of a bath

varies inversely with the decoherence time. This result holds in the spin-boson model, where the bath is treated as a set of harmonic oscillators [19,20], or in the frozen Gaussian formulation [21–23], where the bath wave function is approximated by a set of Gaussian wave packets [24]. Within this Gaussian wave packet approximation, the average decay of the overlap integral and corresponding nondiagonal matrix elements in Eq. (2) is described by the decoherence function given by Eq. (39) of Ref. [23]

$$D(t) = (\phi_1^B | \phi_2^B) = \exp\left[-\left\langle \sum_n \frac{\Delta F_n^2}{4a_n \hbar^2} \right\rangle t^2 \right], \quad (3)$$

where the angular brackets indicate thermal averaging. $\Delta F_n = F_{1n} - F_{2n}$ is the difference in the quantum forces experienced by the nth bath degree of freedom, i.e., the difference of energy gradients for the initial and final states of the subsystem taken in the direction of the nth bath mode. In the adiabatic representation these are the Hellmann-Feynman forces

$$F_{\alpha n} = -(\phi_\alpha^S | \nabla_n H | \phi_\alpha^S), \qquad \alpha = 1, 2. \quad (4)$$

We note that here we do not consider the dynamical effect of the bath on the subsystem energy eigenvalues. In the presence of bath induced fluctuations in these values, the phases of c_1 and c_2 in Eq. (2) are randomized, and a new "dephasing" contribution (see Refs. [23,25]) to the decay of the off-diagonal elements of the reduced density matrix can potentially contribute as well. The dephasing term, generally, decays slower than the nuclear overlap. This term becomes important on the longer time scale, and when averaging of transition probabilities over many states of slightly different energies is performed. The decay of the nuclear overlap is responsible for the quantum Zeno effect, while the "random-phase approximation" for the product of c_1 and c_2 leads to constant transition rates, in particular, to the Fermi's golden rule [26].

In the low temperature regime the width $a_n^{-1/2}$ of the Gaussian wave packet in Eq. (3) equals the width of the coherent state of a corresponding harmonic oscillator, i.e., $a_n = m_n \omega_n / \hbar$. For higher temperatures, the width of the wave packet incorporates quantum thermal ensemble averaging. The thermal width is analytic for harmonic baths

$$a_n = \frac{m_n \omega_n}{\hbar} \tanh\left(\frac{\hbar \omega_n}{2k_B T} \right). \quad (5)$$

For arbitrary baths, the width can be defined via the thermal de Broglie wavelength $\lambda_T = (2\pi \hbar^2 / mk_B T)^{1/2}$. An alternative expression for the thermal width is derived in Ref. [21], Sec. IV by comparing the exact and Gaussian wave packet results for the transition rate in a double-well system

$$a_n = \frac{m_n \omega_n}{\hbar} A_n,$$

$$A_n = \left[\coth\left(\frac{\hbar \omega_n}{2k_B T} \right) - \frac{2k_B T}{\hbar \omega_n} \right]^{-1}. \quad (6)$$

This expression reduces to the coherent state width in the low temperature case, and gives

$$a_n = \frac{6m_n k_B T}{\hbar^2} \simeq \left(\frac{\lambda_T}{6} \right)^{-2}, \quad (7)$$

in the high temperature limit. The last formula is particularly useful, since it yields a width which is independent of the frequency; Eq. (7) is designed [21] for use in molecular dynamics simulations, where thermal averaging over bath states is performed classically.

Turning to solvation dynamics, the response of the solvent bath to a quantum transition within the solute subsystem characterizes the rate of solvent adjustment to a change in the state of the solute and is quantified by the normalized correlation function C of the energy gap U between the initial and final quantum states [8,27]. The fluctuation-dissipation theorem relates this nonequilibrium solvent response to the regression of fluctuations δU of the gap U in equilibrium, e.g., before the quantum transition or after the solvent has already stabilized the newly created state,

$$C(t) = \frac{\langle \delta U(t) \cdot \delta U(0) \rangle}{\langle (\delta U)^2 \rangle}. \quad (8)$$

The short-time solvation dynamics that is of relevance in the present discussion, the so-called Gaussian or inertial response, depends solely on the change in the solute-solvent coupling due to the quantum transition. The microscopic *short-time* expression for $C(t)$ has been obtained in Ref. [27] [Eqs. (2.18), (2.19)] by expanding $C(t)$ in a set of independent modes, and in time yielding

$$C(t) = \exp\left[-\frac{k_B T}{\langle 2(\delta U)^2 \rangle} \left\langle \sum_n (U_n')^2 \right\rangle t^2 \right], \quad (9)$$

where U_n' is the derivative of U with respect to the nth mass-weighted solvent coordinate

$$U_n' = m_n^{-1/2} \frac{dU}{dx_n} = m_n^{-1/2} \Delta F_n. \quad (10)$$

The decoherence τ_D and Gaussian solvation τ_g time scales are given by the variances of the decoherence $D(t)$ and solvent response $C(t)$ functions of Eqs. (3) and (9), respectively. The structure of the equations is clearly similar, and by comparison we obtain

$$\left[\frac{\tau_D}{\tau_g} \right]^2 = \frac{2k_B T}{\langle (\delta U)^2 \rangle} \frac{\sum_n \Delta F_n^2 (m_n)^{-1}}{\sum_n \Delta F_n^2 (a_n \hbar^2)^{-1}}. \quad (11)$$

With the high temperature limit expression for the width [Eq. (7)] the formula simplifies to

$$\left[\frac{\tau_D}{\tau_g} \right]^2 = \frac{12(k_B T)^2}{\langle (\delta U)^2 \rangle} = \frac{6k_B T}{\lambda}. \quad (12)$$

Here, 2λ is the Stokes shift defined as the difference between the equilibrium absorption and emission maxima. The Stokes shift arises due to the fact that equilibrium

solvent configuration stabilizing the first and the second quantum states differ. The energies of the states are not the same in the two equilibria. The equilibrium absorption of the first state does not coincide with the equilibrium emission from the second state, leading to a Stokes shift. Within a linear response regime, the Stokes shift is related [20] to the fluctuations in the quantum energy gap by the fluctuation-dissipation theorem: $\langle(\delta U)^2\rangle = 2\lambda k_B T$. Equation (12) establishes direct proportionality between the short-time evolution of decoherence and of solvent response. In the high temperature limit for the bath the proportionality coefficient is determined by the ratio of the thermal energy fluctuations $(k_B T)^2$ to the fluctuations in the system-bath coupling $\langle(\delta U)^2\rangle$. The latter can be expressed in terms of the Stokes shift in the linear response regime. We note that the dependences are sensible: High temperatures accelerate solvation dynamics; large equilibrium fluctuations in the coupling, as well as large Stokes shifts, are indicative of fast decoherence.

Equation (12) should be compared with Eq. (5.4) for the decoherence time given in Ref. [1]:

$$\tau_D = \gamma^{-1}(\lambda_T/\Delta x)^2. \tag{13}$$

Here, γ^{-1} is the relaxation time, equivalent to τ_g in our notation. λ_T is the thermal de Broglie wave length. Δx is the "distance" between the initial and final states, related to the Stokes shift. Apart from a possible proportionality coefficient, $6k_B T/\lambda$ of Eq. (12) equals to $(\lambda_T/\Delta x)^2$ of Eq. (13). The ratio of the decoherence and solvation times enters the two equations in qualitatively different ways: quadratically in Eq. (12) and linearly in Eq. (13). The expression for the decoherence time derived in this Letter is valid in the short-time limit for an *individual* quantum event and is closely related to the quantum Zeno effect. On the other hand, the golden rule related result of Ref. [1] is obtained from a master equation, where averaging over an *ensemble* of quantum events is performed. Further discussion on the origins of the quadratic and linear forms of the decay rate can be found in Ref. [26].

We note that the relationship between the decoherence and solvation time scales presented above using the Gaussian wave packet approximation for the bath wave function also necessarily pertains to the spin-boson model. The spin-boson Hamiltonian describes a two-level system linearly coupled to a harmonic bath [19]

$$H_{\mathrm{SB}} = -\frac{1}{2}\hbar\Delta\sigma_x + \frac{1}{2}U_0\sigma_z$$
$$+ \sum_n\left(\frac{1}{2}m_n\omega_n x_n^2 + \frac{p_n^2}{2m_n}\right) + \frac{1}{2}q_0\sigma_z\sum_n c_n x_n, \tag{14}$$

where, U_0 and q_0 are the energy and coordinate displacements between the pair of potential minima, Δ is the intrinsic coupling between the two quantum states, c_n is the system-bath coupling constant, and σ_z, σ_x are the Pauli

matrices. The terms containing σ_z describe the energy gap

$$U_{\mathrm{SB}} = U_0 + q_0\sum_n c_n x_n. \tag{15}$$

According to Eqs. (9) and (10), the short-time solvent response function of the spin-boson model is

$$C_{\mathrm{SB}} = \exp\left[-\frac{1}{2}\frac{k_B T}{\langle(\delta U)^2\rangle}\sum_n\frac{q_0^2 c_n^2}{m_n}t^2\right]. \tag{16}$$

The decoherence function can be extracted from the Fermi golden rule result for the spin-boson problem [Eqs. (3.2), (3.35), and (3.36) of Ref. [19]]

$$D_{\mathrm{SB}} = \exp[-(q_0^2/\pi\hbar)Q_2(t)], \tag{17}$$

with

$$Q_2(t) = \int_0^\infty \frac{J(\omega)(1-\cos\omega t)}{\omega^2}\coth(\hbar\omega/2k_B T)\,d\omega, \tag{18}$$

and

$$J(\omega) = \frac{\pi}{2}\sum_n\frac{c_n^2}{m_n\omega_n}\delta(\omega-\omega_n). \tag{19}$$

The short-time expansion of $Q_2(t)$ gives

$$D_{\mathrm{SB}} = \exp\left[-\frac{1}{4}\sum_n\frac{q_0^2 c_n^2}{m_n\hbar\omega_n}\coth(\hbar\omega_n/2k_B T)t^2\right] \tag{20}$$

$$= \exp\left[-\frac{1}{4}\sum_n\frac{q_0^2 c_n^2}{a_n\hbar^2}t^2\right], \tag{21}$$

with a_n as in Eq. (5). The expression in Eq. (21) is a specific case of Eq. (3) with $\Delta F_n = -q_0 c_n$. Comparison of Eqs. (16) and (21) leads to the relationship given in Eq. (11) between the decoherence and Gaussian solvation times.

We can directly test Eq. (12) for the case of relaxation following transition from the first excited to the ground state of the hydrated electron, whose time dependent properties are well studied theoretically (see Refs. [21–23,25,29], and references therein). Based on a molecular dynamics trajectory for the first excited state of the hydrated electron [28], the equilibrium energy gap U is 0.56 eV and the fluctuation in the energy gap $\langle(\delta U)^2\rangle^{1/2}$ is 0.21 eV, which corresponds to a 1.7 eV Stokes shift (2λ) at room temperature. This Stokes shift corresponds closely to that found in nonadiabatic simulations [30]. The short-time component of the solvent response function $C(t)$ of Eq. (8) is found to be characterized by a 10.6 fs Gaussian time scale τ_g. From these data, the decoherence time τ_D of the first excited state of the hydrated electron calculated via Eq. (12) is 4.5 fs. This estimate falls within the previously reported range of 2.7–5.1 fs [21–23], with the value of 5.1 fs obtained in the high temperature approximation for Eq. (6).

The properties of the solute and the nature of the quantum transition define the difference in the solute-solvent potential for the initial and final states and, therefore, determine the magnitude of the Stokes shift in the relationship (12) between the decoherence and solvation times. Intrinsic solvent properties also, to some extent, affect the magnitude of the Stokes shift. However, the major solvent influence on the duration of quantum coherence is due to solvent's ability to respond to a perturbation in the solute, i.e., as reflected in the rate of solvent response τ_g. Based on the success above for the hydrated electron, one can address other systems, which will demonstrate the variability of decoherence times. For a styryl dye in methanol [31], experiment yields an estimated τ_g of 40 fs and a Stokes shift of 115 nm yielding a decoherence time of 6.8 fs. Acetonitrile $[CH_3-CN]$, the next solvent in a logical series exhibits a 100 fs experimental short-time solvent response [32]. Simulation of the electronic transition of the betaine-30 molecule in acetonitrile is characterized by a similar 91 fs short-time solvation [33]. The value for τ_g, together with the 0.16 eV electronic energy gap fluctuation evaluated along the ground state trajectory [33], leads via Eq. (12) to a substantially longer 49 fs decoherence time. Compared to the protic solvents, acetonitrile is much less effective in destroying quantum coherence.

In summary, we have presented an analytical relationship between the time scale for quantum decoherence and that governing the short time response of solvent to a perturbation in the solvent-solute coupling. The proportionality constant relating these requires knowledge of only the Stokes shift associated with the change in solute state. The expression successfully reproduces results obtained directly by other routes, and allows the prediction of decoherence times for other solution systems. It is expected that since the required input data is becoming readily accessible experimentally for even the most rapidly responding condensed phase environments, the derived relation will be very valuable to advancing the study of both decoherence and condensed phase chemical dynamics more generally.

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