Energy Gap Dependence of Vibrational Dephasing Rates in a Bath: A Semigroup Description

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Abstract.

The quantum dynamical semigroup formalism provides an appealing general framework for discussing factors that affect pure vibrational dephasing rates in chemical systems. Within this framework, we formulate a Poisson model of pure vibrational dephasing which is more generally applicable than the commonly employed stochastic Gaussian dephasing model. In the limit of small and frequent phase changes, the Poisson model reduces to the stochastic Gaussian form. We
find that for certain vibrational states of the lithium dimer in argon, the stochastic Gaussian model is valid, while for other states large and abrupt phase changes clearly require application of the Poisson model. In the former case, dephasing rates increase with the difference in quantum number between constituent vibrational states, while in the latter case, the dependence on quantum number difference or energy gap can become negligible. Recent experimental advances described by Amitay and Leone are expected to permit experimental tests of our theoretical predictions.

1. Introduction

Fully quantum mechanical treatment of complex chemical systems is generally computationally intractable. However, one is often concerned only with observables characterizing a subsystem of interest. In this case, it is most appropriate and convenient, when possible, to consider only the effective (or “reduced”) dynamics governing the evolution of these observables [1]. When the subsystem is weakly coupled to the remaining (“bath”) degrees of freedom, Redfield theory can be used to incorporate important bath effects into the reduced dynamics in an approximate way [1]. This approach has been used by Mukamel, Friesner, Nitzan and others [2-6] to address such issues as bath effects on electron transfer rates and mechanisms. However, the Redfield approach has important disadvantages, including the fact that one's choice of subsystem-bath boundary is constrained by the requirement of small coupling, and the occurrence of unphysical “negative populations” as a result of approximations inherent in the theory [7,8].
One promising alternative approach for modeling the reduced dynamics of a subsystem interacting with its environment was pioneered by Lindblad in the 1970s [9,8]. Lindblad determined the general form that all reduced dynamical equations must take if the bath is Markovian and the reduced density matrix retains certain required attributes (such as positivity of state populations). Practical dynamical methods based on the Lindblad approach include semigroup methods and stochastic (nonlinear) Schrödinger equation methods [8,10,11]. The simplicity and generality of the Lindblad approach are especially useful for categorizing and characterizing the different kinds of reduced dynamical processes that can be observed, as well as the experimental conditions that will promote one process over another [8].

Vibrational dephasing experiments provide important opportunities to test reduced dynamical methods in general. While vibrational dephasing processes have long been the subject of intense experimental and theoretical research [12], recent experimental advances developed by Leone and others have drastically increased both the range of vibrational dephasing processes that can be studied experimentally and the accuracy with which initial vibrational populations and phase relationships are known [13,14]. In addition to creating opportunities to test the applicability of semigroup and other reduced dynamical methods, these experimental methods also have potential applications in the areas of quantum control and quantum computing [13,14,15,16]. In these two developing areas, dephasing processes can be expected to play a particularly important role.
One prediction that follows from the application of the quantum dynamical semigroup formalism is that under certain experimental conditions the usual energy gap dependence of vibrational dephasing rates will be modified. A particularly promising system for testing this prediction is that of a lithium dimer in argon [13]. This system, which has been studied extensively by Leone and others, has a number of attractive features. These include the high tunability of the bath conditions and the great variability in the properties of different vibrational states. But most importantly, Leone and others [15] have demonstrated that a wide range of different initial superposition states can be created, and the resulting dynamics observed experimentally. This measurement capability provides a very attractive testing area for dynamical theories.

The remainder of this paper is organized as follows. In the second section, pure vibrational dephasing processes are described from a theoretical standpoint. In the third section, the transition to a region of energy gap independence is discussed within a semigroup framework. A “Poisson” model of dephasing is discussed which has more general applicability than traditional “stochastic Gaussian” models. In the fourth section, we consider the specific case of vibrational dephasing of a lithium dimer in argon, and make more explicit the conditions under which energy gap independent dephasing rates are expected to be observed experimentally. The fifth section discusses our conclusions.

2. Pure vibrational dephasing
For simplicity, we begin by considering the subsystem space to contain only two orthogonal vibrational states; the generalization to further states is straightforward. In the energy eigenstate representation the Hamiltonian of the subsystem “$S$” is

$$\hat{H}_S = |0\rangle \hbar \omega_0 \langle 0 | + |1\rangle \hbar \omega_1 \langle 1 |$$

(1)

where $\hbar \omega_0$ and $\hbar \omega_1$ are the energies of the two eigenstates $|0\rangle$ and $|1\rangle$. The reduced density operator in this eigenstate representation will then at all times take the form [17]

$$\hat{\rho}(t) = |0\rangle \rho_{00}(t) \langle 0 | + |1\rangle (1 - \rho_{00}(t)) \langle 1 | + |0\rangle \rho_{01}(t) \langle 1 | + |1\rangle \rho^\ast_{01}(t) \langle 0 |$$

(2a)

where $\rho_{00}$ is a positive integer, $\rho_{01}$ is complex, and the following relation is always satisfied

$$\rho^\ast_{01} \leq \rho_{00}(1 - \rho_{00})$$

(2b)

We note that the energy of the subsystem depends on the value of $\rho_{00}$, but is independent of the value of $\rho_{01}$.
Interaction with a bath will induce energy gap fluctuations in the subsystem [1]. Dephasing associated with such energy gap fluctuations is commonly referred to as “pure dephasing [1,18].” At high temperatures, this is expected to be the dominant dephasing process, and a classical description of the bath is expected to be valid. We adopt such a classical description of the bath in this work, but note here that our primary conclusions in this study would be unaffected even if the so-called “quantum decoherence [19,20,21]” associated with bath quantum effects played a non-negligible role in the reduced dynamics. We also note that the applicability of the classical bath approach is well established for predicting line shapes [12].

Evolution of $\rho_{00}$ over typical vibrational dephasing times can be neglected [22,12]. As such, over a time period on the order of the vibrational dephasing time, the subsystem may be taken to interact with the environment nearly elastically, such that only the value of $\rho_{01}$ evolves in time. As a result, over the time scale of dephasing, the reduced dynamics may be taken to be determined by an approximately diagonal Hamiltonian. In the classical bath approximation, the short time reduced dynamics for a given classical bath trajectory is then determined by an approximate Hamiltonian of the form

$$\hat{H} = \hat{H}_s + |0\rangle V_{00}(t)\langle 0| + |1\rangle V_{11}(t)\langle 1|$$

(3)
where $V_{ii}(t)$ is the time dependent interaction energy between the bath (evaluated along a specific classical bath nuclear trajectory) and the system (in a specific vibrational state $|i\rangle$).

Two aspects of Eq. (3) warrant particular emphasis. First, the term “classical trajectory” defining $V_{ii}(t)$ is used in the most general sense, to refer to the classical trajectory of the entire bath. In other words, multiple collisions and many body effects can contribute to the time evolving interaction energy. Second, the separation of time scales for dephasing and relaxation is the sole justification for consideration of the elastic effects in isolation, according to a short-time effectively diagonal Hamiltonian. At longer times, off-diagonal terms in the Hamiltonian become important, and result in population relaxation (evolution of $\rho_{00}$).

The evolution of the reduced density matrix in the interaction representation [17], over the time scale of dephasing, is then given according to the Hamiltonian of Eq. (3) by

$$\tilde{\rho}_{01}(t) = \tilde{\rho}_{01}(0) \exp\left\{-(i/\hbar)\int_0^t dt' [V_{11}(t') - V_{00}(t')]\right\} \quad (4a)$$

$$\tilde{\rho}_{00}(t) = \tilde{\rho}_{00}(0) \quad (4b)$$

where we have employed the fact that $H_s$ commutes with $V_{00}$ and $V_{11}$ for an elastic process, and the “tildes” denote the interaction representation. So the effect of the classical bath trajectories is to
induce a phase change in $\tilde{\rho}_{01}$. If one averages over a distribution of initial bath states, the off-diagonal reduced density matrix element takes the form

$$\langle \tilde{\rho}_{01}(t) \rangle_B = \tilde{\rho}_{01}(0) \left\langle \exp \left\{ -\frac{i}{\hbar} \int_0^t dt' [V_{11}(t') - V_{00}(t')] \right\} \right\rangle_B \quad (4c)$$

Each possible initial classical bath state determines a different phase change in $\tilde{\rho}_{01}$. The average over different evolving phases in Eq. (4c) leads to the loss of phase coherence usually referred to as pure dephasing [22,12,18].

In the simplest (low density and low temperature) case, pure vibrational dephasing is the result of isolated gas phase binary collisions which individually result in small phase changes in $\tilde{\rho}_{01}$. We denote the characteristic dephasing time (which is to say the time it characteristically takes for the probability distribution of $\tilde{\rho}_{01}$ phases to approach uniformity) by $\tau_{ph}$. If the probability distribution for the single (isolated) collision-induced phase changes is given by a Gaussian function about an average (thermal) value, and the decay of the vibrational correlation function is assumed to be single exponential [22,12,24] then the dephasing rate $\tau_{ph}^{-1}$ is related to the collision rate $\tau_c^{-1}$ by [22,12]

$$\tau_{ph}^{-1} \approx \tau_c^{-1} \langle \phi^2 \rangle_B / 2 \quad (5)$$
where $\phi$ is the phase change during an isolated collision, and the angular brackets denote a thermal average over possible initial trajectories for the individual bath molecule involved in the collision.

In general, the assumptions of small phase changes and single exponential decay are not always justified [23,24]. In the next section, we discuss the conditions under which a stochastic model in which phase changes are small and Gaussian-distributed is valid.

### 3. Semigroup methodology

In this section, we show that Eq. (4) is consistent with the Lindblad approach, and further that a simpler semigroup form for the dynamics can be employed which emphasizes the physical content and facilitates generalization beyond the stochastic Gaussian dephasing model. According to the Lindblad equation [9,8], any reduced dynamical process in which the bath is Markovian must take the form

$$\frac{\partial \tilde{\rho}_{\text{mn}}}{\partial t} = \langle m | \hat{F} \tilde{\rho} \hat{F}^+ | n \rangle - \left\{ \langle m | \hat{F}^+ \hat{F} \tilde{\rho} | n \rangle + \langle m | \hat{F} \hat{F}^+ \tilde{\rho} | n \rangle \right\} / 2$$  \hspace{1cm} (6)

where $\hat{F}$ is an operator on the subsystem variables, and we have dropped the operator caret from $\tilde{\rho}$ for notational convenience. We note that for the general case of pure dephasing between two
vibrational energy eigenstates $|0\rangle$ and $|1\rangle$, a finite difference expression for $\hat{F}$ can be determined based on Eq. (4a):

$$\hat{F} = \tau^{-1/2} \left\{ |0\rangle e^{(i/\hbar) \int_{t_0}^{t} \delta V_{ii}(t') dt'} \langle 0| + |1\rangle e^{(i/\hbar) \int_{t_0}^{t} \delta V_{i1}(t') dt'} \langle 1| \right\}$$

(7)

where $\tau$ is an appropriate finite duration of time (about which we say more shortly). We emphasize that, as noted after Eq. (3), the time dependent interaction energy $V_{ii}$ can incorporate multiple collisions in the general case.

At low densities, when an isolated binary collision model is valid and the collision duration times can be neglected, a simple approximate Markovian form for $\hat{F}$ can be employed within the semigroup approach, which elucidates the physical content:

$$\hat{F} = \tau^{-1/2} \hat{S}$$

(8)

Here (as in Eq. (5)) $\tau^{-1}$ is the collision rate, and the operation of the single-collision scattering operator $\hat{S}$ results in a phase change in the off-diagonal elements of the reduced density matrix due to a single collision. The primary approximations in Eq. (8) are that (a) exactly one collision usually takes place during the collision time and (b) correlations between collisions, which can be
included in Eq. (7), are neglected (Markovian approximation). In section 4, we investigate vibrational dephasing of the lithium dimer in argon using a simple linear classical collision model. It is important to note here that Eq. (8) is much more general than these considerations might suggest, and is applicable for any scattering operator inducing changes in phase relationships between subsystem states. As such, the formalism is general enough to accommodate more detailed treatment of the scattering process.

As has been noted, the Lindblad equation is derived for the case of Markovian bath dynamics only. And for the simple (lithium dimer in argon) system considered in section 4, the Markovian approximation is expected to be acceptable. But it is important to note that an isolated binary collision model of dephasing has also been successful, at least qualitatively, in explaining dephasing in liquids [22]. This provides encouraging evidence that the semigroup approach may find application even in cases where the Markovian bath assumption is difficult to justify. This is very encouraging because the semigroup method has significant potential advantages for studying phenomena such as condensed phase electron transfer, where explicit treatment of all degrees of freedom is not convenient [25].

If one assumes single exponential decay of the vibrational correlation function, and small isolated phase changes, then the vibrational dephasing rate $\tau_{ph}^{-1}$ for a harmonic oscillator depends quadratically on the difference in vibrational quantum number (and correspondingly on the energy gap) [22,12]. As noted previously, the assumptions of small phase changes and single exponential
decay are not always justified [23,24]. However, for notational convenience we assume this quadratic dependence for the case of small collision-induced phase changes; the discussion is easily extended to more general energy gap dependence. For this quadratic case, we find that $\hat{S}$ may be written in the form

$$\hat{S} = \exp[-i(\hat{H}_S/\hbar \omega_0)\phi_B]$$

(9)

where the operation of the subsystem Hamiltonian $\hat{H}_S$ insures that the scattering operator will commute with the Hamiltonian (so that the process will be elastic), and $\phi_B$ contains the dependence of the phase change on the bath variables, in particular on the velocity of a bath molecule prior to collision. (Other constant quantities, such as molecule masses and the subsystem electronic surface curvature, also affect $\phi_B$, but do not result in any variability in the phase changes).

If the probability distribution of phase changes is given by $P(\phi_B)$, then the evolution of the density matrix according to the scattering operator of Eq. (9) is given by

$$\frac{\partial}{\partial t} \langle \hat{\rho}_{mn} \rangle_B = \tau_e^{-1} \langle \hat{\rho}_{mn} \rangle_B \int d\phi_B P(\phi_B)[e^{-i(\omega_m/\omega_0)\phi_B} - 1]$$

(10)

For the case of a Gaussian distribution (i.e. $P(\phi_B) = [1/2\pi \sigma^2]^{1/2} \exp(-\phi_B^2/2\sigma^2)$) this becomes
\[
\frac{\partial \langle \tilde{\rho}_{mn} \rangle_B}{\partial t} = -\tau_c^{-1} \langle \tilde{\rho}_{mn} \rangle_B \left[ 1 - e^{-\frac{(\omega_{mn} / \omega_0)^2 \sigma^2}{2}} \right] \tag{11}
\]

where \( \omega_{mn} = \omega_m - \omega_n \). In the limit of large isolated phase changes in Eq. (11), complete randomization of phase is obtained after the average collision time, and the appropriate reduced dynamical equation is

\[
\frac{\partial \langle \tilde{\rho}_{mn} \rangle_B}{\partial t} = -\tau_c^{-1} \langle \tilde{\rho}_{mn} \rangle_B \tag{12}
\]

in which case there is no dependence on the energy gap. Sensibly, the upper limit of the dephasing rate is seen here to be equal to the collision rate, as discussed in earlier work by Yamaguchi [23].

For small average squared phase changes, on the other hand, the dephasing rate indeed goes as the square of the energy gap, or quantum number difference:

\[
\frac{\partial \langle \tilde{\rho}_{mn} \rangle_B}{\partial t} = -\tau_c^{-1} \langle \tilde{\rho}_{mn} \rangle_B \left[ (\omega_{mn} / \omega_0)^2 \sigma^2 / 2 + \vartheta(\sigma^4) \right] \tag{13}
\]
This energy gap dependence is a signature of a “stochastic Gaussian” process. Stochastic processes are commonly modeled using the semigroup method, though the result given as Eq. (13) is usually obtained by employing a Hermitian operator for \( \hat{F} \) which commutes with the Hamiltonian, as discussed in Ref. [8]; the simplest (linear in \( \hat{H} \)) such operator, \( \hat{F} = k\hat{H} \), leads to agreement with Eq. (13) if \( k = \tau_c^{-1/2}\sigma i(\hbar \omega_b) \).

Formulation of the dephasing process in terms of the unitary scattering operator \( \hat{S} \) rather than the Hermitian operator \( \hat{F} = k\hat{H} \) is advantageous not only because the physical content is elucidated. The primary advantage is that formulation in terms of \( \hat{S} \) yields a “Poisson” model of dephasing (as described by Eq. (10)) which is more generally applicable than the “stochastic Gaussian” model (as described by Eq. (13)) in two important respects. First, the Poisson model does not require that collision-induced phase changes be small. This aspect is the primary focus of this paper, and in the next section we consider a physical system in which the Poisson model is required due to large and abrupt phase changes. But it is also the case that Eq. (10) allows for non-Gaussian distributions of phases. Consideration of physical systems that may require non-Gaussian phase change distributions is an ongoing subject of study in our research group. Here we simply note that if, for example, the probability distribution is exponential (i.e. \( P(\phi_b) = (\alpha/2)e^{-\alpha|\phi_b|} \) in Eq. (10)) then the density matrix evolves according to
\[
\frac{\partial \langle \hat{\rho}_{mn} \rangle_B}{\partial t} = -\tau^{-1} \langle \hat{\rho}_{mn} \rangle_B (\omega_{mn} / \omega_0)^2 / [\alpha^2 + (\omega_{mn} / \omega_0)^2]
\]  

(14)

In the limit of small \( \alpha \) (large \( |\phi_0| \)), the same gap-independent upper bound of the dephasing rate is obtained as in the case of Gaussian distribution (see Eq. (12)). And in the opposite limit of large \( \alpha \) (small phase changes), the dependence on the energy gap is quadratic, as in the case of the stochastic Gaussian model of Eq. (13). So if one assumes that phase changes are small and frequent, the Poisson model in general reduces to the stochastic Gaussian model, illustrating the generality. A survey of the phase change distributions found in chemically important physical systems is clearly an important direction for future study, as there is the potential to discover a variety of dephasing mechanisms.

To underscore the potential importance of different dephasing mechanisms, we illustrate in Fig. 1 the evolution of a wavepacket in a harmonic potential. Initially, the wavepacket is in the coherent state with average excitation level \( \langle n \rangle = 14 \). Snapshots of the density operator \( \rho(v,v') \) are shown, with the colors representing different phases. For both the Poisson dephasing model with exponential phase distribution (Eq. (14)) and the stochastic Gaussian dephasing model (Eq. (13)), the dephasing time constant is 5 periods (\( 1/T_2 = 0.2 \omega_0 \)). For the Poisson model, \( \alpha = 2(\omega_{mn} / \omega_0) \).

An appreciable difference in dynamical behavior is evident, showing the dynamical effects of relaxing the stochastic Gaussian assumption.
For the case of vibrational dephasing between two states, the most immediate conclusions one can draw from consideration of the Poisson model are the conditions under which phase changes will be large and abrupt, and a stochastic Gaussian model of dephasing consequently inappropriate. In the next section, we discuss the experimental conditions under which energy gap independence and Poisson dephasing behavior are expected to be realized for the specific case of vibrational dephasing of a lithium dimer in argon.

4. Lithium dimer in argon gas

To construct a simple model of head-on collisions, we take the interaction potential between the lithium dimer and argon atoms to be of the form employed by Fischer and Laubereau [22]

\[
V = V_0 \exp[-(R - Q/2)/L] \\
= V_0 [1 + Q/2L + Q^2/8L^2 + \vartheta(Q^3)] \exp[-R/L]
\]

(15)

where \( Q \) is the lithium dimer bond displacement from its equilibrium value, and \( R - Q/2L \) is the distance between the colliding argon atom and the closest lithium atom. We will see that for large vibrational quantum numbers on the \( E^3 \Sigma^+_g \) Li\(_2\) electronic surface, the polarizability of argon gives rise to an important additional interaction term (the contribution of lithium dimer polarizability,
which varies with bond length, is less important), but we begin by considering only the potential
described by Eq. (15).

During a head-on collision, the expectation value of this potential as a function of time for
the vibrational state $|i\rangle$, evaluated along the classical trajectory of the colliding argon atom, is then
given to second order in $Q$ by [22]

$$V_i(t) = E_0[1 + \langle Q\rangle_{ii}/2L + \langle Q^2\rangle_{ii}/8L^2]\text{sech}^2[(E_0/2M)^{1/2}t/L]$$  \hspace{1cm} (16a)

where $E_0$ is the initial relative kinetic energy, $t = 0$ is taken to be the time at which the classical
turning point is reached, and $M$ is defined in terms of the atomic masses of lithium and argon as

$$M = 2m_{Ar}m_{Li}/(m_{Ar} + 2m_{Li})$$
$$= 10.3m_p$$  \hspace{1cm} (16b)

where $m_p$ is the mass of a proton. The phase change in $\tilde{\rho}_{mn}$ during the collision is therefore

$$\phi_{mn} = (1/\hbar)\int_{-\infty}^{\infty} dt' [V_{mn}(t') - V_{mn}(t')]$$
$$= (2ML^2E_0/\hbar^2)^{1/2}[q_{mn}/2L + q_{mn}^2/8L^2]$$  \hspace{1cm} (17a)
where $q_{mn} = \langle Q \rangle_{mn} - \langle Q \rangle_{mm}$ and $q_{mn}^2 = \langle Q^2 \rangle_{mm} - \langle Q^2 \rangle_{mn}$. Correspondingly, if all collisions were head-on, then the average (thermal) squared phase change would be [22]

$$
\langle \phi_{mn}^2 \rangle = (2ML^2kT/h^2)[q_{mn}/2L + q_{mn}^2/8L^2]^2
$$

(17b)

However, since not all collisions are head-on, a more accurate value is obtained by replacing $q_{mn}$ by the average component of the bond length displacement in the direction of the colliding argon atom’s trajectory. Specifically, we assume a nearly uniform distribution of incident angles $\theta$ (where $\theta = 0$ is a head-on collision), and take the limit of large $R$ (i.e. we replace $Q/2$ by $(Q/2)\cos\theta$ in Eq. (15)), and obtain the modified expression

$$
\langle \phi_{mn}^2 \rangle = (2ML^2kT/h^2)[q_{mn}/4L + q_{mn}^2/24L^2]^2
$$

(18)

where the $q_{mn}^2$ term is similarly modified. The modified quantity in square brackets is of the same order as in the case of strictly head-on collisions, but is reduced due to the fact that typical collisions are less efficient than head-on collisions in inducing dephasing.

The configurational energy of Li$_2$ in the $E^1\Sigma^+_g$ electronic state, as a function of bond length, is shown in Fig. 2. This figure is based on a spline fit [26] of data taken from Bernheim et.
al. [27,13]. Also shown are the vibrational energy levels. For each vibrational state, we approximate the values of $\langle Q \rangle$ and $\langle Q^2 \rangle$ by the corresponding values for harmonic oscillator stationary states with the same classical turning points. Specifically, if $x_-$ and $x_+$ represent the two classical turning points (where the configurational energy is equal to the vibrational state energy), we approximate $\langle Q \rangle$ and $\langle Q^2 \rangle$ as [28]

$$\langle Q \rangle = (x_+ + x_-)/2$$  \hspace{1cm} (19a)

$$\langle Q^2 \rangle = (x_+ - x_-)^2/8$$  \hspace{1cm} (19b)

The results are shown in Table 1.

The difference in mean bond length ($q_{10}$) between the first two vibrational states for the lithium dimer on the “E” state is found to be 0.0352 Å, while the difference in mean square bond displacement ($q_{10}^2$) is found to be 0.0414 Å$^2$. We note by way of comparison that $q_{10}^2$ is quite similar for the ground electronic state for Li$_2$, but that $q_{10}^2$ for the ground electronic surface of the commonly studied nitrogen dimer [12] is 0.00207 Å$^2$, which is significantly smaller. This is because the vibrational frequency of the weakly bound lithium dimer is much lower than triple-bonded N$_2$. The result is that dephasing rates for the lithium dimer can be expected to be exceptionally high.
\( L \) is expected to be about 0.18Å for lithium-argon collisions [22,29]. At a temperature of 1073K, evaluation of Eq. (18) for the case of the first two vibrational states then indicates an average squared phase change of 0.15. By way of comparison, the typical average squared phase change for the two lowest vibrational states in liquid nitrogen is of order 10^{-3} [22]. We note that in the stochastic Gaussian model, the ratio of the dephasing rate to the collision rate is \( \frac{\langle \phi^2 \rangle}{2} \), while in the Poisson model with a Gaussian distribution, the ratio is \( 1 - \exp\left(-\frac{\langle \phi^2 \rangle}{2}\right) \). Since \( 1 - e^{-0.15/2} = 0.072 \), the stochastic Gaussian and Poisson dephasing models are in reasonable agreement for this case, and a stochastic Gaussian description of the dephasing process would seem to be acceptable.

The average squared phase changes for other initial vibrational superposition states are readily evaluated in the same manner, based on the appropriate values of \( q_{nn} \) and \( q_{nn}^2 \). As indicated in Table 1, \( \langle \phi_{n+1,n}^2 \rangle \) reaches a maximum for the states 13 and 14, since one is above the potential energy shelf on the “E” surface and the other is below. (While there is some uncertainty over whether the maximum may in fact occur between the states with quantum numbers 12 and 13 [27], these considerations are not crucial with respect to our goals in this work.) In particular, evaluation of this maximum average squared phase change to second order in \( Q \) gives 32.0, which is quite large. Higher order terms in \( Q \) in Eq. (15) can serve to increase this value even further in this case of significantly different vibrational state properties. But the exact value of \( \langle \phi_{\max}^2 \rangle \) is not
required to ascertain the fact that the limit \( \langle \phi_{\text{max}}^2 \rangle \gg 1 \) is obtained. It is clear that in this case a stochastic Gaussian description of the dephasing process is inappropriate. The dephasing rate is not only at a maximum for these two states, but is expected to be nearly equivalent to its upper bound, the collision rate.

An additional cause of increased average squared phase changes is the effect of an argon atom’s polarizability on its interaction with lithium dimer states above the shelf region, where the vibrations have a strongly ionic character. We crudely approximate the “effective” dipole moment of the lithium dimer, in a given vibrational state with average bond length \( l \), interacting with an argon atom as follows. Supposing that the average bond lengths of the vibrational states, as shown in Table 1, are an indication of the ionic character according to

\[
l = c_{\text{ion}}^2 l_{\text{ion}} + c_{\text{cov}}^2 l_{\text{cov}}
\]

where \( l_{\text{cov}} \) is equal to the bond length in the lowest energy vibrational state (3.1 Å), \( l_{\text{ion}} \) is equal to the maximum average bond length (4.7 Å), and the effective dipole moment is

\[
\mu = -c_{\text{ion}}^2 e l_{\text{ion}}
\]
then the maximum phase change due to this effect is seen for the states 13 and 14 (where the
difference in $c^2_{ion}$ is 0.23). Following Ref. [30], we note that the “polarizability volume” of argon
(i.e. the product of the polarizability and $(4\pi\varepsilon_0)^{-1}$) is about $1.66\,\text{Å}^3$, and so this maximum phase
change if all collisions were head on would be about

\[
\phi = 0.23[\mu^2\alpha_{\text{Ar}}/\pi\hbar\varepsilon_0]\int_{-\infty}^{\infty} dt'[R(t')]^{-6}
= 0.23[(4.7\varepsilon_0)^2(1.66\,\text{Å}^3)/\pi\hbar\varepsilon_0]\int_{-\infty}^{\infty} dt'[R(t')]^{-6}
= 0.23[35.35.07a_0^6E_h/\hbar]\int_{-\infty}^{\infty} dt'[R(t')]^{-6}
= 0.23[2.04 \times 10^5\,\text{Å}^6\hbar J/\hbar N_A]\int_{-\infty}^{\infty} dt'[R(t')]^{-6}
\]

(22)

where $R(t)$ for an initial relative velocity equal to the root mean square relative velocity is
approximately [31]

\[
R(t) = (3\,\text{Å}) - (0.18\,\text{Å})\ln\{\text{sech}^2[(9.31\,\text{Å}/\text{ps})t/0.18\,\text{Å}]\}
\]

(23)

assuming that the collision trajectories are similar to those determined prior to consideration of the
ionic character of the lithium dimer vibrational states. Substituting Eqs. (23) into (22) would give
an average square phase change of about 1400. The correct value would be smaller due to the fact
that not all collisions are head on. However, it is clear that the argon polarizability alone would
cause the dephasing rate to be nearly equal to the collision rate, a conclusion that would be unaltered by a more careful treatment of either the collision trajectories or the extent of ionic character of the lithium dimer vibrational states.

To get a collision rate in dilute argon gas (neglecting the difference in lithium dimer and argon atom scattering cross sections and thermal velocities), we note that for hard spheres with diameters of about 4Å, the collision time (at a temperature $T$ and density $\rho$) is given by [32]:

$$
\tau_c = \left(\frac{m_A}{\pi kT}\right)^{1/2} / 4 \rho d^2
= \left[40 m_p / \pi kT\right]^{1/2} / [(64 \text{Å}^2)(\rho)]
$$

such that if, for example, the temperature is 1073K and there is an a density of 1 argon atom per $2.7 \times 10^7$ Å$^3$, the collision time is 50,000ps. This is in on the order of 100,000 times as infrequent as in liquid argon, where the collision rate is about 2.3/ps [32].

For the case of two vibrational states, one above and one below the potential “shelf,” the dephasing rate is expected to be nearly equal to the collision rate, as noted above. Lower average squared phase changes correspond to lower dephasing rates according to the factor $1 - \exp[-\langle \phi^2 \rangle / 2]$. Ongoing experiments performed by Zohar Amitay and others are expected to permit experimental tests of our theoretical conclusions. Here we note only that based on
preliminary experiments with \( \text{Li}_2 \) in a noble gas buffer, Amitay has estimated that the dephasing time scale for a wavepacket with average excitation level \( \langle n \rangle = 14 \) is close to 7ns.

5. Conclusions

We find that a Poisson model of pure vibrational dephasing can be formulated within a semigroup framework which has a number of important advantages over traditional stochastic Gaussian treatments. Both models are consistent with the quantum dynamical semigroup approach to reduced dynamics, an approach that is widely used because of its generality and straightforward implementation. But the stochastic Gaussian treatment is only correct when collision-induced changes in the phase relationship between vibrational states are small and Gaussian distributed. The Poisson model reduces to the Gaussian model in this limit, but can also be applied for a larger range of distributions and magnitudes of phase changes. The Poisson model also clarifies the nature of the physical processes responsible for dephasing. We find that for certain vibrational states of the lithium dimer in argon, large phase changes clearly require application of the Poisson model. Exploration of the range of phase distributions observed in chemical systems is an important direction for future study.

Acknowledgements
We thank Lorenzo Pesce, Neil Snyder, Zohar Amitay, and Steve Leone for helpful discussions, and NSF-Chemistry for support. Work was also financed by the United States Israel Binational Science Foundation (BSF).

References


[21] We follow Refs. [18]-[20] in our use of the terms “quantum decoherence” and “pure dephasing.” Specifically, dephasing due to decay in the magnitude of overlap between bath wavefunctions reacting to different subsystem states is referred to as quantum decoherence. And dephasing due to changes in relative phase between subsystem states, as a result of bath-induced subsystem energy gap fluctuations, is referred to as pure dephasing. Quantum decoherence is
expected to become more important under conditions of increasing density and decreasing temperature.


Table 1. For the vibrational states on the $E^1 \Sigma_g^+$ electronic surface of Li$_2$, the mean bond lengths and mean squared displacements are shown. Also shown are the mean-squared, collision-induced changes in phase between neighboring vibrational states, neglecting polarizability, under experimental argon bath conditions described in the text. An asterisk is used to denote values which, due to error in the fit to the potential surface, may not be accurate beyond the first digit.
Table 1.

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<th>$\langle Q^2 \rangle$/Å$^2$</th>
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Figure. 1. Dephasing of an initially-prepared coherent state on a harmonic surface. The two limits shown are the Poisson process with exponential distribution (Eq. (14)) and the stochastic Gaussian model of Eq. (13). After ten periods, the dephasing is essentially complete in both models. Colors show phase behavior. See text for parameters.

Figure. 2. The potential energy surface as a function of bond length is shown for the $E^1 \Sigma^+_g$ electronic surface of Li$_2$. Also shown are the vibrational energy levels.