

Optical dephasing of the electronic transitions of delocalized molecular dimer states

H. W. H. Lee^{a)} and M. D. Fayer

Department of Chemistry, Stanford University, Stanford, California 94305

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We present a theoretical study of the optical dephasing of the electronic transitions of delocalized molecular dimer states. The dephasing arises from the dynamical interactions of the dimer states with the phonon bath of the host crystal. We introduce a general dephasing model for dimers with strong intermolecular interactions and analyze the consequences of the model with optical Redfield theory. A quantum mechanical microscopic model is developed in which the interaction Hamiltonian of the dimer states and the phonon bath states is clearly delineated. We treat both linear and quadratic excitation-phonon coupling in which the two molecules comprising the dimer may be coupled differently to the phonons. Couplings to acoustic, optical, and pseudolocal phonons (librations) are considered explicitly. The temperature dependence of the dephasing rates are obtained for scattering between delocalized dimer states, scattering to dimer librations and phonon-induced pure dephasing. These results are used to analyze the photon echo studies on pentacene dimers and tetracene dimers in *p*-terphenyl and on naphthalene dimers in perdeuterated naphthalene. In the pentacene dimers and tetracene dimers, we conclude that the dephasing results from scattering to the dimer librations via a one-phonon process. In addition, a quantitative value for the libron-phonon coupling is determined. In the naphthalene dimer system, we find scattering between delocalized dimer states, induced by linear excitation-phonon coupling, to be the predominant dephasing mechanism. A quantitative value is determined for the phonon coupling matrix element responsible for scattering between the delocalized states.

I. INTRODUCTION

The electronic excitation of a system of interacting molecules can result in a delocalization of the excitation energy. The dynamical behavior of such delocalized states has been a subject of great interest for many years. Particularly, the problem of delocalized electronic excitations (excitons) in both pure and mixed molecular crystals and their dynamical interactions with the phonon bath of the crystal has received much attention in the literature.^{1,2} Of central interest has been the question of coherent and incoherent electronic energy transport and the study of the relaxation pathways of these delocalized states.

The simplest system for the experimental and theoretical understanding of these processes in a delocalized system is an interacting pair of guest molecules in a molecular mixed crystal, i.e., a dimer.² These dimers consist of isolated pairs of guest molecules substitutionally imbedded in a host crystalline lattice. The relative orientations of the molecules in the dimer pair are usually taken to be similar to the orientation of host molecules in the pure crystal. Thus, there are a variety of possible dimer pairs having various intermolecular interactions. An excited dimer has been referred to as a "mini-exciton". An understanding of dimer systems can lead to a better understanding of other interesting delocalized systems such as excitons and impurity bands.

The study of dimer dynamics is not a new endeavor and has been experimentally and theoretically pursued by numerous authors in the hopes of understanding these impor-

tant systems and possibly relating them to exciton dynamics. Most of the early work was done on triplet dimer states. Since the experiments of Schworer and Wolf³ who in 1967 observed the EPR transitions of translationally inequivalent dimers of naphthalene-*h*₈ in naphthalene-*d*₈, many other magnetic resonance studies were performed on delocalized dimer states. Hutchison and King⁴ observed the hyperfine structure of the EPR lines and the electron-nuclear double resonance (ENDOR) of the protons in similar dimers in isotopically mixed naphthalene crystals. Hochstrasser and Zewail⁵ recorded the optically detected magnetic resonance (ODMR) spectra of translationally equivalent 1,4-dibromonaphthalene dimers, while Zewail and Harris⁶ recorded the ODMR spectra of translationally equivalent 1,2,3,5-tetrachlorobenzene-*h*₂ in the perdeuterated host.

Of particular interest has been the experiments of Botter *et al.*⁷ who have examined the EPR dephasing times of triplet states of both translationally equivalent and inequivalent naphthalene-*h*₈ dimers in a perdeuterated naphthalene host using spin echo and ODMR techniques. They interpreted their results using the exchange model of van't Hof and Schmidt,⁸ and ascribed the dephasing to spin exchange between the $|+\rangle$ and $|-\rangle$ dimer states. However, the van't Hof model, which uses modified Bloch equations, allows only qualitative interpretations at low temperatures because of the approximate treatment of the crystal phonons.

Useful to the early interpretation of many of these experiments has been the Haken-Strobl stochastic model.⁹ This model has been remarkably successful, considering its relative simplicity. Its major shortcoming is its lack of any microscopic description of the dephasing process. This mod-

^{a)} Permanent address: Chemistry and Physics Laboratory, The Aerospace Corporation, P. O. Box 92957, Los Angeles, CA 90009.

el represents a classical stochastic treatment in which the fluctuations in the site energies and resonance interaction energies are modeled as randomly fluctuating Gaussian Markov processes with nonzero averages and delta function correlation times. In addition, the cross correlations between the fluctuations in the site energies and between the site energies and the resonance interaction energy were ignored. This made their model applicable only at high temperatures, and, as pointed out previously,^{1,10} their model leads to an unrealistic non-Boltzmann population distribution of the dimer excited states. Detailed balance is lost. Nonetheless, there have been a number of modifications and applications of the Haken–Strobl model.¹¹

Recently, however, Schmid and Reineker¹² and Köhler and Reineker¹³ introduced a theory of temperature dependent ESR line shapes of triplet dimers using projection operator techniques in which the bath is treated with the microscopic model of linear excitation–phonon coupling. Schmid and Reineker used their model to interpret the results of Botter *et al.*⁷ and found that scattering of the triplet dimer between the two Davydov components is the dominant dephasing mechanism. In addition, their predictions at high temperatures agree with the Haken–Strobl model, as expected. Wertheimer and Silbey¹⁴ developed a similar microscopic model to describe relaxation pathways of triplet multilevel systems. These same authors analyzed dimer dephasing dynamics using Redfield theory.¹⁵ However, their latter treatment left the bath and its interactions with the dimer unspecified.

A natural progression from these experiments on triplet states of dimers is studies on the dimer singlet states. Fayer and co-workers¹⁶ have studied the optical dephasing of singlet electronic transitions of pentacene dimers in *p*-terphenyl and tetracene dimers in *p*-terphenyl with photon echoes. Using the theory presented here, they concluded that these dimers, which are chemically distinct from the host molecules, dephase predominately by phonon scattering of the dimer librations. Also with photon echoes, Morsink and Wiersma¹⁷ have investigated the optical dephasing of singlet electronic transitions of translationally equivalent dimers of naphthalene in perdeuterionaphthalene (the *AA* dimer). They suggested that phonon-induced scattering between the delocalized dimer singlet states is the dominant dephasing process. However, we expect dimers which are not merely isotopically different from the host to have other dephasing pathways which may effectively compete with scattering between dimer states. These chemically distinct dimers do not have their librations amalgamated into the host optical phonon bands. This gives rise to pseudolocal modes which may effectively dephase the dimer transitions. This mechanism has been shown to be operative for monomers in mixed molecular crystal systems.¹⁸

In a recent paper, Skinner *et al.*¹⁹ presented a theory of photon echoes from weakly interacting dimers, focusing on the energy transfer process. Other authors have also focused on energy transfer in dimer systems²⁰ and exciton systems.²¹ In the most detailed papers,²⁰ only linear excitation-phonon coupling was considered. The principal exception has been papers by Munn *et al.*²² in which the effect of quadratic exci-

tation-phonon coupling on exciton transport is treated. It is certainly recognized that quadratic coupling is important in that, for example, the excited state vibrational frequencies are in general unequal to those of the ground state due to quadratic coupling.

Thus, in spite of this rich literature, a complete microscopic theory of dimer dephasing is lacking. In view of this, we introduce in this paper a general dephasing model for strongly interacting dimers and analyze the consequences of the model with optical Redfield theory (ORT).^{18,23,24} This model is unique in the following regards:

(1) We develop a quantum mechanically microscopic model describing dimer dephasing in which the interaction Hamiltonian of the dimer states and the phonon bath states is clearly delineated. This is generally more satisfying than stochastic models.

(2) We treat both linear and quadratic excitation-phonon coupling in which the two molecules may be coupled differently to the phonons.

(3) We remove the dimer librations (mini-librons) from the “fast” bath states and treat them on the same level as the electronic dimer states. This is analogous to the model used for monomers by de Bree and Wiersma.²⁴

We find three basic processes that are responsible for the dephasing of the dimer transitions: (A) scattering between delocalized dimer states (T_1 process), (B) scattering to dimer librations (T_1 process), and (C) phonon-induced pure dephasing (T_2^* process). Explicit expressions are given for the temperature dependent dephasing rates arising from these processes. In addition, we point out that our Redfield perturbation results have been demonstrated to be exact to all orders for the specific case of scattering between delocalized dimer states induced by linear excitation-phonon coupling only.²⁵

These results are then used to analyze the photon echo dephasing studies on pentacene dimers and tetracene dimers in *p*-terphenyl,¹⁶ and on naphthalene dimers in perdeuterionaphthalene.¹⁷ In the pentacene dimer and tetracene dimer systems, we conclude that the dephasing results from scattering of the dimer librations via a one-phonon process. In addition, a quantitative value for the libron–phonon coupling is determined. In the naphthalene dimer system, we find scattering between delocalized dimer states, induced by linear excitation-phonon coupling, to be the predominant dephasing mechanism. A quantitative value is also determined for the phonon coupling. Furthermore, as mentioned above, this value for the phonon coupling is exact.

II. MODEL HAMILTONIAN

The model Hamiltonian operator we will use for a guest dimer in a molecular crystal is given by

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{int}}. \quad (2.1)$$

H_{ex} represents the Hamiltonian for a pair of coupled two-level systems and is given in the site representation by

$$H_{\text{ex}} = \epsilon_1 a_1^+ a_1 + \epsilon_2 a_2^+ a_2 + V(a_1^+ a_2 + a_2^+ a_1). \quad (2.2)$$

Each guest is assumed to have one excited electronic state with energy ϵ_n , and these states interact via the static

intermolecular potential V which may arise, for example, from dipole-dipole coupling. Here, a_n^+ (a_n) represents the Fermion creation (destruction) operator for an excitation on site n ($n = 1, 2$). For convenience, we have chosen V to be real.

The treatment of the electronic excitation separately from the phonons stems from the Born-Oppenheimer (BO) approximation.²⁶ In the adiabatic BO approximation, the electronic problem is solved first and the electronic energies thus obtained depend parametrically on the nuclear coordinates and serve as potential surfaces for the vibrational motions. Since these potentials will, in general, be different for each electronic state, electronic excitation is usually accompanied by lattice deformation and vibrational frequency changes.

One usually expands the ground state potential in a Taylor series around the equilibrium configuration. In the harmonic approximation, one retains only the linear and quadratic terms and transforms to a set of normal coordinates which diagonalizes the vibrational Hamiltonian and gives rise to the crystal phonons. The excitation-phonon coupling arises from expanding the difference of the excited state and ground state potentials in a Taylor series of the ground state coordinates. Thus, in this model where the ground state is taken as the reference, the excitation-phonon coupling only acts on the excited states.

The Hamiltonian for the phonons and the excitation-phonon coupling can be written as

$$H_{\text{ph}} = \hbar \sum_{\alpha} \omega_{\alpha} (b_{\alpha}^{+} b_{\alpha} + \frac{1}{2}), \quad (2.3a)$$

$$H_{\text{int}} = \sum_{n\alpha\alpha'} a_n^{+} a_n [G_{n\alpha} \delta_{\alpha\alpha'} (b_{\alpha} + b_{-\alpha}^{+}) + K_{n\alpha\alpha'} (b_{\alpha} + b_{-\alpha}^{+}) (b_{\alpha'} + b_{-\alpha'}^{+})] + (a_1^{+} a_2 + a_2^{+} a_1) \sum_{\alpha\alpha'} [P_{\alpha} \delta_{\alpha\alpha'} (b_{\alpha} + b_{-\alpha}^{+}) + W_{\alpha\alpha'} (b_{\alpha} + b_{-\alpha}^{+}) (b_{\alpha'} + b_{-\alpha'}^{+})]. \quad (2.3b)$$

Here, b_{α}^{+} (b_{α}) is a Boson creation (destruction) operator of a phonon with wave vector α . These phonons consist of both lattice phonons and intramolecular vibrations.

We have included both local and nonlocal linear and quadratic excitation-phonon coupling. $G_{n\alpha}$ and $K_{n\alpha\alpha'}$ represent, respectively, the local linear and quadratic excitation-phonon coupling. This gives rise, respectively, to lattice deformation, and to phonon scrambling (nondiagonal quadratic terms) or frequency shifts (diagonal quadratic terms) as a result of site electronic excitation. P_{α} and $W_{\alpha\alpha'}$ represent the nonlocal linear and quadratic coupling. $G_{n\alpha}$ and $K_{n\alpha\alpha'}$ arise from the phonon induced modulation of the site energies while P_{α} and $W_{\alpha\alpha'}$ originate from the phonon modulation of the resonance interaction.

The lattice dynamics of defects in a host crystal have been discussed extensively in the literature. We will not re-consider it here, but refer the reader to the numerous articles on the subject.²⁷ Here we adopt a generalized definition of the phonon quantum numbers α to apply to the solutions of the defect lattice equations of motion.

We now remove the static interaction V with the following unitary transformation:

$$\tilde{H} = e^{\theta} H e^{-\theta}, \quad (2.4a)$$

where

$$S = \frac{1}{2} \theta (a_1^{+} a_2 - a_2^{+} a_1) \quad (2.4b)$$

and

$$\theta = \tan^{-1} \left(- \frac{2V}{(\epsilon_1 - \epsilon_2)} \right). \quad (2.4c)$$

This results in a Hamiltonian in the dimer representation

$$H = H_{\text{ex}}^0 + H_{\text{ph}} + H_{\text{int}}^0, \quad (2.5a)$$

where

$$H_{\text{ex}}^0 = \sum_n E_n c_n^{+} c_n, \quad (2.5b)$$

$$H_{\text{ph}} = \hbar \sum_{\alpha} \omega_{\alpha} (b_{\alpha}^{+} b_{\alpha} + \frac{1}{2}), \quad (2.5c)$$

$$H_{\text{int}}^0 = \sum_{n\alpha} L_{n\alpha} (b_{\alpha} + b_{-\alpha}^{+}) c_n^{+} c_n + \frac{1}{2} \sum_{n\alpha\alpha'} Q_{n\alpha\alpha'} (b_{\alpha} + b_{-\alpha}^{+}) (b_{\alpha'} + b_{-\alpha'}^{+}) c_n^{+} c_n + (c_1^{+} c_2 + c_2^{+} c_1) \left[\sum_{\alpha} F_{\alpha} (b_{\alpha} + b_{-\alpha}^{+}) + \sum_{\alpha\alpha'} D_{\alpha\alpha'} (b_{\alpha} + b_{-\alpha}^{+}) (b_{\alpha'} + b_{-\alpha'}^{+}) \right], \quad (2.5d)$$

where

$$L_{1\alpha} = G_{1\alpha} \cos^2 \gamma + G_{2\alpha} \sin^2 \gamma - P_{\alpha} \sin 2\gamma, \quad (2.6a)$$

$$L_{2\alpha} = G_{1\alpha} \sin^2 \gamma + G_{2\alpha} \cos^2 \gamma + P_{\alpha} \sin 2\gamma, \quad (2.6b)$$

$$Q_{1\alpha\alpha'} = 2(K_{1\alpha\alpha'} \cos^2 \gamma + K_{2\alpha\alpha'} \sin^2 \gamma - W_{\alpha\alpha'} \sin 2\gamma), \quad (2.6c)$$

$$Q_{2\alpha\alpha'} = 2(K_{1\alpha\alpha'} \sin^2 \gamma + K_{2\alpha\alpha'} \cos^2 \gamma + W_{\alpha\alpha'} \sin 2\gamma), \quad (2.6d)$$

$$F_{\alpha} = [\frac{1}{2} \sin 2\gamma (G_{1\alpha} - G_{2\alpha}) + P_{\alpha} \cos 2\gamma], \quad (2.6e)$$

$$D_{\alpha\alpha'} = 2[\frac{1}{2} \sin 2\gamma (K_{1\alpha\alpha'} - K_{2\alpha\alpha'}) + W_{\alpha\alpha'} \cos 2\gamma], \quad (2.6f)$$

and where

$$c_1 = e^{\theta} a_1 e^{-\theta} = a_1 \cos \gamma - a_2 \sin \gamma, \quad (2.7a)$$

$$c_2 = e^{\theta} a_2 e^{-\theta} = a_1 \sin \gamma + a_2 \cos \gamma, \quad (2.7b)$$

$$\gamma = \theta / 2, \quad (2.7c)$$

and

$$E_{1,2} = \frac{1}{2} [(\epsilon_1 + \epsilon_2) \pm \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4V^2}]. \quad (2.8)$$

In Eq. (2.5b), c_n^{+} creates a delocalized dimer excitation. The first and second terms in Eq. (2.5d) represent the linear and quadratic phonon-induced pure dephasing of dimer states $|1\rangle$ and $|2\rangle$ (a T_2^* process), while the final term gives rise to linear and quadratic phonon-induced scattering between the two delocalized dimer states $|1\rangle$ and $|2\rangle$ (a T_1 process).

It has been well established that pseudolocal phonons play a dominant role in the dephasing of monomer electronic transitions of pentacene and tetracene in mixed molecular crystals.^{16,18,24} The pseudolocal phonon responsible for monomer dephasing has been identified as a libration ("hindered rotation") of the impurity molecules. In the systems of pentacene monomers in naphthalene and in *p*-terphenyl, convincing evidence was given by Hesselink and Wiersma^{18(a)} to indicate that phonon-induced scattering to monomer librations is the predominate dephasing mechanism of the impurity electronic transition. In Lee *et al.*,^{16(b)} qualitative arguments were given to suggest that phonon-induced scattering to delocalized dimer librations is a plausible dephasing pathway of electronically excited pentacene dimers in *p*-terphenyl.

In the above reference, optical Redfield theory (ORT)^{18,23,24} was used to theoretically analyze the experimental data. It was shown that within the framework of ORT, it is convenient and sometimes necessary to include the pseudolocal phonons as part of the "slow subsystem" consisting of the impurity electronic states, and leave the band phonons as the "fast" bath subsystem. There are several valid reasons that prompted us to use a similar model. First, like local phonons and unlike lattice phonons, pseudolocal phonons exhibit an enhanced vibrational amplitude at the impurity site but at large distances from the impurity, resemble unperturbed delocalized lattice modes.^{27,28} As a consequence, the electronic transition will couple selectively with these pseudolocal modes. In such cases, it would be more convenient to treat them on the same level as the electronic levels. Second, sharp spectral features corresponding to the excitation of the librational mode are often observed in the absorption (or emission) spectra of mixed molecular crystals.¹⁸ The observation of sharp spectral features such as the zero phonon line (ZPL) apart from the broad phonon band is important in that it validates the Markov approximation used in ORT and indicates that ORT is applicable and realistic. Thus the observation of sharp features in the spectrum as narrow as the ZPL indicates a separation of time scales more appropriate for the "slow" subsystem rather than the "fast" bath system. Third, included in the excitation-phonon interaction is both diagonal and nondiagonal adiabatic quadratic coupling. For band phonons, the nondiagonal coupling contribution to optical dephasing will dominate the diagonal contribution, while the reverse is true for local phonons.²⁹ Consequently, Lubchenko³⁰ and Krivoglaz²⁹ demonstrated that it is appropriate to treat the local phonons separately from the band phonons. The similarity of local and pseudolocal phonons prompts us to do the same. Finally, the commonly employed two-level reduction scheme of optical dephasing in ORT is valid only if the phonons comprising the heat bath either show an appreciable anharmonic width or belong to a phonon branch of sufficiently broad bandwidth.²⁴ Acoustic phonons easily satisfy this condition; however, problems arise when one considers "dispersionless" optical phonons or pseudolocal modes, both of which we consider in this treatment.

Thus, in analogy with de Bree *et al.*²⁴ we will remove the dimer librational modes (pseudolocal modes) from the

phonon bath. These modes will be indicated by creation annihilation operators B_λ^+ and B_λ . The following assumptions are made:

(1) We will consider only one librational mode on each monomer comprising the dimer. This results in two delocalized dimer librations in the ground and in the singly excited states.

(2) The dimer librations are coupled to the dimer electronic excitation both linearly and quadratically:

$$\sum_{n\lambda} c_n^+ c_n \{L_{n\lambda} (B_\lambda + B_\lambda^+) + Q_{n\lambda\lambda} (B_\lambda + B_\lambda^+)^2\}. \quad (2.9)$$

This linear and quadratic coupling can be transformed away in a manner similar to the band phonons,²² giving rise to a renormalized dimer electronic energy and changed pseudolocal phonon frequencies in the ground and excited states.

(3) There will be terms that induce scattering between delocalized dimer states via linear and quadratic coupling to dimer librations. These arise from the modulation of the resonance electronic interaction by the libration. These terms will be ignored.

In addition, it is convenient to renormalize the Hamiltonian such that $\langle H_{\text{int}} \rangle = 0$ where $\langle \dots \rangle$ indicates an equilibrium thermal average over the phonon (bath) states:

$$\langle \dots \rangle = \text{Tr}_p (\rho_p^e \dots), \quad (2.10a)$$

where

$$\rho_p^e = \frac{e^{-H_{\text{ph}}/kT}}{\text{Tr}_p e^{-H_{\text{ph}}/kT}}. \quad (2.10b)$$

This renormalization can be accomplished by redefining

$$H_{\text{ex}} = H_{\text{ex}}^0 + \langle H_{\text{int}}^0 \rangle, \quad (2.11)$$

$$H_{\text{int}} = H_{\text{int}}^0 - \langle H_{\text{int}} \rangle. \quad (2.12)$$

Finally, we utilize the rotating wave approximation³¹ by truncating the adiabatic quadratic interaction terms so that they conserve the number of phonons to first order. In addition, we include an anharmonic interaction of the pseudolocal phonon with the band phonons to describe the decay of the pseudolocal phonon. We will also include the diagonal part of the intrinsic pseudolocal phonon anharmonicity in the mode frequency. This results in the final form of the Hamiltonian:

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{int}}, \quad (2.13)$$

where

$$H_{\text{ex}} = \sum_n \left[E_n + \sum_\alpha Q_{n\alpha, -\alpha} (\bar{n}_\alpha + \frac{1}{2}) \right] c_n^+ c_n + \hbar \sum_\lambda \Omega_\lambda (B_\lambda^+ B_\lambda + \frac{1}{2}) + \hbar \sum_{n\lambda} c_n^+ c_n (\Omega_{n\lambda} - \Omega_\lambda) (B_\lambda^+ B_\lambda + \frac{1}{2}), \quad (2.14a)$$

$$H_{\text{ph}} = \hbar \sum_\alpha \omega_\alpha (b_\alpha^+ b_\alpha + \frac{1}{2}), \quad (2.14b)$$

$$H_{\text{int}} = H_{e-p} + V_{1-p}, \quad (2.14c)$$

and where

$$H_{e-p} = \sum_n c_n^+ c_n (V_n^{(1)} + V_n^{(2)} + V_n^{(3)}) + \sum_{n\lambda} c_n^+ c_n (B_\lambda + B_\lambda^+) V_{n\lambda}^{(4)} + \sum_{\substack{mn \\ (m \neq n)}} c_m^+ c_n (V^{(5)} + V^{(6)}), \quad (2.15a)$$

$$V_{1-p} = \sum_\lambda (B_\lambda + B_\lambda^+) [V_\lambda^{(7)} + V_\lambda^{(8)}], \quad (2.15b)$$

and

$$V_n^{(1)} = \sum_\alpha L_{n\alpha} (b_\alpha + b_{-\alpha}^+), \quad (2.16a)$$

$$V_n^{(2)} = \sum_{\alpha\alpha'} Q_{n\alpha\alpha'} b_{-\alpha}^+ b_{\alpha'}, \quad (\alpha \neq -\alpha') \quad (2.16b)$$

$$V_n^{(3)} = \sum_\alpha Q_{n\alpha, -\alpha} (b_\alpha^+ b_\alpha - \bar{n}_\alpha), \quad (2.16c)$$

$$V_{n\lambda}^{(4)} = \sum_\alpha Q_{n\alpha\lambda} (b_\alpha + b_{-\alpha}^+), \quad (2.16d)$$

$$V_n^{(5)} = \sum_\alpha F_\alpha (b_\alpha + b_{-\alpha}^+), \quad (2.16e)$$

$$V_n^{(6)} = \sum_{\alpha\alpha'} D_{\alpha\alpha'} (b_\alpha + b_{-\alpha}^+) (b_{\alpha'} + b_{-\alpha'}^+), \quad (2.16f)$$

$$V_\lambda^{(7)} = \sum_\alpha H_{\alpha\lambda} (b_\alpha + b_{-\alpha}^+), \quad (2.16g)$$

$$V_\lambda^{(8)} = \sum_{\alpha\alpha'} A_{\alpha\alpha'\lambda} (b_\alpha + b_{-\alpha}^+) (b_{\alpha'} + b_{-\alpha'}^+), \quad (2.16h)$$

$$\bar{n}_\alpha = \langle b_\alpha^+ b_\alpha \rangle = [e^{\beta \hbar \omega_\alpha} - 1]^{-1}, \quad \beta = (kT)^{-1}; \quad (2.17)$$

and Ω_λ and $\Omega_{n\lambda}$ are the dimer librational frequencies in the ground and excited electronic states, respectively.

Before proceeding further, we would like to comment on the problem of vibronic coupling in a dimer. The vibronic states of a dimer are a classic example in which the Born-Oppenheimer approximation may fail.³² This failure arises when the electronic resonance interaction V is weak, resulting in an electronic splitting smaller than the vibrational splitting. However, we are considering strongly interacting dimers where V is large and the dimer peaks are split far from the constituent monomer peak. In addition, the vibrations we consider (the pseudolocal phonon) is a delocalized librational mode that corresponds to a hindered rotation of the molecules. We would expect the vibrational coupling of such a mode to be small, as is evidenced by the reduced bandwidth of vibrational excitons in comparison to electronic excitons.³³ Thus we treat the limiting case of strong electronic coupling. This gives rise to the energy level scheme in Fig. 1.

Thus in Fig. 1, $|0\rangle$ is the dimer ground state while $|1\rangle$ and $|2\rangle$ correspond to the singly excited delocalized electronic singlet states. $|0, L_\lambda\rangle$ ($\lambda = 1, 2$) are the dimer librations in the ground state, and $|n, L_\lambda\rangle$ ($n = 1, 2; \lambda = 1, 2$) are the librations in the excited states.

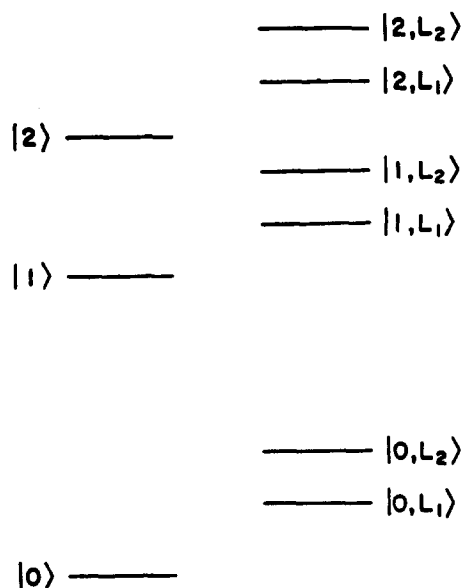


FIG. 1. Dimer energy levels. $|0\rangle$, $|1\rangle$, and $|2\rangle$ are the dimer ground and singly excited delocalized electronic singlet states. $|0, L_\lambda\rangle$ ($\lambda = 1, 2$) are the dimer librations in the ground state, and $|n, L_\lambda\rangle$ ($n = 1, 2; \lambda = 1, 2$) are the dimer librations in the excited states.

In this representation of the Hamiltonian, it is immediately recognized that $V_n^{(i)}$ ($i = 1-3$) are responsible for the adiabatic pure dephasing (T_2^*) of the $|0\rangle \leftrightarrow |n\rangle$ ($n = 1, 2$) dimer transitions. $V_n^{(1)}$ corresponds to the linear excitation-phonon coupling interaction while $V_n^{(2)}$ and $V_n^{(3)}$ are respectively the nondiagonal and diagonal quadratic excitation-phonon interaction describing the usual resonance Raman scattering processes with the band phonons.

In contrast, $V_{n\lambda}^{(4)}$, $V^{(i)}$ ($i = 5-6$), $V_\lambda^{(7)}$, and $V_\lambda^{(8)}$ are responsible for the T_1 -type nonadiabatic dephasing process. $V_{n\lambda}^{(4)}$ causes scattering from the dimer excited electronic states to the excited state librations and involves the direct exchange of the pseudolocal phonon and a band phonon. $V_\lambda^{(7)}$ and $V_\lambda^{(8)}$ however, describe the coupling of the librations to the band phonons and cause scattering to the librations in both the ground and excited dimer states. $V_\lambda^{(7)}$ describes the harmonic interaction of the libration with the band phonons and results in the direct exchange of a band phonon and a pseudolocal phonon, while $V_\lambda^{(8)}$ describes the anharmonic interactions and cause nonadiabatic decay of the pseudolocal phonon into two band phonons. Quartic and higher-order interactions are neglected as they are important only at high temperatures. $V^{(i)}$ ($i = 5-6$) cause scattering between dimer states $|1\rangle$ and $|2\rangle$.

Since we are dealing with strongly coupled dimers, examination of Eq. (2.14) reveals this Hamiltonian to be isomorphic with a multilevel monomer Hamiltonian. Thus we expect, and do find, the dephasing dynamics of this dimer model to be qualitatively similar to that of a monomer^{18a, 29, 34} with the differences being in the interpretation of the dephasing parameters. For example, we expect the phonon-induced pure dephasing of the $|0\rangle \leftrightarrow |1\rangle$ and $|0\rangle \leftrightarrow |2\rangle$ dimer transitions to exhibit the same functional form of the temperature dependence as the monomer. How-

ever, the pure dephasing of the dimer includes, in addition to the phonon modulation of the constituent monomer site energies, phonon modulation of the electronic resonance interaction. This contribution is obviously absent in the monomer. Also, the dimer has additional T_1 -type dephasing pathways which are lacking in the monomer, e.g., phonon-induced scattering between delocalized dimer states.

In our model, the optical dephasing rates for the dimer transitions are written as

$$\left[\frac{1}{T_2} \right]_n = \frac{1}{2\tau_n} + \left[\frac{1}{T_2'} \right]_n, \quad (2.18a)$$

where

$$\left[\frac{1}{T_2'} \right]_n = \left[\frac{1}{T_2^*} \right]_n + \left[\frac{1}{2T_1} \right]_n. \quad (2.18b)$$

The subscript n indicates the particular dimer transition $|0\rangle \leftrightarrow |n\rangle$ ($n = 1, 2$). τ_n is the excited state lifetime out of $|n\rangle$, while $(1/T_2')_n$ includes all other dephasing processes such as adiabatic pure dephasing $(T_2^*)_n$ and nonadiabatic population relaxation processes $(T_1)_n$. For example, phonon modulation of the dimer excited state energy is a pure dephasing process, T_2^* , while phonon-induced scattering between delocalized dimer states is a T_1 process. Both processes are included in T_2' .

We remark that the designation of the process of scattering to dimer librations as a T_1 process is a consequence of our removing the librations from the bath and including them in the dimer subsystem. An equivalent treatment consists of leaving the dimer librations in the bath. In this case, excitation of the dimer libration would be designated as a T_2^* adiabatic pure dephasing process.

III. REDFIELD THEORY

The use of Redfield theory to analyze relaxation processes in magnetic resonance has been very successful. The application of this theory to optical dephasing processes has been equally fruitful. Optical Redfield theory (ORT) has been discussed elsewhere.^{18,23,24} We highlight the results here of the quantum mechanical version of ORT in order to derive results pertaining to cross-correlation relaxation effects which were ignored by Cohen-Tannoudji²³ and by Wiersma and co-workers.^{18,24}

The total system is characterized by the Hamiltonian

$$H = H_A + H_R + V_{AR}. \quad (3.1)$$

H_A represents the slow subsystem of interest, H_R represents the fast bath subsystem, which is assumed to always be in thermal equilibrium, and V_{AR} gives the coupling between the two subsystems. All operators in the A subsystem are assumed to commute with the bath operators, and V_{AR} is assumed to be of the form

$$V_{AR} = \sum_{\mu} A^{(\mu)} R^{(\mu)}, \quad (3.2)$$

where $A^{(\mu)}$ operates on the A subsystem, and $R^{(\mu)}$ operates on the R subsystem. Both $A^{(\mu)}$ and $R^{(\mu)}$ are taken to be Hermitian.

The dynamics of the entire system is governed by the Liouville equation

$$i\hbar \dot{\rho} = [H, \rho], \quad (3.3)$$

where ρ is the density operator for the total system. However, since we are principally interested in the dynamics of subsystem A , we trace over the bath variables to yield the equation of motion for the reduced density operator for subsystem A (σ_A):

$$\dot{\sigma}_A = \text{Tr}_R \dot{\rho}. \quad (3.4)$$

The following assumptions are then made.

- (1) The bath states are always in thermal equilibrium.
- (2) $\rho(t)$ can be factorized as

$$\rho(t) = \sigma_A(T) \times \sigma_R(0). \quad (3.5)$$

Here, $\sigma_R(0)$ is the reduced density operator for the bath at thermal equilibrium.

- (3) The bath correlation functions decay away much faster than the observables in the A subsystem, i.e., the bath has a short memory time τ_c . This allows the approximation $\sigma_A(t - \tau) = \sigma_A(t)$ for $0 < \tau < \tau_c$. This is the Markov approximation.
- (4) σ_{ij} will couple to σ_{lm} only if $|(\omega_i - \omega_j) - (\omega_l - \omega_m)| \ll$ the coupling between these two. This is the secular approximation.

With the above assumptions and Eqs. (3.2)–(3.4) we arrive at the following equation of motion for the off-diagonal matrix elements of the reduced density operator of subsystem A :

$$\frac{d}{dt} \sigma_{ij} = -i \left(\omega_{ij} + \frac{\Delta_{ij}}{\hbar} \right) \sigma_{ij} - \Gamma_{ij} \sigma_{ij} + \sum_{rs} \Gamma_{rs \rightarrow ij} \sigma_{rs}, \quad (3.6)$$

where

$$\Gamma_{ij} = \Gamma_{ij}^A + \Gamma_{ij}^{NA}, \quad (3.7a)$$

$$\Gamma_{ij}^A = \frac{1}{\hbar^2} \text{Re} \sum_{\mu\nu} [A_{ii}^{\mu} A_{jj}^{\nu} I_{\mu\nu}(0) - A_{jj}^{\mu} A_{ii}^{\nu} I_{\mu\nu}^*(0)], \quad (3.7b)$$

$$\Gamma_{ij}^{NA} = \frac{1}{\hbar^2} \text{Re} \sum_{\mu\nu} \left[\sum_{m \neq i} A_{im}^{\mu} A_{mi}^{\nu} I_{\mu\nu}(\omega_{im}) + \sum_{m \neq j} A_{jm}^{\nu} A_{mj}^{\mu} I_{\mu\nu}^*(\omega_{jm}) \right], \quad (3.7c)$$

$$\Gamma_{rs \rightarrow ij} = \frac{1}{\hbar^2} \text{Re} \sum_{\mu\nu} \sum_{rs} [A_{ir}^{\nu} A_{sj}^{\mu} I_{\mu\nu}(\omega_{ri}) + A_{sj}^{\nu} A_{ir}^{\mu} I_{\mu\nu}^*(\omega_{sj})], \quad (3.7d)$$

$$\Delta_{ij} = \frac{1}{\hbar} \text{Im} \sum_{\mu\nu} \left\{ \sum_m [A_{im}^{\mu} A_{mi}^{\nu} I_{\mu\nu}(\omega_{im}) + A_{jm}^{\nu} A_{mj}^{\mu} I_{\mu\nu}^*(\omega_{im})] - A_{ii}^{\nu} A_{jj}^{\mu} I_{\mu\nu}(0) - A_{jj}^{\nu} A_{ii}^{\mu} I_{\mu\nu}^*(0) \right\}, \quad (3.7e)$$

and where

$$I_{\mu\nu}(\omega) \equiv \pi J_{\mu\nu}(\omega) + iP \int_{-\infty}^{\infty} \frac{d\omega'}{\omega - \omega'} J_{\mu\nu}(\omega'), \quad (3.8a)$$

$$J_{\mu\nu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau c_{\mu\nu}(\tau) e^{i\omega\tau}, \quad (3.8b)$$

$$c_{\mu\nu}(\tau) = \langle R^{(\mu)}(t)R^{(\nu)}(t-\tau) \rangle = \langle R^{(\mu)}(\tau)R^{(\nu)} \rangle, \quad (3.8c)$$

where $c_{\mu\nu}(\tau)$ is the time correlation function of the bath operators in V_{AR} , and P indicates the principal part.

Several terms relating to the dephasing of the $|i\rangle \leftrightarrow |j\rangle$ transition can be identified in Eq. (3.6). Δ_{ij} gives the second order frequency shift of the transition. $\Gamma_{rs \rightarrow ij}$ represents the coherence transfer feeding terms and results from the correlated scattering of the bath with the subsystem A in the states $|i\rangle$ and $|j\rangle$. This term is important only when $|\omega_{rs} - \omega_{ij}| < \Gamma_{rs \rightarrow ij}$ and in our model, is allowed only between near-resonant transitions.

In the absence of coherence transfer, the dephasing rate $1/T_2'$ is given by Γ_{ij} . From Eq. (3.7) we see that there are two contributions to Γ_{ij} , an adiabatic (Γ_{ij}^A) and a nonadiabatic (Γ_{ij}^{NA}) contribution. The adiabatic contribution gives rise to the pure dephasing (T_2^*) of the transition and involves elastic collisions with the bath without any transition in subsystem A . This contribution is determined by $J_{\mu\nu}(0)$, i.e., the zero frequency limit of the Fourier transform of correlation functions of the bath operators in V_{AR} . The nonadiabatic contribution, however, results in T_1 -type dephasing processes and involves inelastic collisions of the bath with A with a concomitant transition in A . This contribution is determined by $J_{\mu\nu}(\omega)$ where $\hbar\omega$ is the energy of the T_1 transition process in A . From Eq. (3.7c) we see that Γ_{ij}^{NA} is the sum of Fermi Golden Rule transition rates out of $|i\rangle$ and $|j\rangle$:

$$\Gamma_{ij}^{NA} = \frac{1}{2} \left[\sum_{m \neq i} \Gamma_{i \rightarrow m} + \sum_{n \neq j} \Gamma_{j \rightarrow n} \right], \quad (3.9a)$$

where

$$\Gamma_{i \rightarrow m} = \frac{2}{\hbar^2} \text{Re} \sum_{\mu\nu} \sum_{m \neq i} A_{im}^\mu A_{mi}^\nu J_{\mu\nu}(\omega_{im}), \quad (3.9b)$$

and where $\Gamma_{i \rightarrow m}$ is the Fermi Golden Rule transition rate from $|i\rangle$ to $|m\rangle$.

The important point is that the dephasing of the transition is determined by the time correlation functions of the bath operators $R^{(\mu)}$. In addition, we have explicitly derived terms relating to dephasing dynamics resulting from cross correlation functions. These cross correlation effects arise from the summation in Eq. (3.2) for the form of the coupling interaction, V_{AR} . This summation generates interference effects between terms in the summation. Thus, the dephasing rate is not simply the sum of the dephasing contributions from each term in the summation, but includes the interference terms also. Specifically, these cross correlation effects are given by the terms in the summation in Eqs. (3.7b)–(3.7e) where $\mu \neq \nu$. Cohen-Tannoudji²³ and Wiersma and co-workers^{18,24} assumed a coupling of the form

$$V_{AR} = AR. \quad (3.10)$$

Though this form precludes any cross correlation effects, it is not generally applicable to the systems described by Wiersma and co-workers,^{18,24} where their coupling interaction consists of a summation of terms. Equation (3.2) is the proper form. However, in the systems treated by Wiersma and co-workers,^{18,24} the cross correlation relaxation effects fortuitously vanish.

IV. APPLICATION OF REDFIELD THEORY TO DIMER DEPHASING

We shall now use the Redfield equations (3.7) to calculate the dephasing dynamics of our dimer model. Within the formalism of ORT, H_A corresponds to H_{ex} , i.e., subsystem A corresponds to the impurity dimer system shown in Fig. 1. The bath subsystem H_R corresponds to H_{ph} and consists of the lattice phonons of the host crystal, while the interaction H_{AR} corresponds to the interaction between the dimer system and the crystal phonons, and is given by H_{int} .

As stated in Sec. III, the dephasing dynamics are determined by the time correlation functions of the phonon operators in H_{int} . We note that the cross correlations $\langle V_n^{(i)}(\tau)V^{(j)} \rangle$ ($i=1-3, j=5-6$) are of no consequences since in the Redfield equations (3.7), these correlation functions are multiplied by

$$A_{im}^\mu A_{mi}^\nu \quad (A^\mu = c_n^+ c_n, \quad A^\nu = c_n^+ c_m, \quad m \neq n), \quad (4.1)$$

which is zero in the above cases. For similar reasons, numerous other cross correlations do not matter. Also, correlations that do not contain an equal number of phonon creation and annihilation operators are strictly zero, such as cross correlations between operators linear and quadratic in phonon operators. The phonon correlation functions used to calculate the bath correlation functions are given in Appendix A. We have phenomenologically modeled the phonon anharmonicity with an α -dependent damping factor ($e^{-\Gamma_\alpha|\tau|}$) representing the finite dephasing time of the phonons. This has been shown to be an accurate description.^{29,35}

We now calculate the temperature dependence of the dimer dephasing rate. As noted earlier, the processes responsible for dephasing a dimer transition are: (A) scattering between delocalized dimer states (T_1 process), (B) scattering to dimer librations (T_1 process), and (C) phonon-induced pure dephasing (T_2^* process). These processes are illustrated in Fig. 2.

A. T_1 -type dephasing: Scattering between dimer levels

Phonon-induced scattering between delocalized dimer states may arise from both linear and quadratic excitation-phonon coupling. Since the cross correlations from these two couplings are strictly zero, the dephasing is determined by the sum of their individual contributions.

From Eqs. (2.16) and (3.7) we calculate the linear excitation-phonon coupling contribution to $(1/T_2)_n$ arising from scattering between dimer states to be

$$\begin{aligned} \left(\frac{1}{T_2'}\right)_1 &= \frac{\pi}{\hbar^2} \sum_\alpha |F_\alpha|^2 [(\bar{n}_\alpha + 1)\Delta(\omega_\alpha, \omega_s) \\ &\quad + \bar{n}_\alpha \Delta(\omega_\alpha, -\omega_s)] \\ &= \frac{\pi}{\hbar^2} \int d\omega \rho(\omega) |F(\omega)|^2 [[\bar{n}(\omega) + 1]\Delta(\omega, \omega_s) \\ &\quad + \bar{n}(\omega)\Delta(\omega, -\omega_s)], \quad (4.2a) \\ \left(\frac{1}{T_2'}\right)_2 &= \frac{\pi}{\hbar^2} \sum_\alpha |F_\alpha|^2 \\ &\quad \times [(\bar{n}_\alpha + 1)\Delta(\omega_\alpha, -\omega_s) + \bar{n}_\alpha \Delta(\omega_\alpha, \omega_s)] \end{aligned}$$

DIMER DEPHASING MECHANISMS

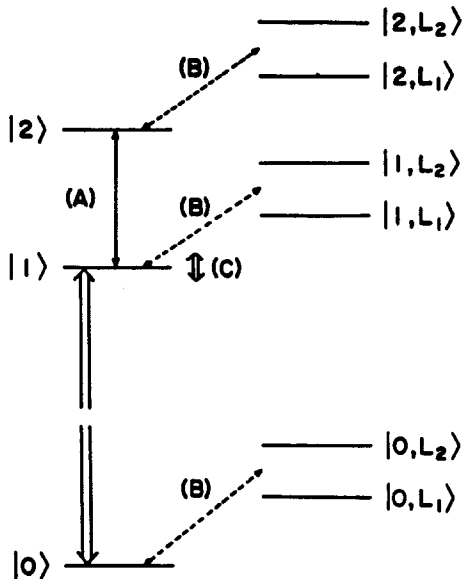


FIG. 2. Dimer dephasing mechanisms. Mechanism (A) involves phonon-induced scattering between delocalized dimer states (a T_1 process). Mechanism (B) involves phonon-induced scattering to dimer librations (a T_1 process). Mechanism (C) involves phonon-induced pure dephasing (a T_2^* process).

$$= \frac{\pi}{\hbar^2} \int d\omega \rho(\omega) |F(\omega)|^2 \{ [\bar{n}(\omega) + 1] \Delta(\omega, -\omega_s) + \bar{n}(\omega) \Delta(\omega, \omega_s) \}, \quad (4.2b)$$

where $\rho(\omega)$ is the density of phonon states, $\hbar\omega_s$ is the energy splitting between dimer states $|1\rangle$ and $|2\rangle$,

$$\Delta(\omega_\alpha, \omega_s) = \frac{\Gamma_\alpha}{\pi [\Gamma_\alpha^2 + (\omega_\alpha + \omega_s)^2]}, \quad (4.2c)$$

and where we have assumed a continuous distribution of phonon states, which allows us to convert the summation over α to an integral with $\Sigma \rightarrow \int d\omega \rho(\omega)$.

If we now consider the case of weak phonon anharmonicities, the limit $\Gamma_\alpha \rightarrow 0$ can be taken. With the following definition of $\delta(x)$:

$$\delta(x) = \lim_{a \rightarrow 0} \frac{a}{\pi(a^2 + x^2)}, \quad (4.3)$$

Eqs. (4.2a) and (4.2b) become

$$\left(\frac{1}{T_2'}\right)_1 = \frac{\pi}{\hbar^2} |F(\omega_s)|^2 \rho(\omega_s) \bar{n}(\omega_s), \quad (4.4a)$$

$$\left(\frac{1}{T_2'}\right)_2 = \frac{\pi}{\hbar^2} |F(\omega_s)|^2 \rho(\omega_s) [\bar{n}(\omega_s) + 1]. \quad (4.4b)$$

Both dephasing rates arise from T_1 -type scattering processes. The up-scattering process [reflected in $(1/T_2')_1$] in-

volves the direct absorption of a single phonon of energy $\hbar\omega_s$, while the down scattering process [reflected in $(1/T_2')_2$] involves either spontaneous or stimulated emission of a phonon of energy $\hbar\omega_s$.

The temperature dependence of Eqs. (4.2a), (4.2b), (4.4a), and (4.4b) results from the factors \bar{n}_α and $(\bar{n}_\alpha + 1)$ evaluated at $\omega_\alpha = \omega_s$. In the temperature region $T \ll \hbar\omega_s/k$, \bar{n}_α is well approximated by $e^{-\beta\hbar\omega}$ where $\tilde{\omega} > \omega_s$, and $(\bar{n}_\alpha + 1)$ is roughly constant. In the limit of low temperatures where $T \ll \hbar\omega_s/k$, $\tilde{\omega}$ equals ω_s and $(\bar{n}_\alpha + 1)$ is 1. Thus we see that at low temperatures, linear excitation-phonon coupling inducing scattering between the dimer states $|1\rangle$ and $|2\rangle$ results in an exponential temperature activation of $(1/T_2')_1$, and a temperature independent rate $(1/T_2')_2$.

Equations (4.4a) and (4.4b) cannot be expressed in more detail without a specific phonon density of states and an explicit expression for the coupling parameter, $F(\omega)$. If we consider acoustic phonons, the Debye density of phonon states³⁶ may be used:

$$\rho(\omega) = 9N(\omega^2/\omega_D^3), \quad (4.5)$$

where an isotropic solid is assumed. This gives

$$\left(\frac{1}{T_2'}\right)_1 = \frac{9\pi}{\hbar} \bar{F}^2 \left(\frac{\omega_s}{\omega_D}\right)^3 \bar{n}(\omega_s), \quad (4.6a)$$

$$\left(\frac{1}{T_2'}\right)_2 = \frac{9\pi}{\hbar} \bar{F}^2 \left(\frac{\omega_s}{\omega_D}\right)^3 [\bar{n}(\omega_s) + 1], \quad (4.6b)$$

where \bar{F} is a constant reflecting the strength of the linear excitation-phonon coupling, and is defined in Appendix B.

Finally, the radiationless relaxation rates for the processes $|1\rangle \leftrightarrow |2\rangle$ are related to the dephasing rates:

$$\Gamma_{|1\rangle \rightarrow |2\rangle} = 2 \left(\frac{1}{T_2'}\right)_1, \quad (4.7a)$$

$$\Gamma_{|2\rangle \rightarrow |1\rangle} = 2 \left(\frac{1}{T_2'}\right)_2. \quad (4.7b)$$

Along with Eqs. (4.4a) and (4.4b), this provides an expression for the lifetime of $|2\rangle$ resulting from phonon scattering between dimer states due to linear coupling:

$$\begin{aligned} (1/T_1) &= \Gamma_{|2\rangle \rightarrow |1\rangle} - \Gamma_{|1\rangle \rightarrow |2\rangle} \\ &= (2\pi/\hbar^2) \rho(\omega_s) |F(\omega_s)|^2. \end{aligned} \quad (4.8)$$

From Eqs. (2.14) and (3.7), we find the quadratic coupling contribution to $1/T_2'$ to be

$$\left(\frac{1}{T_2'}\right)_1 = \frac{1}{2\hbar^2} \text{Re} \int_{-\infty}^{\infty} e^{-i\omega_s\tau} \langle R(\tau)R \rangle d\tau, \quad (4.9a)$$

$$\left(\frac{1}{T_2'}\right)_2 = \frac{1}{2\hbar^2} \text{Re} \int_{-\infty}^{\infty} d\tau e^{i\omega_s\tau} \langle R(\tau)R \rangle, \quad (4.9b)$$

where

$$\begin{aligned} \langle R(\tau)R \rangle &= \sum_{\alpha\alpha'} \sum_{ss'} D_{\alpha\alpha'} D_{ss'} \{ \langle (b_\alpha b_{\alpha'}) (\tau) b_\pm^\dagger b_\pm^\dagger \rangle + \langle (b_\pm^\dagger b_\pm^\dagger) (\tau) b_s b_s \rangle + \langle (b_\pm^\dagger b_{\alpha'}) (\tau) b_\pm^\dagger b_s \rangle \\ &\quad + \langle (b_\pm^\dagger b_{\alpha'}) (\tau) b_s b_\pm^\dagger \rangle + \langle (b_\alpha b_\pm^\dagger) (\tau) b_s b_\pm^\dagger \rangle + \langle (b_\alpha b_\pm^\dagger) (\tau) b_\pm^\dagger b_s \rangle \}, \end{aligned} \quad (4.10)$$

and where the phonon correlation functions are given in Appendix A.

If we again consider small phonon anharmonicities, the expressions for the dephasing rates simplify considerably. We obtain

$$\left(\frac{1}{T'_2}\right)_1 = \frac{2\pi}{\hbar^2} \int d\omega \rho(\omega) \bar{n}(\omega) \{ |D(\omega, \omega_s - \omega)|^2 \rho(\omega_s - \omega) \bar{n}(\omega_s - \omega) + 2|D(\omega, \omega - \omega_s)|^2 \rho(\omega - \omega_s) [\bar{n}(\omega - \omega_s) + 1] \}, \quad (4.11a)$$

$$\left(\frac{1}{T'_2}\right)_2 = \frac{2\pi}{\hbar^2} \int d\omega \rho(\omega) [\bar{n}(\omega) + 1] \{ |D(\omega, \omega_s - \omega)|^2 \rho(\omega_s - \omega) [\bar{n}(\omega_s - \omega) + 1] + 2|D(\omega, \omega - \omega_s)|^2 \rho(\omega - \omega_s) \bar{n}(\omega - \omega_s) \}. \quad (4.11b)$$

Equations (4.11a) and (4.11b) show that scattering between dimer states induced by quadratic excitation-phonon coupling proceeds by two distinct processes. In up-scattering [Eq. (4.11a)], the first process involves two-phonon absorption into the higher dimer state, where the two phonons make up the energy difference. The second process involves a Raman scattering Stokes mechanism, where the difference of the two phonon energies make up the dimer splitting. In down scattering [Eq. (4.11b)], the first process involves two-phonon emission, where one or both phonons emitted results from spontaneous or stimulated emission. The second process proceeds via a Raman anti-Stokes mechanism.

The temperature dependence of the dephasing rates given in Eqs. (4.11a) and (4.11b) cannot be determined for the general case. However, if we again assume coupling to only acoustic phonons, we find

$$\left(\frac{1}{T'_2}\right)_1 = 486\pi\bar{D}^2\omega_D\left(\frac{T}{T_D}\right)^7 \times \int_0^{T_D/T} dx \left(\frac{x^3}{e^x - 1}\right) \frac{(x_s - x)^3}{(e^{x_s - x} - 1)}, \quad (4.12a)$$

$$\left(\frac{1}{T'_2}\right)_2 = 486\pi\bar{D}^2\omega_D\left(\frac{T}{T_D}\right)^7 \times \int_0^{T_D/T} dx \frac{x^3(x - x_s)^3 e^x}{(e^x - 1)(e^{x - x_s} - 1)}, \quad (4.12b)$$

where $x = \beta\hbar\omega$, $x_s = \beta\hbar\omega_s$, and \bar{D} is a constant reflecting the strength of the quadratic excitation-phonon coupling and is defined in Appendix B.

The radiationless relaxation rates resulting from quadratic coupling can be determined from Eqs. (4.7a), (4.7b), (4.11a), and (4.11b). From this, we calculate the lifetime of the upper delocalized dimer state arising from quadratic phonon scattering processes between dimer states:

$$\frac{1}{T_1} = \frac{4\pi}{\hbar^2} \int d\omega \rho(\omega) \{ |D(\omega, \omega_s - \omega)|^2 \rho(\omega_s - \omega) \times [\bar{n}(\omega_s - \omega) + \bar{n}(\omega) + 1] + |D(\omega, \omega - \omega_s)|^2 \times \rho(\omega - \omega_s) [\bar{n}(\omega - \omega_s) - \bar{n}(\omega)] \}. \quad (4.13)$$

B. T_1 -type dephasing: Scattering to librations

As noted earlier, $V_{n\lambda}^{(4)}$, $V_{\lambda}^{(7)}$, and $V_{\lambda}^{(8)}$ are responsible for the T_1 -type dephasing resulting from scattering to dimer librations. $V_{n\lambda}^{(4)}$ operates only on the excited electronic states while $V_{\lambda}^{(7)}$ and $V_{\lambda}^{(8)}$ operate on both the ground and excited states. These operators describe the creation or destruction of a dimer libration at the expense or creation of band phonons. However in this case, the dephasing rate is not determined simply by the sum of the individual contributions from $V_{n\lambda}^{(4)}$, $V_{\lambda}^{(7)}$, and $V_{\lambda}^{(8)}$. There is an additional term that arises from the cross correlation between $V_{\lambda}^{(7)}$ and $V_{n\lambda}^{(4)}$ (i.e., from $\langle V_{n\lambda}^{(4)}(\tau) V_{\lambda}^{(7)} \rangle \neq 0$).

$V_{n\lambda}^{(4)}$ and $V_{\lambda}^{(7)}$ describe one-phonon processes that scatter the dimer libration (i.e., one band phonon and one dimer libration). They describe the direct exchange of the pseudo-local phonon and a band phonon. Their individual contributions to the dephasing is calculated from Eqs. (2.16) and (3.7) to be, respectively,

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n^{(4)} &= \frac{\pi}{\hbar^2} \sum_{\lambda\alpha} |Q_{n\lambda}|^2 [(\bar{n}_\alpha + 1)\Delta(\omega_\alpha, \Omega_{n\lambda}) + \bar{n}_\alpha \Delta(\omega_\alpha, -\Omega_{n\lambda})] \\ &= \frac{\pi}{\hbar^2} \sum_{\lambda} \int d\omega \rho(\omega) |Q_{n\lambda}(\omega)|^2 \{ [\bar{n}(\omega) + 1]\Delta(\omega, \Omega_{n\lambda}) + \bar{n}(\omega)\Delta(\omega, -\Omega_{n\lambda}) \}, \end{aligned} \quad (4.14a)$$

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n^{(7)} &= \frac{\pi}{\hbar^2} \sum_{\lambda\alpha} |H_{\alpha\lambda}|^2 \{ (\bar{n}_\alpha + 1)[\Delta(\omega_\alpha, \Omega_\lambda) + \Delta(\omega_\alpha, \Omega_{n\lambda})] + \bar{n}_\alpha [\Delta(\omega_\alpha, -\Omega_\lambda) + \Delta(\omega_\alpha, -\Omega_{n\lambda})] \} \\ &= \frac{\pi}{\hbar^2} \sum_{\lambda} \int d\omega \rho(\omega) |H_{\lambda}(\omega)|^2 \{ [\bar{n}(\omega) + 1][\Delta(\omega, \Omega_\lambda) + \Delta(\omega, \Omega_{n\lambda})] + \bar{n}(\omega)[\Delta(\omega, -\Omega_\lambda) + \Delta(\omega, -\Omega_{n\lambda})] \}, \end{aligned} \quad (4.14b)$$

while the contribution from their cross correlation is

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n^{(4,7)} &= \frac{2\pi}{\hbar^2} \sum_{\lambda\alpha} \text{Re}(Q_{n\alpha\lambda} H_{\alpha\lambda}) [(\bar{n}_\alpha + 1)\Delta(\omega_\alpha, \Omega_{n\lambda}) + \bar{n}_\alpha \Delta(\omega, -\Omega_{n\lambda})] \\ &= \frac{2\pi}{\hbar^2} \sum_{\lambda} \int d\omega \rho(\omega) \text{Re}[Q_{n\lambda}(\omega) H_{\lambda}(\omega)] \{[n(\omega) + 1]\Delta(\omega, \Omega_{n\lambda}) + \bar{n}(\omega)\Delta(\omega, -\Omega_{n\lambda})\}. \end{aligned} \quad (4.14c)$$

If small phonon anharmonicities are considered, Eqs. (4.14a)–(4.14c) become, respectively,

$$\left(\frac{1}{T'_2}\right)_n^{(4)} = \frac{\pi}{\hbar^2} \sum_{\lambda} |Q_{n\lambda}(\Omega_{n\lambda})|^2 \rho(\Omega_{n\lambda}) \bar{n}(\Omega_{n\lambda}), \quad (4.15a)$$

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n^{(7)} &= \frac{\pi}{\hbar^2} \sum_{\lambda} [|H_{\lambda}(\Omega_{\lambda})|^2 \rho(\Omega_{\lambda}) \bar{n}(\Omega_{\lambda}) \\ &\quad + |H_{\lambda}(\Omega_{n\lambda})|^2 \rho(\Omega_{n\lambda}) \bar{n}(\Omega_{n\lambda})], \end{aligned} \quad (4.15b)$$

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n^{(4,7)} &= \frac{2\pi}{\hbar^2} \sum_{\lambda} \text{Re}[Q_{n\lambda}(\Omega_{n\lambda}) H_{\lambda}(\Omega_{n\lambda})] \\ &\quad \times \rho(\Omega_{n\lambda}) \bar{n}(\Omega_{n\lambda}). \end{aligned} \quad (4.15c)$$

The total dephasing rate arising from one-phonon process is then given by the sum of the contributions from Eqs. (4.15a)–(4.15c),

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n &= \frac{\pi}{\hbar^2} \sum_{\lambda} [|H_{\lambda}(\Omega_{\lambda})|^2 \rho(\Omega_{\lambda}) \bar{n}(\Omega_{\lambda}) \\ &\quad + |Q_{n\lambda}(\Omega_{n\lambda}) + H_{\lambda}(\Omega_{n\lambda})|^2 \rho(\Omega_{n\lambda}) \bar{n}(\Omega_{n\lambda})]. \end{aligned} \quad (4.15d)$$

Note that the contribution to dimer dephasing given by Eqs. (4.15a) and (4.15c) reflect one phonon induced scattering processes to the dimer excited state librations ($\Omega_{n\lambda}$, $n = 1, 2$), while Eq. (4.15b) reflects phonon induced scattering to both the dimer ground and excited state librations (Ω_{λ} , $\Omega_{n\lambda}$).

If we again consider coupling to acoustic phonons, the Debye density of states can be used in Eqs. (4.15a)–(4.15c) to yield the following dephasing rates due to $V_{n\lambda}^{(4)}$, $V_{\lambda}^{(7)}$, and their cross correlations, respectively:

$$\left(\frac{1}{T'_2}\right)_n^{(4)} = \frac{9\pi}{\hbar} \sum_{\lambda} |\bar{Q}_{n\lambda}|^2 \left(\frac{\Omega_{n\lambda}}{\omega_D}\right)^3 \bar{n}(\Omega_{n\lambda}), \quad (4.16a)$$

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n^{(7)} &= \frac{9\pi}{\hbar} \sum_{\lambda} [|\bar{H}_{\lambda}|^2 \left(\frac{\Omega_{\lambda}}{\omega_D}\right)^3 \bar{n}(\Omega_{\lambda}) \\ &\quad + \left(\frac{\Omega_{n\lambda}}{\omega_D}\right)^3 \bar{n}(\Omega_{n\lambda})], \end{aligned} \quad (4.16b)$$

$$\left(\frac{1}{T'_2}\right)_n^{(4,7)} = \frac{18\pi}{\hbar} \sum_{\lambda} \text{Re}(\bar{Q}_{n\lambda} \bar{H}_{\lambda}) \left(\frac{\Omega_{n\lambda}}{\omega_D}\right)^3 \bar{n}(\Omega_{n\lambda}), \quad (4.16c)$$

The total dephasing rate is again given by the sum of the contributions from Eqs. (4.16a)–(4.16c),

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n &= \frac{9\pi}{\hbar} \sum_{\lambda} \left[|\bar{H}_{\lambda}|^2 \left(\frac{\Omega_{\lambda}}{\omega_D}\right)^3 \bar{n}(\Omega_{\lambda}) \right. \\ &\quad \left. + |\bar{Q}_{n\lambda} + \bar{H}_{\lambda}|^2 \left(\frac{\Omega_{n\lambda}}{\omega_D}\right)^3 \bar{n}(\Omega_{n\lambda}) \right]. \end{aligned} \quad (4.16d)$$

The constants \bar{H}_{λ} and $\bar{Q}_{n\lambda}$ reflect the strength of the phonon coupling and are defined in Appendix B.

The temperature dependence of Eqs. (4.15a)–(4.15d) is also determined by the factor $\bar{n}(\omega)$ evaluated at the librational frequencies. As noted previously, this factor displays an exponentially activated temperature behavior at low temperatures ($T \ll \hbar\Omega_{\lambda}/k$, $\hbar\Omega_{n\lambda}/k$) with the activation energy given by the particular dimer libration. The final expression for the dimer dephasing rate arising from one phonon processes is then given by Eq. (4.15d). We thus observe that at low temperatures ($T \ll \hbar\Omega_{\lambda}/k$, $\hbar\Omega_{n\lambda}/k$), one-phonon scattering processes give rise to a tetraexponentially activated temperature dependence of the dephasing rate (one exponential for each libration in the ground and excited dimer states) with activation energies given by the four dimer librational energies. We point out, however, that one could observe experimentally a temperature behavior ranging from a quadruple to a single exponential. The apparent functional form depends on the relative magnitudes of the librational energies and the occupation of phonons at those energies. In addition, scattering to one or more librations in the ground or excited states may dominate.

Contributions to dimer dephasing from two phonon processes that scatter the dimer librations arise from $V_{\lambda}^{(8)}$, i.e., the anharmonic interaction between a dimer libration and two band phonons. This interaction describes the nonadiabatic decay of the pseudolocal phonon into two band phonons. This contribution is shown by Eqs. (2.16) and (3.7) to be given by

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n &= \frac{1}{2\hbar^2} \sum_{\lambda} \text{Re} \int_{-\infty}^{\infty} d\tau \\ &\quad \times (e^{-i\Omega_{\lambda}\tau} + e^{-i\Omega_{n\lambda}\tau}) \langle R_{\lambda}(\tau) R_{\lambda} \rangle, \end{aligned} \quad (4.17)$$

where $\langle R_{\lambda}(\tau) R_{\lambda} \rangle$ is given by $\langle R(\tau) R \rangle$ in Eq. (4.10), with $A_{\alpha\alpha'\lambda}$ and $A_{s's'\lambda}$ substituting for $D_{\alpha\alpha'}$ and $D_{s's'}$, respectively.

If we consider weak phonon anharmonicities, Eq. (4.17) becomes

$$\begin{aligned} \left(\frac{1}{T'_2}\right)_n &= \frac{2\pi}{\hbar^2} \sum_{\lambda} \sum_{\alpha\alpha'} \{ |A_{\alpha\alpha'\lambda}|^2 [\bar{n}_{\alpha} \bar{n}_{\alpha'} \delta(\omega_{\alpha} + \omega_{\alpha'} - \Omega_{\lambda}) \\ &\quad + 2\bar{n}_{\alpha} (\bar{n}_{\alpha'} + 1) \delta(\omega_{\alpha} - \omega_{\alpha'} - \Omega_{\lambda}) \} \end{aligned}$$

$$+ \bar{n}_\alpha \bar{n}_{\alpha'} \delta(\omega_\alpha + \omega_{\alpha'} - \Omega_{n\lambda}) \\ + 2\bar{n}_\alpha (\bar{n}_{\alpha'} + 1) \delta(\omega_\alpha - \omega_{\alpha'} - \Omega_{n\lambda}) \}. \quad (4.18)$$

As in the case of two-phonon induced scattering between dimer states, the above contribution to dimer dephasing reflects two distinct phonon scattering processes that occur for each libration in the dimer ground and excited electronic states. The first process involves the absorption of two band phonons to create the dimer libration, where the sum of the energies of the two band phonons equals the dimer librational energy. The second process involves a Raman scattering Stokes mechanism, where the difference of the energies of the two band phonons involved equals the dimer librational energy.

To determine the functional form of the temperature dependence of the dephasing rate given in Eq. (4.18) requires knowledge of the frequency dependence of $|A_{\alpha\alpha'\lambda}|^2$. Unfortunately, an accurate crystal potential surface function is needed to describe the anharmonicity. However, it was recently suggested by Della Valle *et al.*³⁷ that in many cases, that $|A_{\alpha\alpha'\lambda}|^2$ is constant in frequency provides a reasonable description of the temperature dependence of phonon lifetimes in various systems. For example, this simple model accurately described the temperature dependent lifetimes of librations in naphthalene and naphthalene- d_8 .³⁸ It was also recently shown to account for the frequency dependence of libron lifetimes in various amino acids and peptides.³⁹

Recognizing the success of this model, we take $|A_{\alpha\alpha'\lambda}|^2$ to be a frequency independent factor $1/N^2|\bar{A}_\lambda|^2$. We then convert the sum over α to an integral and again, assuming coupling to only acoustic phonons, we use the Debye density of states. This gives

$$\left(\frac{1}{T_2^*}\right)_n = \frac{162\pi}{\hbar^2 \omega_D} \left(\frac{T}{T_D}\right)^5 \sum_\lambda |\bar{A}_\lambda|^2 f_\lambda(\beta\hbar\Omega_\lambda, \beta\hbar\Omega_{n\lambda}), \quad (4.19)$$

where

$$f_\lambda(\beta\hbar\Omega_\lambda, \beta\hbar\Omega_{n\lambda}) = \int_0^{T_D/T} dx \frac{x^2}{e^x - 1} \\ \times \left[\frac{(x - x_\lambda)^2}{1 - e^{x_\lambda - x}} + \frac{(x - x_{n\lambda})^2}{1 - e^{x_{n\lambda} - x}} \right], \quad (4.20)$$

and where $x = \beta\hbar\omega$, $x_\lambda = \beta\hbar\Omega_\lambda$, and $x_{n\lambda} = \beta\hbar\Omega_{n\lambda}$.

C. Pure dephasing from linear coupling

As was noted in Sec. II, the temperature dependence of the pure dephasing of these dimer transitions is analogous to the temperature dependent dephasing of a two level monomer,^{18(a),29,34} as is evidenced by the form of the Hamiltonian, Eqs. (2.14). Therefore, as in the monomer, we expect linear excitation-phonon coupling involving harmonic phonons to contribute no pure dephasing broadening of the dimer transitions. Similarly, we expect the inclusion of phonon anharmonicity to result in only a weak temperature dependence.^{24,29}

These points are verified by Eqs. (2.16) and (3.7) from which we calculate that the linear coupling contribution to the pure dephasing (T_2^*) of the dimer $|0 \leftrightarrow |n\rangle$ ($n = 1, 2$) transitions is given by

$$\left[\frac{1}{T_2^*}\right]_n = \frac{\pi}{N\hbar} \sum_\alpha \frac{\Gamma_\alpha}{\pi[\Gamma_\alpha^2 + \omega_\alpha^2]} \bar{L}_n^2 \omega_\alpha (2\bar{n}_\alpha + 1), \quad (4.21)$$

where \bar{L}_n is a frequency independent function defined in Appendix B. In the limit of harmonic phonons, $\Gamma_\alpha \rightarrow 0$. In this case, we obtain

$$\left[\frac{1}{T_2^*}\right]_n = \frac{\pi}{N\hbar} \sum_\alpha \bar{L}_n^2 \omega_\alpha (2\bar{n}_\alpha + 1) \delta(\omega_\alpha) = 0. \quad (4.22)$$

Thus, as in the monomer, we see that linear excitation-phonon coupling involving perfectly harmonic phonons contributes no pure dephasing broadening of these dimer transitions. Taking into account phonon anharmonicities, we find two limiting cases:

$$\left[\frac{1}{T_2^*}\right]_n = \frac{\pi}{N\hbar} \sum_\alpha \frac{\Gamma_\alpha}{\pi(\Gamma_\alpha^2 + \omega_\alpha^2)} \bar{L}_n^2 \omega_\alpha \quad (\text{low temp.}), \quad (4.23a)$$

$$\left[\frac{1}{T_2^*}\right]_n = \frac{2\pi}{N\hbar^2} \left\{ \sum_\alpha \frac{\Gamma_\alpha}{\pi(\Gamma_\alpha^2 + \omega_\alpha^2)} \bar{L}_n^2 \right\} kT \quad (\text{high temp.}). \quad (4.23b)$$

We see that even with anharmonic phonons, linear excitation-phonon coupling results in no temperature dependence at low temperature and only a weakly temperature dependent linewidth at high temperature.

D. Pure dephasing from quadratic coupling

As with monomers, there are two contributions to $1/T^*$ resulting from quadratic excitation-phonon coupling. These contributions are the diagonal and nondiagonal quadratic coupling contributions and are given respectively by

$$\left[\frac{1}{T_2^*}\right]_n = \frac{1}{\hbar^2} \sum_\alpha \frac{|Q_{n\alpha, -\alpha}|^2}{2\Gamma_\alpha} \bar{n}_\alpha (\bar{n}_\alpha + 1), \quad (4.24a)$$

$$\left[\frac{1}{T_2^*}\right]_n = \frac{\pi}{\hbar^2} \sum_{\alpha\alpha'} \frac{\Gamma_\alpha + \Gamma_{\alpha'}}{\pi[(\Gamma_\alpha + \Gamma_{\alpha'})^2 + (\omega_\alpha - \omega_{\alpha'})^2]} \\ \times |Q_{n\alpha\alpha'}|^2 \bar{n}_\alpha (\bar{n}_{\alpha'} + 1). \quad (4.24b)$$

Once again, the temperature dependence of the pure dephasing is analogous to that of the two level monomer.^{18(a),29,34} Thus we expect, as in the monomer case, that the nondiagonal quadratic excitation-phonon coupling to the crystal band phonons will dominate the diagonal one, and that the phonon anharmonicity will be small, i.e., $\Gamma_\alpha \simeq 0$. Hence in the case of acoustic phonons, we shall predict a low temperature, T^7 and a high temperature T^2 dependence of $1/T_2^*$ in analogy with the monomer. To see this, we take the limit of small phonon anharmonicity and convert the sum in Eq. (4.24b) to an integral. The nondiagonal contribution can then be written as

$$\left[\frac{1}{T_2^*}\right]_n = \frac{\pi}{N^2} \bar{Q}_n^2 \int d\omega \rho^2(\omega) \omega^2 \bar{n}(\omega) [\bar{n}(\omega) + 1], \quad (4.25)$$

where \bar{Q}_n^2 represents a constant defined in Appendix B, and N is the number of unit cells in the crystal.

Using the Debye model for acoustic phonons,³⁶ we finally arrive at the following expression for the temperature dependence of the dephasing rate of the dimer transitions:

$$\left[\frac{1}{T_2^*} \right]_n = 81\pi \bar{Q}_n^2 \frac{kT_D}{\hbar} \left[\frac{T}{T_D} \right]^7 \int_0^{T_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx \quad (4.26)$$

where $x = \hbar\omega/kT$ and T_D is the Debye temperature given by $T_D = \hbar\omega_D/k$.

Thus we see that the temperature dependence of dimer pure dephasing resulting from quadratic excitation-phonon coupling to acoustic phonons is analogous to that of the monomer. Equation (4.26) predicts the familiar T^7 temperature dependence at low temperatures and T^2 at high temperatures.³⁴

We now consider quadratic coupling to optical phonons. If we assume a sharp peaking in the phonon density of states [as might be exhibited by the often-used Einstein model where $\rho_E(\omega) = N\delta(\omega - \bar{\omega})$ or by a sharply peaked Lorentzian or Gaussian density of states], then the integral in

$$\rho(\omega) = \begin{cases} \frac{2N}{\pi(\Gamma_B/2)^2} \left([\Gamma_B/2]^2 - (\omega - \bar{\omega})^2 \right)^{1/2}, & \bar{\omega} - (\Gamma_B/2) \leq \omega \leq \bar{\omega} + (\Gamma_B/2) \\ 0, & \text{elsewhere} \end{cases} \quad (4.28)$$

we find at low temperatures ($kT \ll \hbar\bar{\omega}$),

$$\left[\frac{1}{T_2^*} \right]_n = \frac{32}{\pi} \left[\frac{\bar{Q}_n}{\Gamma_B} \right]^2 \bar{\omega}^2 \sinh \left[\beta \hbar \frac{\Gamma_B}{2} \right] e^{-\beta \hbar \bar{\omega}} \quad (4.29)$$

Thus, we see that even in the case of a small bandwidth optical phonon branch ($\hbar\Gamma_B/2 \ll kT$) modified exponentials are predicted. This analogous result was also derived by de Bree²⁴ for monomers.

Thus at low temperatures, our model predicts that quadratic excitation-phonon coupling to acoustic phonons results in a T^7 temperature dependent pure dephasing of the dimer $|0\rangle \leftrightarrow |1\rangle$ and $|0\rangle \leftrightarrow |2\rangle$ transitions, while quadratic coupling to a sharply peaked optical phonon branch results in an exponential activation of $1/T_2^*$. In general, however, the temperature dependence resulting from optical phonons is dependent on the density of states of the optical phonon branch. Again, the above results are analogous to those derived for monomers.

V. DISCUSSION

To our knowledge, there have been only two experimental investigations into the dephasing dynamics of dimer transitions involving singlet states: A study on translationally equivalent naphthalene- h_8 dimers in naphthalene- d_8 by Morsink and Wiersma,¹⁷ and a study on pentacene dimers and tetracene dimers in *p*-terphenyl by Fayer *et al.*¹⁶ In both studies, exponential temperature activations were observed for the dephasing rates.

In the study on pentacene and tetracene dimers,^{16(b)} the experimental results were interpreted with the theory presented here. In that study it was concluded that dimer transitions of pentacene dimers and tetracene dimers in *p*-terphenyl dephase by phonon scattering to dimer librations.

Eq. (4.25) can be ignored and the frequency dependence can be evaluated at the peaking of $\rho(\omega)$ at say, $\bar{\omega}$. This gives

$$\left[\frac{1}{T_2^*} \right]_n = \frac{\pi}{N^2} \bar{Q}_n^2 \bar{\omega}^2 \rho^2(\bar{\omega}) \bar{n}(\bar{\omega}) [\bar{n}(\bar{\omega}) + 1] \quad (4.27)$$

The temperature dependence of Eq. (4.27) arises from $\bar{n}(\bar{\omega}) [\bar{n}(\bar{\omega}) + 1]$. In the temperature region $T \ll \hbar\bar{\omega}/k$, this factor closely approximates $e^{-\beta\hbar\bar{\omega}}$, in which $\bar{\omega} \gg \bar{\omega}$. In the limit of low temperatures where $T \ll \hbar\bar{\omega}/k$, $\bar{\omega}$ is precisely $\bar{\omega}$.

Thus, a sharp peaking in the density of phonon states results in the often-seen exponentially activated temperature dependence of the dephasing rate, regardless of the precise form of the density of states. This result is again analogous to the monomer case.²⁴

However, it must be stressed that the functional form of the temperature dependence is dependent, in general, on the particular density of states (and hence dispersion model) of the optical phonon band. For example, if the semicircular density of states⁴⁰ is used where

This conclusion was arrived at by comparing the apparent activation energies for the temperature dependent dephasing rates of pentacene dimers in *p*-terphenyl and tetracene dimers in *p*-terphenyl.

The observation of an exponential temperature activated dephasing rate is consistent with our theoretical result arising from one-phonon processes that scatter the dimer libration. This result is expressed in Eqs. (4.15) and (4.16). Two-phonon processes that scatter the dimer libration results in a dimer dephasing rate given by Eqs. (4.18)–(4.20). The functional form of this theoretical temperature dependence is apparently not exponentially activated. We thus conclude that one-phonon processes dominate in scattering the dimer libration in these systems.

In theory, our results [Eqs. (4.15) and (4.16)] indicate that one-phonon processes that scatter the dimer libration should result in a tetraexponential temperature activation of the dephasing rate. Since a single exponential was observed, it is likely that scattering to only one libration or near degenerate librations occurs. It also indicates that scattering to either the ground or excited state libration dominates. Precedent for this is provided by the system of pentacene monomers in benzoic acid,⁴¹ where ground state scattering dominates at low temperatures. These conditions would collapse the theoretical tetraexponential temperature activation [Eqs. (4.15)–(4.16)] to the experimentally observed single exponential.

With these simplifications of Eqs. (4.15) and (4.16), and if we make the reasonable assumption of coupling to only acoustic phonons at the temperatures involved in the experiments, quantitative values for the phonon coupling constants can be determined. If ground state scattering dominates, Eq. (4.16d) gives at low temperature

$$\left(\frac{1}{T'_2}\right)_n = \frac{9\pi}{\hbar} |\bar{H}_\lambda|^2 \left(\frac{\Omega_\lambda}{\omega_D}\right)^3 e^{-\beta\hbar\Omega_\lambda}, \quad (5.1)$$

where Ω_λ is the ground state librational frequency. If excited state scattering dominates, Eq. (4.16d) gives at low temperatures

$$\left(\frac{1}{T'_2}\right)_n = \frac{9\pi}{\hbar} |\bar{Q}_{n\lambda} + \bar{H}_\lambda|^2 \left(\frac{\Omega_{n\lambda}}{\omega_D}\right)^3 e^{-\beta\hbar\Omega_{n\lambda}}, \quad (5.2)$$

where $\Omega_{n\lambda}$ is the excited state frequency.

For illustrative purposes, let us consider ground state scattering. This would permit the determination of $|\bar{H}_\lambda|^2$. (With excited state scattering, $|\bar{Q}_{n\lambda} + \bar{H}_\lambda|^2$ would be determined.) Fayer and co-workers^{16b} were able to fit their data with an equation of the form (in their notation)

$$\frac{1}{T'_2} = \frac{1}{T'_2(\infty)} e^{-\Delta E/kT}. \quad (5.3)$$

Comparison of Eq. (5.1) with Eq. (5.3) allows the following identifications:

$$\Delta E = \hbar\Omega_g, \quad (5.4a)$$

$$\frac{1}{T'_2(\infty)} = \frac{9\pi}{\hbar} |\bar{H}_\lambda|^2 \left(\frac{\Omega_\lambda}{\omega_D}\right)^3. \quad (5.4b)$$

The fitted values of ΔE and $1/T'_2(\infty)$ for the pentacene dimers and tetracene dimers are presented in Ref. 16(b). The Debye energy ($\hbar\omega_D$) for *p*-terphenyl can be estimated from low temperature spectroscopic data to be roughly 80 cm⁻¹. This, along with Eqs. (5.4a) and (5.4b), permits the quantitative determination of $|\bar{H}_\lambda|^2$ (or $|\bar{Q}_{n\lambda} + \bar{H}_\lambda|^2$ for excited state scattering) for the dimer states studied in Ref. 16(b). The results are summarized in Table I.

We note that coherence transfer between the librationless and librational hot transition may also result in a single exponential temperature behavior. If this were the case, the dephasing rate would then be given by Eq. (3.7d).

These results on pentacene and tetracene dimers in *p*-terphenyl are in contrast to the results obtained by Morsink and Wiersma¹⁷ in the system of naphthalene-*h*₈ dimers in naphthalene-*d*₈. They suggested the dephasing mechanism in this system involves phonon-induced scattering between delocalized dimer states. This is not surprising since dimers which are isotopically different from the host have their librations amalgamated into the host optical phonon bands. Pseudolocal modes are thus precluded from dephasing the dimer transition.

TABLE I. Calculated libron-phonon coupling constants ($|\bar{H}_\lambda|^2$) for pentacene dimers and tetracene dimers studied in Ref. 16b. See the text.

Dimer peak ^a	$ \bar{H}_\lambda ^2$ (cm ⁻¹) ^b
PD ₁	2.40
PD ₂	1.58
PD ₃	0.87
TD ₁	8.73
TD ₂	3.26

^a Notation from Ref. 16(b).

^b Taking $\hbar\omega_D = 80$ cm⁻¹.

It would be useful to also analyze the data of Morsink and Wiersma¹⁷ with our theory. The dimer splitting for the *AA* naphthalene-*h*₈ dimers is known to be 17 cm⁻¹.⁴³ Morsink and Wiersma studied the temperature dependent dephasing rate of the $|0\rangle \leftrightarrow |1\rangle$ dimer transition from 1.5–3.75 K (which is in the low temperature limit, i.e., $kT \ll \hbar\omega_s$) and observed an exponential temperature activation of the dephasing rate. Since the observed activation energy of 14 ± 3 cm⁻¹¹⁷ corresponded closely to the 17 cm⁻¹ dimer splitting, they postulated that the dephasing is due to scattering between delocalized dimer states.

Our theory specifies two contributions to the dephasing resulting from scattering between delocalized dimer states: one from linear coupling [Eqs. (4.6) and (4.8)] and one from quadratic coupling [Eqs. (4.11) and (4.12)]. It is convenient at this point to again assume coupling to only acoustic phonons. This is very reasonable since optical phonons in naphthalene are greater than 17 cm⁻¹ in energy.⁴² Using a Debye density of phonon states, we arrived at the following low temperature ($kT \ll \hbar\omega_s$) expression for the dephasing rate due to linear coupling

$$\left(\frac{1}{T'_2}\right)_1 = \frac{9\pi}{\hbar} \bar{F}^2 \left(\frac{\omega_s}{\omega_D}\right)^3 e^{-\beta\hbar\omega_s}, \quad (4.6a)$$

while the corresponding expression arising from quadratic coupling is given by

$$\left(\frac{1}{T'_2}\right)_1 = 486\pi \bar{D}^2 \omega_D \left(\frac{T}{T_D}\right)^7 \int_0^{T_D/T} dx \frac{x^3(x_s - x)^3}{(e^x - 1)(e^{x_s - x} - 1)}, \quad (4.12a)$$

where $x = \beta\hbar\omega$ and $x_s = \beta\hbar\omega_s$.

It is immediately obvious from Eq. (4.16a) that the linear coupling contribution to the temperature-dependent dephasing rate is in the form of an exponential activation, with the dimer splitting as the activation energy. This is consistent with the 14 ± 3 cm⁻¹ activation energy observed by Morsink and Wiersma.¹⁷ However, the functional form for the temperature dependence of the dephasing rate resulting from quadratic coupling is apparently not an exponential one, as shown in Eq. (4.12a). Thus in the system of naphthalene-*h*₈ dimers in naphthalene-*d*₈, the phonon scattering process between the delocalized dimer states is dominated by linear coupling.

In addition, it was demonstrated that in the specific case of scattering between delocalized dimer states induced by linear excitation-phonon coupling, our perturbation result is exact,²⁵ i.e., Eq. (4.6a) provides an exact description of the low temperature dephasing dynamics of naphthalene-*h*₈ dimers in naphthalene-*d*₈.

We also point out that Morsink and Wiersma were able to fit their data by assuming the following form for the dephasing rate (written in their notation):

$$\frac{1}{T_2(T)} = \frac{1}{T_2(0)} + \frac{1}{\Gamma(0)} e^{-E/kT}, \quad (5.5)$$

where $T_2(0)$ was taken as the low temperature (1.5 K) dephasing time of 50 ns, $E = 14 \pm 3$ cm⁻¹, and $\Gamma(0) = 100$

ps. Comparison of Eqs. (4.6a) and (2.18) with (5.5) lead us to interpret $1/T_2(0)$ as

$$\frac{1}{T_2(0)} = \frac{1}{2\tau_1} + \left(\frac{1}{T_2^*}\right)_1, \quad (5.6)$$

where $(1/T_2^*)_1$ is the adiabatic pure dephasing contribution. If we make the reasonable assumption that $(1/T_2^*)_1 \rightarrow 0$ as $T \rightarrow 0$, this would indicate a low temperature lifetime of approximately 25 ns for the lower delocalized dimer state.

A further comparison of Eqs. (4.6a) and (5.5) allows us to make the identification

$$\frac{1}{\Gamma(0)} e^{-E/kT} = \frac{9\pi}{\hbar} \bar{F}^2 \left(\frac{\omega_s}{\omega_D}\right)^3 e^{-\beta\hbar\omega_s}. \quad (5.7)$$

The above contribution to $(1/T_2')_1$ also vanishes as $T \rightarrow 0$. This would indicate that $T_2 = 2\tau$ as $T \rightarrow 0$. Morsink and Wiersma argued that $T_2 \neq 2\tau$ by comparing the observed 50 ns T_2 value for the dimer with the 75 ns value for T_2 for the monomer at the same low temperature (1.5 K). This is not a valid comparison. There is no obvious relationship between the lifetime of a dimer and its constituent monomers.^{16(c)} An experimental measurement of the low temperature lifetime of the lower dimer state is needed.

Equation (5.7) also indicates the following relationship:

$$\frac{1}{\Gamma(0)} = \frac{9\pi}{\hbar} \bar{F}^2 \left(\frac{\omega_s}{\omega_D}\right)^3. \quad (5.8)$$

Using the experimentally determined value of 78.5 cm^{-1} for $\hbar\omega_D$,⁴⁴ we are able to calculate a value for the linear excitation-phonon coupling constant: $\bar{F}^2 = 0.19 \text{ cm}^{-1}$.

Finally, the lifetime of state $|2\rangle$ arising from phonon scattering between dimer states can be calculated from Eq. (4.8). Using a Debye density of phonon states yields the following expression for the lifetime (T_1) of $|2\rangle$:

$$\frac{1}{T_1} = \frac{18\pi}{\hbar} \bar{F}^2 \left(\frac{\omega_s}{\omega_D}\right)^3. \quad (5.9)$$

Comparison with Eq. (5.8) gives a lifetime of 50 ps for $|2\rangle$.

To summarize, we have introduced a model for dimer dephasing in which the interactions between the dimer and bath states are clearly delineated in a quantum mechanically microscopic sense. We have included both local and nonlocal, linear and quadratic excitation-phonon coupling and have analyzed the model using the quantum mechanical version of Redfield theory. In addition, we have removed the dimer librations from the bath states and treated them on the same level as the dimer electronic states.

Nonadiabatic dephasing is caused by phonon-induced scattering between dimer electronic states and scattering to dimer librations in the ground and excited states. Scattering between delocalized dimer states, induced by one-phonon processes, exhibit a low temperature exponential activation of the dephasing rate $(1/T_2')_1$ [Eq. (4.4a)], and a temperature independent dephasing rate $(1/T_2')_2$ [Eq. (4.4b)]. The activation energy is given by the dimer splitting. The temperature dependence due to two-phonon processes is given in Eqs. (4.11a) and (4.11b) and is not easily specified. Uncorrelated phonon scattering to dimer librations, induced by

one-phonon processes, formally results in a low temperature tetraexponential activation of the dephasing rate with activation energies determined by the four librational energies [Eq. (4.15d)]. However, the observed temperature dependence can vary from a tetraexponential to a single exponential depending on the librational frequencies and the occupation of phonon states at these frequencies and experimental temperatures. Also, scattering to one or more librations in the ground or excited state may dominate. Contributions to the dephasing rate from two-phonon processes are expressed in Eq. (4.18) and are again not easily specified.

We also found that the adiabatic pure dephasing of the dimer transitions exhibits the analogous functional form of the temperature dependence as that of the monomer. Linear excitation-phonon coupling to harmonic phonons does not dephase the transition. Linear coupling to anharmonic phonons produces a weak temperature dependence of the linewidth [Eq. (4.23)]. Quadratic excitation-phonon coupling to acoustic phonons results in a low temperature T^7 temperature dependence of the pure dephasing [Eq. (4.26)], while quadratic coupling to an optical phonon branch with a sharply peaked phonon density of states at ω gives rise to an exponential activation of the adiabatic dephasing rate with the activation energy determined by ω [Eq. (4.27)]. In general, however, the exact form of the pure dephasing is dependent on the density of states (and hence dispersion) of the optical phonon branch. For example, the often used semicircular density of phonon states yields a modified exponential temperature activation given in Eq. (4.29).

VI. CONCLUDING REMARKS

We remark that our treatment is strictly applicable only in the limit of weak excitation-phonon coupling. In the case of strong coupling, Redfield theory (which is accurate to second order in the perturbation) becomes inappropriate and other methods must be used. Many authors have, in the case of linear excitation-phonon coupling and in the context of excitation transfer, resorted to using a canonical transformation to renormalize the Hamiltonian and minimize the perturbation.²⁰ Similar transformations exist for quadratic coupling.²² However, it can be shown that these transformations to date are not sufficient to minimize the perturbation.⁴⁵

Recently, Skinner *et al.*⁴⁶ and Osad'ko⁴⁷ were able to solve the monomer dephasing problem using a nonperturbative approach, thus making their results applicable to all strengths of the excitation-phonon coupling. Skinner *et al.* were then able to quantitatively fit existing monomer dephasing experimental data with their theoretical expressions which prior weak coupling theories were only able to fit using unphysical parameters.⁴⁶

However, a similar nonperturbative approach to the dimer dephasing problem has not appeared. Thus, though our model is strictly applicable and quantitative only in the weak coupling limit, we point out that it is able to correctly identify the dephasing mechanism operative in the system of interest. More importantly, our model affords a physical picture to the dephasing dynamics. Our results provide the rela-

relationship between the microscopic coupling and the dephasing pathway and spectroscopic observations.

Finally, we point out that since the dimer pure dephasing is analogous in form to the monomer pure dephasing, the nonperturbative results of Skinner *et al.*⁴⁶ may be used to describe the dimer pure dephasing in the regime of interme-

diates to strong excitation-phonon coupling.

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APPENDIX A

The following phonon correlation functions were used to derive the bath correlation functions:

$$\langle b_\alpha(\tau)b_{\alpha'}^\dagger \rangle = \delta_{\alpha\alpha'}(\bar{n}_\alpha + 1)e^{-i\omega_\alpha\tau - \Gamma_\alpha|\tau|}, \quad (\text{A1})$$

$$\langle b_{\alpha'}^\dagger(\tau)b_{\alpha'} \rangle = \delta_{\alpha\alpha'}\bar{n}_{\alpha'}e^{i\omega_{\alpha'}\tau - \Gamma_{\alpha'}|\tau|}, \quad (\text{A2})$$

$$\begin{aligned} \langle (b_\alpha b_{\alpha'}) (\tau) b_s^\dagger b_{s'}^\dagger \rangle &= (1 - \delta_{\alpha\alpha'}) (\delta_{\alpha s} \delta_{\alpha' s'} + \delta_{\alpha s'} \delta_{\alpha' s}) (\bar{n}_{\alpha'} + 1) (\bar{n}_\alpha + 1) e^{-i(\omega_\alpha + \omega_{\alpha'})\tau - (\Gamma_\alpha + \Gamma_{\alpha'})|\tau|} \\ &\quad + 2\delta_{\alpha\alpha'} \delta_{ss'} \delta_{\alpha s} (\bar{n}_\alpha + 1)^2 e^{-2[i\omega_\alpha\tau + \Gamma_\alpha|\tau|]}, \end{aligned} \quad (\text{A3})$$

$$\langle (b_{\alpha'}^\dagger b_\alpha^\dagger) (\tau) b_s b_{s'} \rangle = (1 - \delta_{\alpha\alpha'}) (\delta_{\alpha s} \delta_{\alpha' s'} + \delta_{\alpha s'} \delta_{\alpha' s}) \bar{n}_\alpha \bar{n}_{\alpha'} e^{i(\omega_\alpha + \omega_{\alpha'})\tau - (\Gamma_\alpha + \Gamma_{\alpha'})|\tau|} + 2\delta_{\alpha\alpha'} \delta_{\alpha s} \delta_{\alpha' s'} \bar{n}_\alpha^2 e^{2[i\omega_\alpha\tau - \Gamma_\alpha|\tau|]}, \quad (\text{A4})$$

$$\begin{aligned} \langle (b_\alpha b_{\alpha'}^\dagger) (\tau) b_s^\dagger b_{s'} \rangle &= \delta_{\alpha\alpha'} \delta_{ss'} \{ \delta_{\alpha s} \bar{n}_\alpha (\bar{n}_\alpha + 1) (1 + e^{-2\Gamma_\alpha|\tau|}) + (1 - \delta_{\alpha s}) \bar{n}_s (\bar{n}_\alpha + 1) \} \\ &\quad + (1 - \delta_{\alpha\alpha'}) \delta_{\alpha s} \delta_{\alpha' s'} \bar{n}_{\alpha'} (\bar{n}_\alpha + 1) e^{i(\omega_{\alpha'} - \omega_\alpha)\tau - (\Gamma_\alpha + \Gamma_{\alpha'})|\tau|}, \end{aligned} \quad (\text{A5})$$

$$\begin{aligned} \langle (b_\alpha b_{\alpha'}^\dagger) (\tau) b_s b_{s'}^\dagger \rangle &= (1 - \delta_{\alpha\alpha'}) \delta_{\alpha s} \delta_{\alpha' s'} \bar{n}_{\alpha'} (\bar{n}_\alpha + 1) e^{i(\omega_{\alpha'} - \omega_\alpha)\tau - (\Gamma_\alpha + \Gamma_{\alpha'})|\tau|} \\ &\quad + \delta_{\alpha\alpha'} \delta_{ss'} \{ (1 - \delta_{\alpha s}) (\bar{n}_\alpha + 1) (\bar{n}_s + 1) + \delta_{\alpha s} [(\bar{n}_\alpha + 1)^2 + \bar{n}_\alpha (\bar{n}_\alpha + 1) e^{-2\Gamma_\alpha|\tau|}] \}, \end{aligned} \quad (\text{A6})$$

$$\begin{aligned} \langle (b_{\alpha'}^\dagger b_\alpha^\dagger) (\tau) b_s b_{s'}^\dagger \rangle &= \delta_{\alpha\alpha'} \delta_{ss'} [\delta_{\alpha s} \bar{n}_\alpha (\bar{n}_\alpha + 1) (1 + e^{-2\Gamma_\alpha|\tau|}) + (1 - \delta_{\alpha s}) \bar{n}_\alpha (\bar{n}_s + 1)] \\ &\quad + (1 - \delta_{\alpha\alpha'}) \delta_{\alpha s} \delta_{\alpha' s'} \bar{n}_{\alpha'} (\bar{n}_\alpha + 1) e^{i(\omega_\alpha - \omega_{\alpha'})\tau - (\Gamma_\alpha + \Gamma_{\alpha'})|\tau|}, \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} \langle (b_{\alpha'}^\dagger b_\alpha^\dagger) (\tau) b_s^\dagger b_{s'} \rangle &= (1 - \delta_{\alpha\alpha'}) \delta_{\alpha s} \delta_{\alpha' s'} \bar{n}_{\alpha'} (\bar{n}_\alpha + 1) e^{i(\omega_\alpha - \omega_{\alpha'})\tau - (\Gamma_\alpha + \Gamma_{\alpha'})|\tau|} + \delta_{\alpha\alpha'} \{ (1 - \delta_{\alpha s}) \delta_{ss'} \bar{n}_\alpha \bar{n}_s \\ &\quad + \delta_{\alpha s} \delta_{ss'} [\bar{n}_\alpha^2 + \bar{n}_\alpha (\bar{n}_\alpha + 1) e^{-2\Gamma_\alpha|\tau|}] \}. \end{aligned} \quad (\text{A8})$$

In addition, the following relationship⁴⁸ was used:

$$\overline{n_\alpha n_\alpha} = \bar{n}_\alpha (1 + 2\bar{n}_\alpha). \quad (\text{A9})$$

Phonon anharmonicities are adequately accounted for by the damping constant Γ_α for the α mode.^{29,35}

APPENDIX B

In this Appendix we derive the frequency dependence for the excitation-phonon coupling constants. First, we define the following:

$$G_{n\alpha} = 1/(N)^{1/2} \bar{G}_{n\alpha}, \quad (\text{B1a})$$

$$P_\alpha = 1/(N)^{1/2} \bar{P}_\alpha, \quad (\text{B1b})$$

$$K_{n\alpha\alpha'} = (1/N) \bar{K}_{n\alpha\alpha'}, \quad (\text{B1c})$$

$$W_{\alpha\alpha'} = (1/N) \bar{W}_{\alpha\alpha'}, \quad (\text{B1d})$$

where N is the number of unit cells in the crystal.

For the constituent monomers, the following forms have been shown to be valid for long wavelength phonons⁴⁹:

$$\bar{G}_{n\alpha} = (\hbar\omega_\alpha \bar{G}_n)^{1/2}, \quad (\text{B2a})$$

$$\bar{P}_\alpha = (\hbar\omega_\alpha \bar{P})^{1/2}, \quad (\text{B2b})$$

$$\bar{K}_{n\alpha\alpha'} = \hbar(\omega_\alpha \omega_{\alpha'})^{1/2} \bar{K}_n, \quad (\text{B2c})$$

$$\bar{W}_{\alpha\alpha'} = \hbar(\omega_\alpha \omega_{\alpha'})^{1/2} \bar{W}, \quad (\text{B2d})$$

where the parameters \bar{G}_n , \bar{P} , \bar{K}_n , and \bar{W} are assumed to be slowly varying functions of frequency. Using Eqs. (B1) and (B2) we arrive at the following forms for the dimer linear

and quadratic excitation-phonon coupling constants:

$$L_{n\alpha} = L_n(\omega_\alpha) = 1/(N)^{1/2} (\hbar\omega_\alpha)^{1/2} \bar{L}_n, \quad (\text{B3a})$$

$$F_\alpha = F(\omega_\alpha) = 1/(N)^{1/2} (\hbar\omega_\alpha)^{1/2} \bar{F}, \quad (\text{B3b})$$

$$Q_{n\alpha\alpha'} = Q_n(\omega_\alpha, \omega_{\alpha'}) = (1/N) \hbar(\omega_\alpha \omega_{\alpha'})^{1/2} \bar{Q}_n, \quad (\text{B3c})$$

$$D_{\alpha\alpha'} = D(\omega_\alpha, \omega_{\alpha'}) = (1/N) \hbar(\omega_\alpha \omega_{\alpha'})^{1/2} \bar{D}, \quad (\text{B3d})$$

where

$$\begin{aligned} \bar{L}_1 &= (\bar{G}_1)^{1/2} \cos^2 \gamma + (\bar{G}_2)^{1/2} \sin^2 \gamma \\ &\quad - (\bar{P})^{1/2} \sin 2\gamma, \end{aligned} \quad (\text{B4a})$$

$$\begin{aligned} \bar{L}_2 &= (\bar{G}_1)^{1/2} \sin^2 \gamma + (\bar{G}_2)^{1/2} \cos^2 \gamma \\ &\quad + (\bar{P})^{1/2} \sin 2\gamma, \end{aligned} \quad (\text{B4b})$$

$$\bar{Q}_1 = 2(\bar{K}_1 \cos^2 \gamma + \bar{K}_2 \sin^2 \gamma - \bar{W} \sin 2\gamma), \quad (\text{B4c})$$

$$\bar{Q}_2 = 2(\bar{K}_1 \sin^2 \gamma + \bar{K}_2 \cos^2 \gamma + \bar{W} \sin 2\gamma), \quad (\text{B4d})$$

$$\bar{F} = \frac{1}{2} [(\bar{G}_1)^{1/2} - (\bar{G}_2)^{1/2}] \sin 2\gamma + (\bar{P})^{1/2} \cos 2\gamma, \quad (\text{B4e})$$

$$\begin{aligned} \bar{D} &= 2 [\frac{1}{2} ((\bar{K}_1)^{1/2} - (\bar{K}_2)^{1/2}) \sin 2\gamma \\ &\quad + (\bar{W})^{1/2} \cos 2\gamma]. \end{aligned} \quad (\text{B4f})$$

In a similar manner, we define

$$Q_{na\lambda} = Q_{n\lambda}(\omega_\alpha) = \sqrt{\frac{\hbar\omega_\alpha}{N}} \bar{Q}_{n\lambda}, \quad (\text{B5a})$$

$$H_{a\lambda} = H_\lambda(\omega_\alpha) = \sqrt{\frac{\hbar\omega_\alpha}{N}} \bar{H}_\lambda. \quad (\text{B5b})$$

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