AIP | The Journal of Chemical Physics

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Citation: J. Chem. Phys. **74**, 686 (1981); doi: 10.1063/1.440827
View online: http://dx.doi.org/10.1063/1.440827
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v74/i1
Published by the American Institute of Physics.

Theoretical studies of relaxation processes in excited state impurity molecules: Application to naphthalene dimers[a)]

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(Received 16 June 1980; accepted 16 September 1980)

We present a theoretical study for the relaxation modes of multilevel impurities embedded in a low temperature matrix. The equations of motion for the relevant macrovariables are derived, and the limits of validity carefully delineated. The theory is applied to triplet excitations of naphthalene dimers; the results provide the relations between the microscopic coupling and relaxation mechanisms and the observed spectroscopic data (phosphorescence, EPR, population relaxation, and energy transfer). Comparison is made with relaxation models developed previously, and the limitations of those are discussed.

I. INTRODUCTION

In recent years, the phenomenon of excitation transfer between molecules in condensed phases has been subject to numerous experimental and theoretical investigations. Among these, the study of electronically excited molecular dimers embedded in a host crystal has been of considerable utility.[1] In particular, low temperature experiments on such systems contain a variety of information about the operative dynamical processes, and its appropriate interpretation provides useful conclusions about the interaction and relaxation properties of excitonic systems.

In 1967, Schwoerer and Wolf observed EPR transitions in isotopically mixed naphthalene crystals; these transitions were due to the excited triplet state of translationally inequivalent h_8 molecules (nearest neighbor).[2] Later, Hutchison and King observed the hyperfine structure of the EPR lines and the electron-nuclear double resonance (ENDOR) of the protons in the naphthalene dimer.[3] Hochstrasser and Zewail measured the ODMR spectrum of a 1, 4-dibromonaphthalene dimer[4] and Zewail and Harris measured the ODMR spectra of 1, 2, 4, 5 tetrachlorobenzene (h_2) dimers in the perdeuterated host crystal.[5] In the latter two systems, the molecules are translationally equivalent. Finally, Botter *et al.* have measured the EPR dephasing time of naphthalene-h_8 dimers at liquid helium temperatures, by making use of spin-echo techniques. They have looked at both translationally inequivalent[6] and translationally equivalent[7] dimers, analyzing their findings in terms of a relaxation model by van't Hof and Schmidt.[8]

According to this model the EPR line broadening originates with thermally activated scattering between the lower and the upper triplet levels. Hence, the experiment indicates that the rate of scattering from the upper to the lower level, Γ, is much smaller than the splitting between the levels, $2J$. Accordingly, Botter *et al.* concluded that the energy transfer between the neighboring sites takes place via coherent tunneling rather than via diffusive hopping. (Alternatively, one can say that the quantum oscillators related to transitions between the lower and the upper dimer orbital state show an oscillatory rather than an overdamped behavior.) In the low temperature limit, where thermally activated scattering is absent, the EPR dephasing can be due to hyperfine-field fluctuations; this has been demonstrated in a more recent experiment by van't Hof and Schmidt.[9]

For an appropriate interpretation of these experiments a general model is needed to cover the various limiting cases: high and low temperature, equivalent and inequivalent molecules, fine and hyperfine interaction, respectively, dominating the EPR broadening. Models developed previously apply only in certain limits. For example, the Haken–Strobl model[10] implies a high temperature approach, and its application to EPR spectra, as proposed by Reineker,[11] leaves hyperfine field fluctuations out of consideration. Zewail and Harris interpreted their experiments on TCB[12] in terms of Kubo–Anderson exchange theory.[13] This is similar in spirit to the model by van't Hof and Schmidt,[8] which was mentioned previously. Recently, Rahman *et al.* have presented a theory for the depolarization of fluorescence in molecular pairs.[14]

In the following we develop a general description for the various relaxation modes (phosphorescence, EPR, energy transfer) of triplet multilevel systems that covers simultaneously the variety of limiting situations. Critical attention is paid to the validity of the underlying approximations and to the relations between different spectral parameters.

In Sec. II we introduce the Hamiltonian and derive the equation of motion for the relevant macrovariables of the system. In Sec. III we classify the various types of relaxation modes and interpret their damping constants in terms of microscopic relaxation mechanisms, on the assumption that the modes are dynamically decoupled. In Sec. IV we consider the coupled mode solutions for optical and EPR transitions, energy transfer, and population relaxation. Finally, in Sec. V we compare with experimental results and discuss previous theoretical models in light of our results.

II. HAMILTONIAN, MICROSCOPIC EQUATIONS OF MOTION, AND COUPLED RATE EQUATIONS

In the present section the Hamiltonian is introduced, the relevant microscopic equations of motion are de-

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[a)] Supported in part by the National Science Foundation Grant CHE 7807515.

[b)] Supported by the Deutsche Forschungs-Gemeinschaft.

0021-9606/81/010686-17$01.00

rived and the coupled rate equations that describe the dynamics of the excitations are set down.

The main issue of this paper is the dynamics of triplet excitations of molecular *dimers* embedded in a host crystal. However, the formalism to be developed applies equally well to other multilevel systems, for instance to monomers, radical pairs, impurity vibronic states, etc. For that reason, and also for the sake of lucidity, we will leave the system under consideration rather unspecified in the beginning, assuming only that:

(i) The energetic coupling between the multilevel system and the reservoir (heat bath) is weak.

(ii) The concentration of the impurity systems in the host is sufficiently small to treat them as statistically independent (this corresponds to a neglect of exciton migration, etc.).

In Sec. II B the general expressions set down in Sec. II A are specified to apply to triplet multilevel systems and Sec. II C is devoted to a discussion of the Hamiltonian and the specific interactions of molecular dimer triplet states.

A. General form of Hamiltonian and relaxation equations

We start the present theory with a Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_{Ex} + \mathcal{H}_B + \delta\mathcal{H} . \tag{1}$$

Here $\mathcal{H}_B$ and $\mathcal{H}_{Ex}$ represent the energy operators of the two subsystems (heat bath and multilevel system, respectively) which are weakly coupled via $\delta\mathcal{H}$. Subsequently, $\mathcal{H}_B$ and $\mathcal{H}_{Ex}$ will be also referred to as host and guest subsystem.

In the occupation number representation the guest Hamiltonian reads

$$\mathcal{H}_{Ex} = \sum_{A,B} \delta_{AB}\,\epsilon_A\,N_{AB} \quad , \tag{2}$$

where $N_{AB} = |A\rangle\langle B|$ represents the quantum transition operator (occupation number operator if $A = B$) from the guest level $B \rightarrow A$. The set $|A\rangle$ is assumed to be complete (i.e., $\sum N_{AA} = 1$) and it is chosen to diagonalize the guest Hamiltonian: $\langle A|\mathcal{H}_{Ex}|B\rangle = \delta_{AB}\epsilon_A$. Accordingly, ϵ_A represents the energy of the guest level A. It is assumed furthermore that ϵ_A represent *dressed* self-energies and this is explained in the following.

In case of dimer excitations the set $\{A\}$ refers to *pair* and not to site states. That is, the *stationary* coupling between the sites is incorporated in $\mathcal{H}_{Ex}$ rather than $\delta\mathcal{H}$. In case of vibronic levels, correspondingly, the stationary interaction between electronic and vibrational degrees of freedom of the molecule is included in $\mathcal{H}_{Ex}$.

The coupling operator $\delta\mathcal{H}$ is of the form

$$\delta\mathcal{H} = \hbar \sum_{A,B} \phi_{AB}\, N_{AB}, \tag{3}$$

where ϕ_{AB} is a quantum operator that depends only on bath degrees of freedom. The hermiticity of $\mathcal{H}$ yields the symmetry relations

$$\phi_{AB} = \phi^{\dagger}_{BA}, \quad N_{AB} = N^{\dagger}_{BA}. \tag{4}$$

We stated that ϵ_A represents (partially) dressed self-energies, which here means that the thermal averages of ϕ_{AB} vanish:

$$\langle \phi_{AB} \rangle_B = 0. \tag{5}$$

$\langle \cdots \rangle_B$ denotes the canonical average with respect to the host $\mathcal{H}_B$. For a given temperature, such a representation of $\delta\mathcal{H}$ is always possible. In fact, for $\langle\phi_{AB}\rangle_B \neq 0$ one could repartition $\mathcal{H}$ according to the replacements $\delta_{AB}\epsilon_A \rightarrow \delta_{AB}\epsilon_A + \langle\phi_{AB}\rangle_B$ and $\phi_{AB} \rightarrow \phi_{AB} - \langle\phi_{AB}\rangle_B$. A subsequent canonical transformation that diagonalizes $\delta_{AB}\epsilon_A + \langle\phi_{AB}\rangle_B$ then yields exactly the form of Eqs. (1)–(5). Hence the dressing of the self-energies corresponds in some sense to the minimization of the coupling operator $\delta\mathcal{H}$. According to this procedure, ϵ_A and ϕ_{AB} depend weakly on temperature. In the following, however, this will be neglected, assuming that the corresponding variances are sufficiently small in the temperature region of interest.

The reservoir operator $\mathcal{H}_B$ (which is left unspecified) corresponds to all subsystems to which the multilevel system might be coupled (e.g., vibrations, phonons, excitons, photons, nuclear spins, etc.). Accordingly, $\delta\mathcal{H}$ causes various phonon assisted dephasing and depopulation processes, optical decays, spin diffusion, spin-lattice relaxation, etc.

The microscopic equations of motion for the dynamic variables N_{KL} of the guest system read

$$\begin{aligned}\dot{N}_{KL} &= (i/\hbar)[H,\ N_{KL}]\\ &= i\omega_{KL}N_{KL} + i\sum_A(\phi_{AK}N_{AL} - \phi_{LA}N_{KA}).\end{aligned} \tag{6}$$

This is obtained by making use of the orthonormality relations

$$N_{AB}N_{CD} = \delta_{BC}\,N_{AD} \ , \tag{7}$$

The terms ω_{KL} that appear on the right-hand side of Eq. (6) are the transition frequencies between the guest levels

$$\omega_{KL} = (\epsilon_K - \epsilon_L)/\hbar. \tag{8}$$

We turn to the macroscopic equations of motion for the (nonequilibrium) multilevel system ensemble averages:

$$N_{KL}(t) = \mathrm{Tr}\{\rho^s(t)\ N_{LK}\} . \tag{9}$$

Here, $\rho^s(t)$ is the nonequilibrium density operator ("*S*": Schrödinger picture) and $\mathrm{Tr} = \mathrm{Tr}_{Ex}\mathrm{Tr}_B$ indicates the complete trace. The expectation values $N_{LK}(t)$ are identical to the elements $\rho^{Ex}_{KL}(t)$ of the reduced density matrix

$$\rho^{Ex}(t) = \mathrm{Tr}_B\,\rho^s(t), \tag{10}$$

which can be represented as $\rho^{Ex}(t) = \sum_{AB}\rho^{Ex}_{AB}(t)N_{AB}$.

From the beginning it was assumed that the energy exchange between host and guest system is slow and that the reservoir has a much larger heat capacity than the guest subsystem. Under such circumstances the host temperature can be approximated as constant. Consequently, the freely relaxing guest system can be described by means of a Langevin matrix equation. Accordingly, $N_{LK}(t)$ is given in terms of equilibrium time correlation functions between the fluctuating forces ϕ, Eq. (3), of the reservoir. When the corresponding frequency spectra are sufficiently smooth [in comparison to those of $N_{LK}(\omega)$] memory effects can be neglected. This yields the Redfield coupled rate equations[15]

$$\dot{N}_{LK}(t)+i\omega_{KL}(t)+\sum_{MN} R_{KLMN}\,N_{NM}(t)=0\ . \tag{11}$$

The relaxation matrix R reads

$$R_{KLMN}=\delta_{LN}\sum_{C} r_{CKCM}(\omega_{MC})+\delta_{KM}\sum_{C} r^{*}_{CLCN}(\omega_{NC}) - r_{LNKM}(\omega_{MK})-r^{*}_{KMLN}(\omega_{NL}), \tag{11a}$$

and the complex rate constants $r(\Delta\omega)$ are given in terms of (Laplace-transformed) coupling correlation functions.

$$r_{ABCD}(\Delta\omega)=\gamma_{ABCD}(\Delta\omega)+id_{ABCD}(\Delta\omega), \tag{12a}$$

$$\gamma_{ABCD}(\Delta\omega)=\frac{1}{2}\int_{-\infty}^{+\infty} dt\ e^{i\Delta\omega t}\,\langle\phi^{+}_{AB}(t)\phi_{CD}(0)\rangle_{B}, \tag{12b}$$

$$d_{ABCD}(\Delta\omega)=\mathrm{P}\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\,\frac{\gamma_{ABCD}(\omega)}{\Delta\omega-\omega}\ . \tag{12c}$$

The argument $\Delta\omega$ represents the mismatch frequency of the specific relaxation mechanism in question, and P denotes the principal value.

The averages $N_{LK}(t)$ can be considered as classical polarizations, which might be linearly coupled to external driving fields $F_{KL}(t)$. An inhomogeneity, $\sum_{MN} N_{NM}(t)F_{MN}(t)$, has to be added to the right-hand side of Eq. (11) to describe such situations.

B. Application to triplet multilevel systems

In Sec. II B we have set down the general form of the Hamiltonian and the rate equations for the nonequilibrium averages $N_{LK}(t)$ that characterize the macrostate of a (weakly coupled) multilevel impurity. Here, this will be applied specifically to triplet impurity systems (i.e., vibronic or dimer *orbital* doublets).

Figure 1 shows a schematic energy level diagram of the reference system. The level subgroups + and − belong to different exciton orbital states, which are split into three spin-sublevels $\alpha=X$, Y, and Z.

In case of dimers the states $|+,\alpha\rangle$, $|-,\alpha\rangle$ represent eigenstates of the coupled Hamiltonian:

$$\mathcal{H}_{Ex}=\mathcal{H}_{A}+\mathcal{H}_{B}+J_{AB}\ .$$

Here, $\mathcal{H}_A$ and $\mathcal{H}_B$, respectively, are the dressed energy operators of the molecules A and B, and J_{AB} is their stationary exchange interaction (a more detailed discussion on the stationary dimer Hamiltonian is given in Sec. II C). In case of monomers the upper orbital triplet corresponds to a nearby vibronic level (e.g., as in the pseudo Jahn–Teller effect).

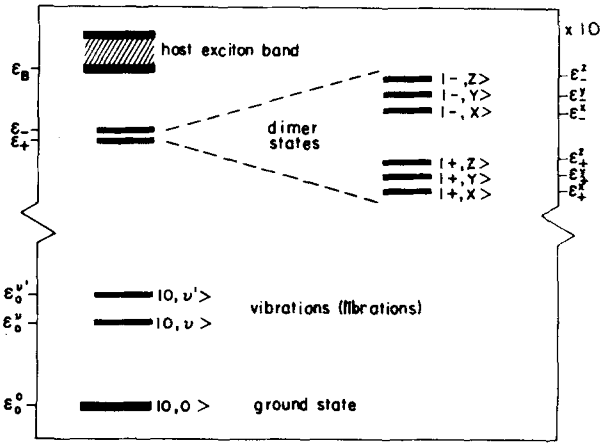

FIG. 1. Schematic energy level diagram. The triplet manifold ϵ_+, ϵ_- may represent dimer states or vibronic monomer states.

For simplicity, we shall assume that there are no further guest vibronic levels of relevance in the temperature region of interest. The interaction of the triplets + and − with the host exciton band will be included, however, at least in some cases.

According to Fig. 1 the quantum number a of the guest state $|a,\ \alpha\rangle$ refers to electronic orbitals [$a=0$: electronic ground state S_0; $a=+,\ -$: lowest energy (vibronic or dimer) triplet states T_0]. The second index α denotes the spin state if $a=\pm$, and the vibrational state of the monomer/dimer if $a=0$. Specific spin quantum numbers are denoted by X, Y, Z, and vibrational states by v, v', ...

We give a brief comment on the energy separations. As a rough rule of thumb we assume that the (dimer) spin sublevels are split by ~ 0.1 cm^{-1}. (~ 3 GHz): this separation is about one order of magnitude smaller than the spacing between the orbital levels $\epsilon_- - \epsilon_+ \approx 1$–$3\ \mathrm{cm}^{-1}$. The guest levels depicted in Fig. 1 are assumed to be well trapped at low temperatures; i.e., $\epsilon_B - \epsilon_- \approx 10$–$20\ \mathrm{cm}^{-1}$. Detrapping processes can be considered as insignificant, therefore, at liquid He temperatures. Experimental examples of such systems are naphthalene $h-8$ dimers in naphthalene $d-8$ host crystals[7] or PBQ$-h_4$ in a PBQ$-d_4$ host (vibronic monomer doublet).[16]

Proceeding from Eq. (11) the dynamics of the triplet manifold is approximately described in terms of the solutions of the eigenvalue problem defined there. The corresponding secular matrix reads

$$L_{KLMN}=\delta_{KM}\,\delta_{LN}\,\omega_{LK}-iR_{KLMN}. \tag{13}$$

[In Eq. (13) it is the *pairs* of quantum numbers KL and MN that denote the matrix elements. In Eq. (14) an individual matrix index is specified by the quantum number quartet $\binom{\kappa\lambda}{kl}$.] The matrix **L** is subsequently referred to as stochastic evolution matrix (SEM). For the system under consideration it is convenient to specify spin (vibrational) quantum numbers and orbital quantum numbers separately: the index K, for instance, is represented by k, κ (orbital index k, spin index κ). Equation (13) becomes

$$L_{klmn}^{\kappa\lambda\mu\nu} = \delta_{km}\, \delta_{ln}\, \delta_{\kappa\mu}\, \delta_{\lambda\nu}\, \omega_{lk}^{\lambda\kappa} + iR_{klmn}^{\kappa\lambda\mu\nu} \,. \tag{14}$$

Here R is defined in terms of the reservoir equilibrium spectral functions $r_{ABCD} =: r_{abcd}^{\alpha\beta\gamma\delta}$, Eq. (12a), which correlate coupling terms of the type $\phi_{AB} =: \phi_{ab}^{\alpha\beta}$, Eq. (3). The explicit form of the matrix R is given in Eq. (12). The transition frequencies $\omega_{KL} =: \omega_{kl}^{\kappa\lambda}$ represent the energy differences $(\epsilon_k^\kappa - \epsilon_l^\lambda)/h$, according to Eq. (8).

The eigenvalues and eigenvectors of the SEM, which provide the characteristic solution of the coupled rate equations (11), depend of course on the magnitude of the individual frequency and relaxation terms. Until now we have introduced these quantities quite formally, neither specifying their magnitude, nor their physical origin. This will be brought up now, specifically for dimer triplet impurities.

C. Dimer triplet states: Stationary Hamiltonian and dynamic interactions

The stationary Hamiltonian of dimer triplet states $\mathcal{H}_{\mathrm{Ex}}$, Eq. (2), as well as the relevant dynamic interaction operator $\delta\mathcal{H}$, Eq. (3), is usually constructed in the molecular site representation, i.e., from the specific interactions of the individual impurity molecules. We will follow here a similar procedure, starting, however, from the dimer rather than the site representation.

To begin with, we shall assume that the six *eigenstates* of the dressed Hamiltonian can be represented as linear combinations of the six product states $|\tilde{a}, \tilde{\alpha}\rangle = |\tilde{a}\rangle\, |\tilde{\alpha}\rangle$ where $|\tilde{a}\rangle$ $(a = +.\ -)$ denotes the two triplet-type orbital states and $|\tilde{\alpha}\rangle$ $(\alpha = X, Y, Z)$ represents three (ortho-normalized) triplet-spin states. This is of course not strictly valid, since there are, e.g., small admixtures of singlet states (spin–orbit coupling) and of band states. The approximation then is, that such distortions have only a negligible effect on both the stationary Hamiltonian $\mathcal{H}_{\mathrm{Ex}}$ as well as the radiationless relaxation mechanisms caused by $\delta\mathcal{H}$. This is so because of the weak coupling and the comparatively large energy separation between the impurity triplet and the band states/impurity singlet states. The only exception concerns optical (phosphorescence) decay mechanisms, which are mainly due to singlet admixtures to the triplet states (singlet triplet spin-orbit coupling). We will comment on this complication later. Subsequently the factorized basis set $|\tilde{a}, \tilde{\alpha}\rangle$ will be referred to as *dimer* representation. We note that it differs from the *eigenstate* representation $|a, \alpha\rangle$ that diagonalizes the stationary Hamiltonian $\mathcal{H}_{\mathrm{Ex}}$; $|a, \alpha\rangle$ is *not* in general of factorized kind.

Once we have chosen the pair-states of pure triplet-type the Hamiltonians $\mathcal{H}_{\mathrm{Ex}}$ and $\delta\mathcal{H}$ can be partitioned according to

$$\mathcal{H}_{\mathrm{Ex}} = \mathcal{H}_{\mathrm{orbit}} + \mathcal{H}_{\mathrm{spin}} + \mathcal{H}_{\mathrm{Zeeman}} + \mathcal{H}_{\mathrm{HF}}, \tag{15a}$$

$$\delta\mathcal{H} = \delta\mathcal{H}_{\mathrm{orbit}} + \delta\mathcal{H}_{\mathrm{spin}} + \delta\mathcal{H}_{\mathrm{Zeeman}} + \delta\mathcal{H}_{\mathrm{HF}} + \delta\mathcal{H}_{\mathrm{phos}} + \delta\mathcal{H}_{\mathrm{band}} \,. \tag{15b}$$

Except for $\delta\mathcal{H}_{\mathrm{phos}}$ and $\delta\mathcal{H}_{\mathrm{band}}$ the individual terms on the right-hand side correspond to specific invariants formed by the axial vector-operators/vectors S (triplet spin matrices $\mathbf{S}_x$, $\mathbf{S}_y$, $\mathbf{S}_z$), $\mathbf{H}_0$ (external magnetic field), and $\mathbf{I}_i$ (nuclear spin-matrices).

The first term (orbital Hamiltonian) is independent of these pseudovectors

$$\begin{aligned}\mathcal{H}_{\mathrm{orbit}} + \delta\mathcal{H}_{\mathrm{orbit}} = {} & (\tilde{\epsilon}_+ + \delta\tilde{\epsilon}_+)\, \tilde{\mathbf{N}}_{++} + (\tilde{\epsilon}_- + \delta\tilde{\epsilon}_-)\tilde{\mathbf{N}}_{--} \\ & + \delta\tilde{J}\, \tilde{\mathbf{N}}_{+-} + \delta\tilde{J}^\dagger\, \tilde{\mathbf{N}}_{-+} \,.\end{aligned} \tag{16}$$

The elements $\tilde{\epsilon}_+$ and $\delta\tilde{\epsilon}_+$, etc. are stationary and fluctuating terms, respectively, of the energy matrix; e.g., $\langle\delta\tilde{\epsilon}_+\rangle_B = 0$. The former represent constant parameters; the latter depend on phonon, librational, and vibrational coordinates, $\delta\tilde{\epsilon}_+ = \delta\tilde{\epsilon}_+(\{\mathbf{X}, \boldsymbol{\Omega}, \mathbf{Q}\})$, etc. The representation chosen here refers to *dimer* states. This is indicated by the tilde and by the subscripts + and −. This representation is characterized by vanishing stationary transition matrix elements $\tilde{J}$ between the orbitals $|\tilde{+}\rangle$ and $|\tilde{-}\rangle$.

Alternatively, $\mathcal{H}_{\mathrm{orbit}} + \delta\mathcal{H}_{\mathrm{orbit}}$ may be given in the so-called *site* representation:

$$\begin{aligned}\mathcal{H}_{\mathrm{orbit}} + \delta\mathcal{H}_{\mathrm{orbit}} = {} & (\hat{\epsilon}_1 + \delta\hat{\epsilon}_1)\, \hat{\mathbf{N}}_{11} + (\hat{\epsilon}_2 + \delta\hat{\epsilon}_2)\, \hat{\mathbf{N}}_{22} \\ & + (\hat{J} + \delta\hat{J})\, \hat{\mathbf{N}}_{21} + (\hat{J}^\dagger + \delta\hat{J}^\dagger)\hat{\mathbf{N}}_{12},\end{aligned} \tag{17}$$

which is unitarily equivalent to the dimer representation. The site representation can be characterized by the requirement that the diagonal energy difference $|\hat{\epsilon}_1 - \hat{\epsilon}_2|$ be minimal (zero in case of translationally equivalent molecules). Since the spin-dependent stationary exchange interactions between the dimer molecules are usually small, this representation is mostly appropriate to obtain the spin, Zeeman, and hyperfine interaction operators.

The spin Hamiltonian is written as

$$\mathcal{H}_{\mathrm{spin}} + \delta\mathcal{H}_{\mathrm{spin}} = \sum_{a,b=1}^{2} \mathbf{S} \cdot (\hat{\mathbf{F}}_{ab} + \delta\hat{\mathbf{F}}_{ab}) \cdot \mathbf{S}\, \hat{\mathbf{N}}_{ab}; \tag{18}$$

invariants of higher than second order with respect to the spin vector S are neglected. $\hat{\mathbf{F}}_{ab}$ and $\delta\hat{\mathbf{F}}_{ab}$ are the stationary and fluctuating parts, respectively, of the fine structure tensor. Both tensors can be considered as traceless with respect to the spin basis; since S is a triplet spin operator we get $\mathbf{S} \cdot \mathbf{S} = 2$; any finite trace contributions have therefore been included in $\mathcal{H}_{\mathrm{orbit}} + \delta\mathcal{H}_{\mathrm{orbit}}$.

If the molecular exchange interactions are sufficiently weak, the site off-diagonal terms $\hat{\mathbf{F}}_{ab}$ and $\delta\hat{\mathbf{F}}_{ab}$ may be omitted, and the spin Hamiltonian of the pair can be constructed from those of the individual molecules, $\hat{\mathbf{F}}_{aa}$ and $\delta\hat{\mathbf{F}}_{aa}$, $a = 1, 2$. The approach which is usually made use of in the relevant literature[7,11] corresponds to a neglect of $\delta\hat{\mathbf{F}}$, of $\hat{\mathbf{F}}_{ab}$ $(a \neq b)$, and to the assumption that the molecular fine structure tensors $\hat{\mathbf{F}}_{aa}$ $(a = 1, 2)$ are identical in the respective principal axis system of the individual molecules. For translationally equivalent molecules the tensors $\hat{\mathbf{F}}_{11}$ and $\hat{\mathbf{F}}_{22}$ have the same principal axis system; in the inequivalent case are $\hat{\mathbf{F}}_{11}$ and $\hat{\mathbf{F}}_{22}$ related by a corresponding orthogonal transformation.

For details and for numerical examples the reader is referred to previous work, i.e., Refs. 7, 11, and 17–19.

We turn to the Zeeman Hamiltonian. In site representation it is of the form

$$\mathcal{H}_{\mathrm{Zeeman}} + \delta\mathcal{H}_{\mathrm{Zeeman}} = \sum_{b,a=1}^{2} \mathbf{H}_0 \cdot (\hat{\mathbf{G}}_{ab} + \delta\hat{\mathbf{G}}_{ab}) \cdot \mathbf{S}\, \hat{\mathbf{N}}_{ab} \ . \tag{19}$$

Again, the fluctuating contributions, $\delta\hat{G}_{ab} = \delta\hat{G}_{ab}(\{\mathbf{X}, \Omega, \mathbf{Q}\})$, as well as the site off-diagonal terms $\hat{\mathbf{G}}_{ab}(a \neq b)$ might be considered as insignificantly small, while $\hat{\mathbf{G}}_{11}$ and $\hat{\mathbf{G}}_{22}$ differ at least for translationally inequivalent molecules.

Similarly, the hyperfine interaction is written as

$$\mathcal{H}_{\mathrm{HF}} + \delta\mathcal{H}_{\mathrm{HF}} = \sum_{a,b} \mathbf{S} \cdot \sum_{j} \hat{\mathbf{K}}_{ab}^{(j)} \cdot (\langle \mathbf{I}_j \rangle + \delta \mathbf{I}_j)\, \hat{\mathbf{N}}_{ab} \ . \tag{20}$$

Here, $\mathbf{I}_j$ refers to individual nuclear spins. The hyperfine tensors $\hat{\mathbf{K}}_{ab}^{(j)}$ are supposed to be independent of bath degrees of freedom, and once more $\hat{\mathbf{K}}_{ab}^{(j)}$ might be omitted for $a \neq b$. The stationary and fluctuating parts $\mathcal{H}_{\mathrm{HF}}$ and $\delta\mathcal{H}_{\mathrm{HF}}$, respectively, are assumed here to originate with the stationary and fluctuating part of the nuclear spin configuration, $\langle \mathbf{I}_j \rangle$ and $\delta I_j = I_j - \langle I_j \rangle$ (full ensemble average $\langle \cdots \rangle$. According to experimental observations,[9] it can occur that some nuclear spins are locked in specific configurations because of their comparatively strong hyperfine interaction; spins at other sites, however, participate in nuclear magnetic moment redistribution processes, and this motivates the decomposition performed in Eq. (20). However, in agreement with experimental results on monomers,[7,9] it is assumed that $\delta\mathcal{H}_{\mathrm{HF}}$ does *conserve* the total nuclear spin (restriction to nuclear spin flip-flop processes); i.e., $\delta\mathcal{H}_{\mathrm{HF}}$ causes only spectral diffusion (pure dephasing).

According to our approximation that the band excitons of the host are only *dynamically* coupled to $\mathcal{H}_{\mathrm{Ex}}$, the dressed Hamiltonian $\mathcal{H}_{\mathrm{Ex}}$ introduced in Sec. II A is given as the sum $\mathcal{H}_{\mathrm{Ex}} = \mathcal{H}_{\mathrm{orbital}} + \mathcal{H}_{\mathrm{spin}} + \mathcal{H}_{\mathrm{Zeeman}} + \mathcal{H}_{\mathrm{HF}}$. Hence, we are now in a position to comment on the relations between the fluctuating interaction terms ϕ, Eq. (3), and the eigenstates and eigenvectors of $\mathcal{H}_{\mathrm{Ex}}$.

The specific form of the eigenstate representation of $\mathcal{H}_{\mathrm{Ex}}$, which has been made use of in Secs. II A and II B, can have significant consequences for the properties of some of the dimer triplet relaxation modes. This is because the stationary Hamiltonian $\mathcal{H}_{\mathrm{Ex}}$ yields a mixing between triplet spin states and orbital states (subsequently referred to as *intrinsic* spin–orbit coupling), at least for translationally inequivalent sites. That is, the eigenstates are not of factorized type, and in particular it is neither the site nor the dimer representation that provides the eigenstate system of $\mathcal{H}_{\mathrm{Ex}}$.

The *dimer* representation $|\tilde{a}\rangle\,|\tilde{a}\rangle$ [it has been used already in Eq. (16)] is defined here so as to diagonalize the (stationary) Hamiltonian

$$\mathcal{H}_{\mathrm{dimer}} = \mathcal{H}_{\mathrm{orbit}} + \tfrac{1}{2}\,\mathrm{Tr}_{\mathrm{orbit}}(\mathcal{H}_{\mathrm{spin}} + \mathcal{H}_{\mathrm{Zeeman}} + \mathcal{H}_{\mathrm{HF}}). \tag{21}$$

$\mathrm{Tr}_{\mathrm{orbit}}$ indicates the trace over the orbital states, e.g.,

$$\mathrm{Tr}_{\mathrm{orbit}}\, \mathcal{H}_{\mathrm{spin}} = \sum_{a=1}^{2} \mathbf{S} \circ \hat{\mathbf{F}}_{aa} \cdot \mathbf{S} \ .$$

Accordingly, the dimer representation has to be considered as optimal representation of the factorized type; it is the remainder, $\mathcal{H}_{\mathrm{Ex}} - \mathcal{H}_{\mathrm{dimer}}$, that causes the (stationary) intrinsic spin–orbit coupling.

The *eigenstates* of $\mathcal{H}_{\mathrm{Ex}}$ read in general terms

$$|b, \beta\rangle = \sum_{a\alpha} U_{ba}^{\beta\alpha}\, |\tilde{a}\rangle\, |\tilde{\alpha}\rangle \ . \tag{22}$$

U is a 6×6 unitary transformation matrix between the eigenstate and the dimer representation. As already mentioned, this form of the eigenstates can have important consequences concerning some of the relaxation matrix elements ϕ [Eq. (3)] and, consequently, in relation to properties of the corresponding relaxation modes. This can be exemplified on the assumption (adhered to throughout this paper) that hyperfine spin-lattice relaxation processes are absent. As a consequence the relaxation matrix elements are spin-diagonal in the *dimer* representation: $\tilde{\phi}_{ab}^{\alpha\beta} = \delta_{\alpha\beta}\, \tilde{\phi}_{ab}^{\alpha\alpha}$. In eigenstate representation we get, however,

$$\phi_{kl}^{\kappa\lambda} = \sum_{ab\alpha} U_{ka}^{\kappa\alpha}\, \tilde{\phi}_{ab}^{\alpha\alpha}\, U_{lb}^{*\lambda\alpha} \ , \tag{23}$$

and this means that there *can* be weakly allowed transitions between triplet sublevels κ and λ of different type. These transitions result from purely orbital relaxation mechanisms, induced, e.g., by $\delta\mathcal{H}_{\mathrm{orbit}}$ [Eq. (16)]. Similarly the coupling term $\delta\mathcal{H}_{\mathrm{orbit}}$ can induce pure dephasing mechanisms for sublevel transitions and even a coupling of the EPR modes.

Relaxation mechanisms of this kind have been introduced by Reineker to describe the line broadening and also a dynamic coupling of dimer triplet EPR modes.[11] However, one must be aware of the fact that the secular spin dephasing processes, which are caused by the hyperfine interaction $\delta\mathcal{H}_{\mathrm{HF}}$ [Eq. (20)], compete with the former mechanism. Experiments on monomers[9] seem to indicate that the nuclear hyperfine field fluctuations are important and may dominate the phase relaxation of the EPR modes at very low temperatures (see Sec. V). In the final part of Sec. V, we compare these two mechanisms.

We conclude this section by introducting the coupling term between the dimer triplet and the radiation field that causes phosphorescence decay. In dimer representation we write

$$\begin{aligned} \delta\mathcal{H}_{\mathrm{phos}} &= \sum_{a\alpha v} \phi_{a0}^{\alpha v}\, \mathrm{N}_{a0}^{\alpha v} + \mathrm{H.c.}, \\ \phi_{a0}^{\alpha v} &= \sum_{\mathbf{k},s} \sqrt{\frac{2\pi\hbar\omega_{\mathbf{k},s}}{V}}\; \mathbf{e}_{\mathbf{k}s} \cdot \mathbf{p}_{a0}^{\alpha v}\, b_{\mathbf{k},s}^{\dagger} \end{aligned} \tag{24}$$

Here $b_{\mathbf{k}s}^{+}$ is the creation operator for a photon with wave vector $\mathbf{k}$, polarization $\mathbf{e}_{\mathbf{k}s}$, and frequency $\omega_{\mathbf{k}s}$. $\mathbf{p}_{a0}^{\alpha v}$ represents the weakly allowed electric dipole transition element from the eigenstate $|a, \alpha\rangle$ to the electronic ground state $|0, v\rangle$ (vibrational state v); $\mathbf{p}_{a0}^{\alpha v}$ still depends on the positions and orientations of the two dimer molecules.

The finite transition dipoles $\mathbf{p}^{\alpha}_{a0}$ are mainly due to stationary singlet state admixtures in the triplet manifold. This is a consequence of direct spin–orbit coupling, which has been neglected up to this point. The transition dipoles $p^{\alpha v}_{a0}$ introduced here are the correct matrix elements between the mixed states and the electronic ground state rather than the matrix elements, which would be calculated using pure triplets. This does not yield any significant inconsistency in the present theory.

III. THE DECOUPLED RELAXATION MODES

Continuing from Eq. (14) we start the investigation of the relaxation modes that occur for the triplet impurity. From Eq. (14) it is seen that the general problem is quite complex. This is because of the *dynamic* coupling (exchange coupling) of the various macrovariables $N^{\lambda\kappa}_{lk}(t)$, which is caused by the off-diagonal terms of the relaxation matrix. [This dynamic coupling should not be confused with the *stationary* coupling between spin and orbital states, which is induced by the Hamiltonian $\mathcal{H}_{\mathrm{Ex}} - \mathcal{H}_{\mathrm{dimer}}$, Eqs. (15) and (21)].

For the sake of lucidity we begin with the most simple situation, assuming that all off-diagonal terms of the relaxation matrix are negligible. Only in Sec. IV the limitations of this approximation will be shown, and more general expressions for solutions of the coupled rate equations will be derived.

A. Damping constants of the decoupled modes

Neglecting the exchange coupling, the temporal behavior of the macrovariables $N^{\lambda\kappa}_{lk}(t)$ is given by

$$N^{\lambda\kappa}_{lk}(t) = N^{\lambda\kappa}_{lk}(0)\exp[i(\Omega^{\lambda\kappa}_{lk} + i\,\Gamma^{\lambda\kappa}_{lk})\,t]. \tag{25}$$

The transition frequencies Ω and decay rates Γ read

$$\Omega^{\lambda\kappa}_{lk} = -\Omega^{\kappa\lambda}_{kl} = \omega^{\lambda\kappa}_{lk} - \mathrm{Im}R^{\lambda\kappa\lambda\kappa}_{lklk}\,, \tag{26a}$$

$$\Gamma^{\lambda\kappa}_{lk} = \Gamma^{\kappa\lambda}_{kl} = \mathrm{Re}R^{\lambda\kappa\lambda\kappa}_{lklk}\,. \tag{26b}$$

Subsequently, it is assumed that the dynamic frequency shifts in $R^{\kappa\lambda\kappa\lambda}_{klkl}$ are insignificantly small. We emphasize that this is an uncontrolled approximation on which we will comment in Sec. III B.

We proceed with a classification of those modes that involve the impurity triplet state. (This classification also applies to the coupled modes, since there is a one-to-one correspondence between coupled and uncoupled modes).

There are six independent population relaxation modes that describe the equilibration of energy among, and the decay out of, the triplet manifold in terms of $N^{\kappa\kappa}_{kk}(k=1, 2)$. In the present situation in which the dynamic coupling between macrovariables is neglected, the decay rates of the population modes are identical with the lifetimes of the states $|k, \kappa\rangle$. We emphasize, however, that this is not valid for the *coupled* rate equations.

All the other modes of interest describe the relaxation of initially phase-correlated states of the ensemble (dephasing). Since the spectrum of the latter modes is related to absorption and emission line shapes they will be subsequently referred to as transition modes.

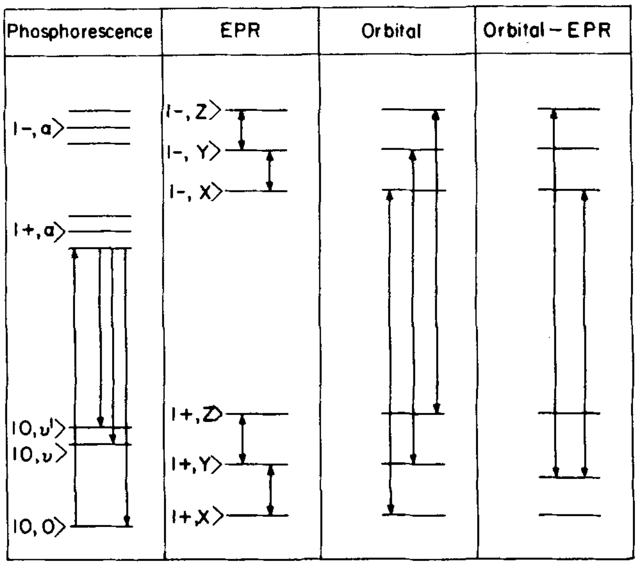

FIG. 2. Schematic sketch of some transition modes. The arrow at the left-hand side indicates optical absorption rather than phosphorescence emission.

There is a large number of phosphorescence modes $N^{\kappa v}_{k0}$ depending on the number of relevant vibrational (librational) states v; at He temperatures the modes related to $N^{0\kappa}_{0k}$ describe the singlet–triplet absorption lines of the impurity. As to the transitions *within* the triplet manifold we distinguish six pairs of EPR modes $|a, \alpha\rangle \leftrightarrow |a, \beta\rangle$ $(a=+, -;\ \alpha \neq \beta = X, Y, Z)$, three pairs of purely orbital transitions $|+, \alpha \leftrightarrow |-, \alpha\rangle$, $(\alpha = X, Y, Z)$, and six pairs of combined orbital EPR transitions $|+, \alpha\rangle \leftrightarrow |-, \beta\rangle$ $(\alpha \neq \beta = X, Y, Z)$. Examples of the relevant transitions are depicted in Fig. 2.

Continuing from Eq. (26), we give more explicit expressions for relaxation constants of the relevant modes. The damping constants of the transition modes can be written in the form

$$\Gamma^{\lambda\kappa}_{lk} = \Gamma_{\mathrm{PD}}\binom{\lambda\kappa}{lk} + \tfrac{1}{2}(\Gamma^{\lambda\lambda}_{ll} + \Gamma^{\kappa\kappa}_{kk}), \tag{27}$$

where $\Gamma^{\lambda\lambda}_{ll}$ and $\Gamma^{\kappa\kappa}_{kk}$ and $\Gamma^{\kappa\kappa}_{kk}$ are the inverse lifetimes of the states $|\,l, \lambda\rangle$ and $|k, \kappa\rangle$, respectively; $\Gamma_{\mathrm{PD}}\binom{\lambda\kappa}{lk}$ is the pure dephasing rate that results from transition frequency fluctuations:

$$\Gamma_{\mathrm{PD}}\binom{\lambda\kappa}{lk} = \frac{1}{2}\int_{-\infty}^{+\infty} dt \langle [\phi^{\lambda\lambda}_{ll}(t) - \phi^{\kappa\kappa}_{kk}(t)] \times [\phi^{\lambda\lambda}_{ll}(0) - \phi^{\kappa\kappa}_{kk}(0)] \rangle_B \tag{28}$$

In case of orbital, spin–orbital, and optical transitions the time dependence of frequency fluctuations, $\phi^{\lambda\lambda}_{ll}(t) - \phi^{\kappa\kappa}_{kk}(t)$, originates mainly with exciton–phonon coupling terms (via the dependence of ϕ on vibrational degrees of freedom and lattice/libration coordinates). The corresponding dephasing rates are expected to be four orders of magnitude larger than those related to the EPR transitions, where the coupling results primarily with fine and hyperfine interactions (see Sec. II D).

TABLE I. Relaxation rates of the decoupled modes.

Type of mode	Macrovariable	Transition frequency	Exemplary decay rate
Population	$\bar{N}^{\kappa\kappa}_{kk}(t)$	0	$\Gamma^{\kappa\kappa}_{--}=\Gamma(-,\kappa\rightarrow+,\kappa)+\sum_v\Gamma(-,\kappa\rightarrow0,v)+\sum_{\nu\neq\kappa}\sum_{\alpha=\pm}\Gamma(-,\kappa\rightarrow a,\nu)+\Gamma(-,\kappa\rightarrow\text{band})$
Optical transition	$\bar{N}^{v\kappa}_{0k}(t)$	$\Omega^{v\kappa}_{0k}$	$\Gamma^{v\kappa}_{0k}=\Gamma_{\text{PD}}\binom{v\kappa}{0k}+\frac{1}{2}\Gamma^{v\kappa}_{kk}+\frac{1}{2}\Gamma^{vv}_{00}$
Spin resonance	$\bar{N}^{\lambda\kappa}_{kk}(t)$	$\Omega^{\lambda\kappa}_{kk}$	$\Gamma^{\lambda\kappa}_{kk}=\Gamma_{\text{PD}}\binom{\lambda\kappa}{kk}+\frac{1}{2}\Gamma^{\kappa\kappa}_{kk}+\frac{1}{2}\Gamma^{\lambda\lambda}_{kk}$
Triplet-orbital	$\bar{N}^{\kappa\kappa}_{lk}(t)$	$\Omega^{\kappa\kappa}_{lk}$	$\Gamma^{\kappa\kappa}_{lk}=\Gamma_{\text{PD}}\binom{\kappa\kappa}{lk}+\frac{1}{2}\Gamma^{\kappa\kappa}_{ll}+\frac{1}{2}\Gamma^{\kappa\kappa}_{kk}$
Triplet spin–orbital transition ($l\neq k$, $\lambda\neq\kappa$)	$\bar{N}^{\lambda\kappa}_{lk}(t)$	$\Omega^{\lambda\kappa}_{lk}$	$\Gamma^{\lambda\kappa}_{lk}=\Gamma_{\text{PD}}\binom{\lambda\kappa}{lk}+\frac{1}{2}\Gamma^{\kappa\kappa}_{kk}+\frac{1}{2}\Gamma^{\lambda\lambda}_{ll}$

We emphasize that the relation established in Eq. (27), between the dephasing rate (left-hand side) the pure dephasing rate and the level lifetimes (right-hand side) applies only in the limit of low impurity concentration: it becomes invalid in the presence of energy migration between different guest subsystems.

The total level decay rates $\Gamma^{\kappa\kappa}_{kk}$, which also contribute to the dephasing of the transition modes, can be expressed as the sum of individual decay constants. (See Table I.)

$$\Gamma^{\kappa\kappa}_{aa}=\Gamma(a,\ \kappa\rightarrow+,\ \kappa)+\sum_v\Gamma(a,\ \kappa\rightarrow0,\ v)$$

$$+\sum_{\nu\neq\kappa}\sum_{a=+,-}\Gamma(a,\ \kappa\rightarrow a,\ \nu)+\Gamma(a,\ \kappa\rightarrow\text{band}),$$

$$\Gamma(+,\ \kappa\rightarrow-,\ \kappa)=\exp[-\beta\hbar\omega^{\kappa\kappa}_{-+}]\Gamma(-,\ \kappa\rightarrow+,\ \kappa). \qquad (29)$$

We have used the notation $\Gamma(a,\ \alpha\rightarrow b,\ \beta)$ to denote individual decay rates (from the initial state $|a,\alpha\rangle$ to the final state $|b,\beta\rangle$):

$$\Gamma(a,\ \alpha\rightarrow b,\ \beta)=\int_{-\infty}^{+\infty}dt\exp[i\omega^{\alpha\beta}_{ab}t]\langle\phi^{\dagger\beta\alpha}_{ba}(t)\,\phi^{\beta\alpha}_{ba}(0)\rangle_B\ . \qquad (30)$$

These rates obey detailed balance relations

$$\Gamma(a,\ \alpha\rightarrow b,\ \beta)=\exp[-\beta\hbar\,\omega^{\alpha\beta}_{ab}]\Gamma(b,\ \beta\rightarrow a,\ \alpha), \qquad (31)$$

and this has been used in Eq. (29) to express $\Gamma(+,\kappa\rightarrow-,\kappa)$ in terms of $\Gamma(-,\kappa\rightarrow+,\kappa)\exp(-\beta\hbar\omega^{\kappa\kappa}_{-+})$. For sufficiently well trapped impurity states (for temperatures sufficiently small with respect to the trap depth), this rate constant dominates $\Gamma^{\kappa\kappa}_{--}$. The second term in Eq. (29) originates with triplet phosphorescence, caused by the photon–exciton coupling Hamiltonian $\delta\mathcal{H}_{\text{phos}}$, Eq. (24). The third terms correspond to sublevel relaxation processes (within the impurity triplet manifold). We have added, finally, the detrapping rates $\Gamma(a,\alpha\rightarrow\text{band})$ from the relevant guest states to the host exciton band. These rates show Arrhenius factors corresponding to the actual activation energies, and they are negligible, therefore, at sufficiently low temperatures.

B. Crucial assumptions and approximations

The expressions derived so far are already subject to various *uncontrolled* approximations on which we would like to comment before we continue the main subject of this article. Some of these approximations are a consequence of the assumption that the relaxation matrix [Eq. (11)] is independent of frequency.

This corresponds, first of all, to the neglect of inhomogeneous relaxation mechanisms. Experimentally and theoretically, it is, however, well known that such an approximation does not necessarily apply. The hyperfine interaction field, for instance, may be different at different impurity sites, as a result of different, comparatively slowly relaxing nuclear spin configurations. Similarly, the exciton–phonon interaction can vary from site to site, because of local defect structure that is often relevant in molecular crystals. Complications like this are well realized in the relevant literature.

Much less attention seems to be paid to the fact that the Markovian approximation, which neglects the explicit frequency dependence of the relaxation matrix, can become invalid for sufficiently low temperatures, i.e., in the extreme quantum limit.

To explain this in more detail we consider any specific relaxation term [Eq. (12b)]. The corresponding spectral function reads

$$\gamma(\omega)=\frac{1}{2}\int_{-\infty}^{+\infty}dt\,e^{i\omega t}\,\langle\phi^{\dagger}(t)\,\phi(0)\rangle_B\geqslant0,$$

where ϕ is the quantum operator for the fluctuations. We introduce the response function, asymmetrized in frequency space:

$$\chi''(\omega)=[\gamma(\omega)-\gamma(-\omega)].$$

This function is real-valued and antisymmetric with respect to the frequency ω.

We make use of the detailed balance relation

$$\gamma(-\omega)=\exp(-\beta\hbar\omega)\gamma(\omega)$$

in order to derive an expression for the slope of γ at frequency zero:

$$\left(\frac{\partial\gamma}{\partial\omega}\right)_{\omega=0}=\tfrac{1}{2}\lim_{\omega\rightarrow0}\frac{[\gamma(\omega)-\gamma(-\omega)]}{\omega}$$

$$=\frac{\hbar\gamma(\omega=0,\ T)}{k_B}=\lim_{\omega\rightarrow0}\frac{\chi''(\omega)}{2\omega}$$

We require that χ'' is a continuously differentiable function of ω at all temperatures, which means that $\gamma(\omega=0, T)$ is at least of order T, as $T\rightarrow 0$. This is in agreement with model calculations,[20] which predict vanishing homogeneous dephasing rates at zero temperature. The positive frequency components of $\gamma(\omega)$, however, remain finite, and low temperature experiments on naphthalene indicate a very strong dependence on ω for $0<\omega<2.5\ \mathrm{cm}^{-1}$.[7,8]

As a consequence, the Markovian limit (where the relaxation kernel is approximated by a frequency independent rate constant) becomes invalid at sufficiently low temperatures, at least for transition modes that are mainly broadened by pure dephasing mechanisms. The corresponding line shapes are then asymmetric with respect to their band centers.

This is not necessarily so for those transition modes that are mainly broadened by population relaxation. In such a case, the Markovian limit remains valid as long as $(\partial\gamma_P/\partial\omega)_{\omega_0}\ll 1$. (mismatch frequency ω_0).

Unfortunately, a further, much more difficult complication occurs in the quantum-mechanical regime. According to Eq. (12c) the relaxation matrix exhibits dynamic frequency shifts. The Kramers–Kronig relations,

$$d(\omega_0)=\mathrm{P}\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\,\frac{\gamma(\omega)}{\omega_0-\omega}\ ,$$

show that the magnitude of the shifts $d(\omega_0)$ depend sensitively on the asymmetry of the spectral functions γ. In the classical regime where $\gamma(\omega)$ is symmetric, $d(\omega_0)$ is rather small, since the relevant mismatch frequencies ω_0 are small in comparison to the spectral widths of the dominant contributions to $\gamma(\omega)$.

At low temperature, however, the negative frequency part of $\gamma(\omega)$ becomes very small compared to its positive frequency part, and $d(\omega_0)$ represents essentially the convolution between $(\omega_0-\omega)^{-1}$ and the positive frequency part of $\gamma(\omega)$.

As to the order of magnitude of the dynamic frequency shifts d, we suppose that the spectral function $\gamma(\omega)$ extends to a frequency region of about τ_c^{-1}; $\omega_0\ll\tau_c^{-1}$. Thus, the order of magnitude of d is very roughly estimated as $\tau_c\int_{-\infty}^{\infty}d\omega\,\gamma(\omega)/2\pi$ and this can even exceed the order of magnitude of the corresponding decay rate. Hence, one must be aware that homogeneous relaxation mechanisms at sufficiently low temperatures may induce dynamic transition frequency shifts as large as the relevant line-broadening parameters.

This might be considered as not too crucial in *well-separated* transition modes, where it just leads to a less important shift of the excitation resonances. We emphasize, however, its significance in terms of the exchange coupling terms between different modes, the magnitude of which depends quadratically on the absolute values of the (complex-valued) off-diagonal relaxation matrix elements.

Because of the slowly decreasing frequency denominator $(\omega_0-\omega)^{-1}$, the disperse shifts $d(\omega_0)$ [Eq. (A10)] collect information from a wide spectral range of the reservoir correlation functions $\gamma(\omega)$. A quantitative inclusion of the dynamic shifts $d(\omega_0)$ would require, therefore, the explicit treatment of the reservoir mode spectra and, furthermore, detailed information about the exciton-bath coupling.

This is, however, beyond the purpose of the present paper, the main emphasis of which is an investigation of the relaxation phenomena in the triplet manifold. Hence, for the sake of simplicity we shall neglect all quantum effects on the relaxation matrix, *except* for the detailed balance relations [Eq. (31)] between the various rate constants. This corresponds to the neglect of the dynamic shifts, or, in terms of Eqs. (12a) and (12b), to the replacement $r_{ABCD}(\omega_0)\rightarrow\gamma_{ABCD}(\omega_0)$.

IV. DYNAMICAL COUPLING OF MODES

The expressions (25)–(31) apply only in certain limits to the relaxation behavior of triplet dimer excitations. Experimental systems are in almost all instances characterized by dynamic coupling of various modes (exchange dephasing, coupled rate equations), and this yields significant alterations of the relaxation dynamics.

The decay rate of the population *mode* $|+,\alpha\rangle$, for instance, agrees, at low temperature with the inverse lifetime of the level $|+,\alpha\rangle$. At higher temperature, however, the excitation is subject to an equilibration between the states $|+,\alpha\rangle$ and $|-,\alpha\rangle$, and the relaxation of the $|+,\alpha\rangle$ mode is characterized by the averaged relaxation rate *out* of the orbital doublet. This rate constant differs significantly from $\Gamma_{++}^{\alpha\alpha}$ [Eq. (26(b)].

Correspondingly, the question arises as to the dynamic coupling of different types of transition modes. The first theoretical models for this so-called exchange coupling have been developed decades ago by Anderson[13a] and Kubo.[13b] In a qualitative way, the phenomenon can be understood in terms of mutually coupled quantum oscillators that drive one another slightly off-resonance. As a consequence, the transition bands can be subject to a mutual attraction in frequency space, and if the coupling is strong enough, it can happen that the two bands coalesce at a single transition frequency. In the case of conjugate modes, $A\rightarrow B$ and $B\rightarrow A$, this occurs at zero frequency, which means that the corresponding quantum oscillators show an over-damped behavior.

In general, the dynamics of multilevel systems provide a difficult problem, because of the high dimension of the related secular matrix. In the present case, however, two major simplifications occur that allow a considerable reduction of the dimensionality of the problem. The first is due to the large transition frequencies between the electronic ground state and the triplet exciton states. As a consequence, the optical transition modes are perfectly decoupled from the population relaxation modes and from the triplet–triplet transition modes as well. The second simplification results from the irrelevance of the radiationless sublevel transitions $|a,\alpha\rangle\leftrightarrow|a,\beta\rangle$ as to a possible dynamic coupling between different sublevel (EPR) modes. Although such transitions are weakly allowed because of intrinsic spin–or-

TABLE II. Mutually coupled macrovariables. It is assumed that the intrinsic spin–orbit relaxation (ISOR) that results from fine structure fluctuations is insignificant. For naphthalene dimers, this assumption is not valid concerning the population relaxation variables $N^{\alpha\alpha}_{++}$ and $N^{\alpha\alpha}_{--}$ ($\alpha = X, Y, Z$) (cf. Appendix A).

Type of mode	Mutually coupled macrovariables	Spin quantum numbers
(1) Optical	$N^{0\kappa}_{0+}$ $N^{0\kappa}_{0-}$	$\kappa = X, Y, Z$
(2) Spin diagonal	$N^{\kappa\kappa}_{++}$, $N^{\kappa\kappa}_{+-}$, $N^{\kappa\kappa}_{-+}$, $N^{\kappa\kappa}_{--}$	$\kappa = X, Y, Z$
(3) Spin transition	$N^{\lambda\kappa}_{++}$, $N^{\lambda\kappa}_{+-}$, $N^{\lambda\kappa}_{-+}$, $N^{\lambda\kappa}_{--}$	$(\lambda, \kappa) = (X, Y)$; (X, Z); (Y, Z); (Y, X); (Z, X); (Z, Y).

bit coupling (see Sec. IIC), we shall anticipate here that they yield only negligible relaxation matrix elements off-diagonal with respect to sublevel quantum numbers. That is, we approximate

$$R^{\kappa\lambda\mu\nu}_{klmn} = \delta_{\kappa\mu}\,\delta_{\lambda\nu}\,R^{\kappa\lambda\kappa\lambda}_{klmn}\ .$$

This relation holds exactly if $\phi^{\kappa\lambda}_{km} = \delta_{\kappa\lambda}\,\phi^{\lambda\lambda}_{km}$, etc. [cf. Eqs. (11) and (12)]; with the exception of the phosphorescence decay rates, it yields a satisfactory description of the various modes, at least in certain systems (including, e.g., naphthalene dimers). The validity of this approximation will be discussed later.

As a consequence, the secular equation (14) reduces to 4×4 problems as far as the triplet–triplet modes are concerned. As to the optical transition modes, we restrict ourselves to transitions between the vibrational ground state and the triplet manifold, assuming that the corresponding part of the optical spectrum is sufficiently well separated in frequency space from vibrational sidebands, etc. Neglecting sublevel relaxation processes of the type $|a, \alpha\rangle \leftrightarrow |a, \beta\rangle$, this leads to 2×2 problems.

The mutually coupled variables are listed in Table II. The following subsections are devoted to the investigation of the dynamics of these mode subgroups.

A. Optical modes

Information about the optical modes can be obtained from the impurity triplet-phosphorescence spectra, and, in favorable cases, also from absorption spectra related to the (weakly allowed) singlet–triplet transitions.

Here, we shall consider only the transitions from the impurity *ground state* to its triplet manifold. We assume that the corresponding spectral bands are sufficiently well separated from phonon sidebands and other host excitations or, at least, that these latter modes are dynamically decoupled from the ground state excitations. Hence, the optical absorption spectrum from the transitions $|0, 0\rangle \rightarrow |+, \alpha\rangle$ and $|0, 0\rangle \rightarrow |-, \alpha\rangle$ can be described in terms of the solutions of the 2×2 secular problem for the macrovariables $N^{0\alpha}_{0a}$.

We start this subsection by setting down explicit expressions for the stochastic evolution matrix L. The relevant diagonal elements have already been given Eq. (26). According to Eqs. (27)–(29), the relaxation elements $R^{\kappa 0\kappa 0}_{k0k0}$ are dominated by the phonon-induced pure dephasing rate $\Gamma_{\rm PD}\binom{\kappa 0}{k0}$ and/or by orbital transition rates $\Gamma(-, \kappa \rightarrow +, \kappa)$. The phonon–orbital coupling terms are essentially independent of the quantum numbers κ of the sublevel; moreover, they dominate the phosphorescence and sublevel-relaxation rates for several orders of magnitude. The diagonal elements of the relevant 2×2 submatrix L can be approximated, therefore, by

$$\begin{aligned} L_{++} &= L^{\kappa 0\kappa 0}_{+0+0} \\ &= \omega^{\kappa 0}_{+0} + (\tfrac{1}{2}i)\left[\langle D_{+0}(0)D_{+0}\rangle_B + A(T)\ \langle P^{+}(\omega_{-+})P\rangle_B\right], \\ L_{--} &= L^{\kappa 0\kappa 0}_{-0-0} \\ &= \omega^{\kappa 0}_{-0} + (\tfrac{1}{2}i)\left[\langle D_{-0}(0)\,D_{-0}\rangle_B + \langle P^{+}(\omega_{-+})P\rangle_B\right]. \end{aligned} \tag{32}$$

These expressions apply as long as thermally activated population relaxation processes $|0, 0\rangle \rightarrow |0, v\rangle$ from the dimer ground state to its vibrational levels v are insignificant ($k_B T \ll \hbar\omega^{v0}_{00}$).

Neglecting dynamic frequency shifts we have used the notation $\langle X^{+}(\omega)Y\rangle_B$ to denote the Fourier transform. The quantity $A(T)$ is the Arrhenius factor

$$A(T) = \exp(-h\omega_{-+}/k_B T). \tag{33}$$

The first terms that appear in the square brackets of Eq. (32) represent the pure dephasing rates, and the second terms the $|-\rangle \rightarrow |+\rangle$ depopulation rate: $D_{-0} = \phi^{\kappa\kappa}_{--} - \phi^{00}_{00}$, $P = \phi^{\kappa\kappa}_{+-}$. [The sublevel indices of the coupling potentials ϕ and of the transition frequencies ω_{-+} have been omitted in Eq. (32)].

For the off-diagonal elements of the matrix L we obtain

$$\begin{aligned} L_{+-} &= L^{\kappa 0\kappa 0}_{+0-0} = \tfrac{1}{2}i\left[\langle D_{+0}(\omega_{-+})P\rangle_B + \langle D_{-0}(0)P\rangle_B\right], \\ L_{-+} &= L^{\kappa 0\kappa 0}_{-0+0} \\ &= (\tfrac{1}{2}i)\left[\langle P^{+}(\omega_{-+})D_{-0}\rangle_B A(T) + \langle P^{+}(0)D_{+0}\rangle_B\right]\ . \end{aligned} \tag{34}$$

It is seen that a *significant* dynamic coupling between the two optical modes occurs only in case that the transition frequency ω_{-+} is comparable to, or smaller than, the magnitude of the cross correlations between the transition frequency- and transition-matrix element fluctuations, D_{l0} and P, respectively ($l = +, -$).

This is most likely for weakly coupled, translationally equivalent dimer molecules: in such a situation, the frequency ω_{-+} is given by the (small) exchange interaction term $\omega_{-+} = 2J$, and the dephasing potentials $\hbar D_{+0}$ and $\hbar D_{-0}$ are essentially identical. Accordingly, the difference $L_{--} - L_{++}$ becomes, in good approximation

$$L_{--} - L_{++} = \omega_{-+} + \tfrac{1}{2}i[1 - A_T(\omega_{-+})]\,\langle P^{+}(\omega_{-+})P\rangle_B.$$

This approaches ω_{-+} as $k_B T \gg h\omega_{-+}$.

The eigenvalues of the secular matrix [Eqs. (32) and (34)], i.e., the effective transition frequencies and the effective linewidths, are easily calculated. Here, we restrict ourselves to the strong coupling limit, where $|L_{++} - L_{--}|^2 \ll |L_{-+}L_{+-}|$, e.g., $\omega_{-+} \lesssim k_B T/\hbar$, $|\langle D_{+0}(\omega_{-+}) \times P\rangle_B| \gg \omega_{-+}$. Hence, the eigenvalues of the optical

TABLE III. Orbital 4×4 damping matrix **Γ**. Only those relaxation terms that originate with exciton–phonon interactions are shown.

	$(+,+)$	$(-,-)$	$\uparrow=(+,-)$	$\downarrow=(-,+)$
$(+,+)$	$A\Gamma$	$-\Gamma$	$+\frac{1}{2}\langle D(0)\,P^{+}\rangle_B$	$\frac{1}{2}\langle D(0)\,P^{+}\rangle_B$
$(-,-)$	$-A\Gamma$	Γ	$-\frac{1}{2}\langle D(0)\,P^{+}\rangle_B$	$-\frac{1}{2}\langle D(0)\,P^{+}\rangle_B$
$\uparrow=(+,-)$	$\frac{1}{2}A\,\langle D(\omega_{-+})P\rangle_B$	$-\frac{1}{2}\langle D(\omega_{-+})P\rangle_B$	$\Gamma_{\mathrm{PD}}+\frac{1}{2}(1+A)\Gamma$	$-\frac{1}{2}(1+A)\,\langle P^{+}(\omega_{-+})P^{+}\rangle_B$
$\downarrow=(-,+)$	$\frac{1}{2}A\,\langle D(\omega_{-+})P\rangle_B$	$-\frac{1}{2}\langle D(\omega_{-+})P\rangle_B$	$-\frac{1}{2}(1+A)\,\langle P^{+}(\omega_{-+})P^{+}\rangle_B$	$\Gamma_{\mathrm{PD}}+\frac{1}{2}(1+A)\Gamma$

$\psi_0=\psi(\omega=0)=\langle D(0)P^{+}\rangle_B$, $D=\phi^{\kappa\kappa}_{--}-\phi^{\kappa\kappa}_{++}$,

$\psi_+=\psi(\omega_{-+})=\langle D(\omega_{-+})P\rangle_B$, $P=\phi^{\kappa\kappa}_{+-}$,

$\Gamma=\Gamma(-,\kappa\rightarrow+,\kappa)=\langle P^{+}(\omega_{-+})P\rangle_B$,

$\Gamma_{\mathrm{PD}}=\frac{1}{2}\langle D(0)D\rangle_B$.

modes read, in lowest order

$$Z_{-+}\cong\tfrac{1}{2}(\omega_{+0}+\omega_{-0})+\tfrac{1}{2}i\,\left[\Gamma_{\mathrm{PD}}\binom{-}{0}+\Gamma_{\mathrm{PD}}\binom{+}{0}\right]$$
$$+\tfrac{1}{2}i\,[1+A(T)]\Gamma(-\rightarrow+)\pm[L_{+-}L_{-+}]^{1/2}\;. \qquad (35)$$

In case that the elements L_{+-} and L_{-+} [Eq. (34)] are purely imaginary, then either the effective transition frequencies or the relaxation constants of the two modes are approximately equally valued, depending on the sign of L_{+-} or L_{-+}. We mention that $L_{-+}\cong-L^{*}_{+-}$ as $k_BT\gg\hbar\omega_{-+}$ and $D_{+0}\approx D_{-0}$, which means that the difference of the effective transition frequencies, $|\mathrm{Re}(z_- - z_+)|$ is significantly smaller than ω_{-+}, at least in this limiting case.

If a dynamic exchange between the two optical modes is operative, it will also affect the relative intensity of their spectral contributions (dynamic borrowing of spectral intensity). Making use of the coupling Hamiltonian [Eq. (24)] and neglecting phonon-assisted processes, the optical spectrum is given in terms of the spectral functions

$$S_\kappa(\omega)\propto\mathrm{Im}\,\mathbf{p}^{+}(\omega\mathbf{l}-\mathbf{L})^{-1}\mathbf{p}\;, \qquad (36)$$

where **p** is the vector of the relevant transition dipole moments

$$\mathbf{p}=(p_+,\,p_-)=(\mathbf{e}\cdot\mathbf{p}^{\kappa 0}_{+0},\;\mathbf{e}\cdot\mathbf{p}^{\kappa 0}_{-0}), \qquad (37a)$$

and **L** is the SEM [Eqs. (32) and (34)]. The inverse of $\omega\mathbf{l}-\mathbf{L}$ is

$$(\omega\mathbf{l}-\mathbf{L})^{-1}=[(\omega-z_-)(\omega-z_+)]^{-1}\begin{pmatrix}\omega-L_{--} & L_{+-}\\ L_{-+} & \omega-L_{++}\end{pmatrix} \qquad (37b)$$

where z_+ and z_- are the eigenvalues of **L**. If one of the transitions is symmetry forbidden (e.g., $p_+=0$), the spectral density $S(\omega)$ becomes

$$S(\omega)\propto\mathrm{Im}\,\{\omega-L_{++})/[(\omega-z_+)(\omega-z_-)]\}.$$

Hence, the spectrum contains contributions from both modes, z_+ and z_-, and their relative strength provides a sensitive measure for the significance of the exchange coupling since $z_+-L_{++}\rightarrow0$ as $L_{+-}L_{-+}\rightarrow0$.

B. Orbital modes

For every pair of sublevel states κ there exist four types of orbital modes, namely, the population modes corresponding to the macrovariables $\bar{N}^{\kappa\kappa}_{++}$, $\bar{N}^{\kappa\kappa}_{--}$, and the transition modes $|+\rangle\rightarrow|-\rangle$ and $|-\rangle\rightarrow|+\rangle$, related to $\bar{N}^{\kappa\kappa}_{-+}$ and $\bar{N}^{\kappa\kappa}_{+-}$.

At the moment we will neglect (exciton-band) detrapping processes, intrinsic spin–orbit relaxation and phosphorescence decay completely; then the variable $\bar{N}^{\kappa\kappa}_{11}+\bar{N}^{\kappa\kappa}_{22}$ is a conserved quantity and the number of relevant modes is three rather than four. This case can be described in analogy to the dynamics of a spin $\frac{1}{2}$ system, a formalism frequently applied to the problem to be discussed here.[1] A main concern of these papers is whether the dimer orbital doublet shows so-called "coherent" or "incoherent" behavior, that is, whether the orbital transition modes *do* or do *not* show an oscillatory behavior. [Since the concept "coherence" is usually used to characterize the temporal-spatial correlation properties of fields, we will prefer here to talk about oscillatory versus overdamped behavior of the relevant $(+\rightarrow-)$ transition modes.]

To decide which case is realized one has to determine the eigenvalues of the relevant secular polynomial, $\det[(z\mathbf{l}-\mathbf{L})]$, the coefficients of which can generally be shown to be real-valued. Accordingly, its roots are either real-valued, or pairwise complex conjugate. Two of the zeros iz_+ and iz_- are always real and definitely negative; these represent the relaxation rates of the population variables. The additional pair of eigenvalues, $z_\uparrow$ and $z_\downarrow$ describes the dynamics of the transition modes. The zeros $iz_\uparrow$ and $iz_\downarrow$ can be: (i) real-valued (overdamped transition modes), (ii) complex, $z_\uparrow=z_\downarrow$ (oscillatory transition modes, $\mathrm{Re}z_\uparrow>0$, by definition), or (iii) real-valued and equal $z_\uparrow=z_\downarrow$ (unphysical aperiodic limit).

Table III shows the elements of the relevant 4×4 secular matrix, including only those relaxation terms that result from exciton–phonon interactions. General expressions for the zeros of the fourth-order secular polynomial can be derived by means of Cardani's formula. This provides however little insight concerning the qualitative behavior of the modes in question, and for that reason we shall discuss here only the case where subsets of population relaxation modes and orbital transition modes are essentially decoupled.

Such a decoupling may occur for different reasons:

(i) The presence of the frequencies $\pm\omega_{-+}$ in the secular matrix, Table III, can be sufficient to ensure that the modes do not couple strongly (i.e., $|\omega_{-+}| \gg \Gamma, \Gamma_{\rm PD}$).

(ii) At high temperatures we expect that the relevant spectral intensities at frequency ω_{-+} and at zero frequency do not differ very much, as long as ω_{-+} is small compared to the Debye frequency. Now, if $\Gamma_{\rm PD} \gg \Gamma$ (or vice versa), $|\psi(0)\psi(\omega_{-+})| \ll \Gamma_{\rm PD}^2 + \Gamma^2$, and consequently the coupling between the two subsets of variables is small.

(iii) At low temperatures, $k_{\rm B}T \ll h\,\omega_{-+}$, we expect that the spectral densities available for quasielastic relaxation mechanisms becomes very small [i.e., $\Gamma_{\rm PD}$, $\psi(0) \to 0$ as $\Gamma \to 0$], so that eventually $\Gamma^2 \gg |\psi(0)\psi(\omega_{-+})|$, $\Gamma_{\rm PD}^2$; hence, the two subsets decouple once more. [In general, however, no statement can be made about the significance of the $\psi(0)$ and $\psi(\omega_{-+})$, unless microscopic arguments are taken into account].

We investigate first the population relaxation modes, taking into account phosphorescence decay but neglecting detrapping and spin lattice relaxation (and assuming the decoupling from the transition modes). The corresponding SEM reads, in this approximation

$$\mathbf{L} = i \begin{pmatrix} A\Gamma + \gamma_+^\kappa & -\Gamma \\ -A\Gamma & \Gamma + \gamma_-^\kappa \end{pmatrix} . \tag{38}$$

Here Γ is the orbital transition rate $\Gamma(-, \kappa \to +, \kappa)$, A denotes the Arrhenius factor [Eq. (33)], and γ_+ and γ_- are the phosphorescence rates of the relevant levels.

The eigenvalues of Eq. (38) read approximately

$$z_+ \cong i\bar{\gamma}_\kappa = i[\gamma_+^\kappa + A(T)\gamma_-^\kappa][1 + A(T)]^{-1} ,$$

$$z_- \cong i[1 + A(T)]\Gamma + i[A(T)\gamma_+^\kappa + \gamma_-^\kappa][1 + A(T)]^{-1} . \tag{39}$$

The error of this result is of the order

$$\lambda = (\gamma_- - \gamma_+)^2 \, \frac{[1 - \tanh^2 \frac{1}{2}\beta h\omega_{-+}]}{[(1 + A)\Gamma]^2} \ll 1$$

at all temperatures, since γ_+, $\gamma_- \ll \Gamma$. [For that reason, the second term in Eq. (39) may be neglected.]

The result [Eq. (39)] is to be interpreted as follows: the rate $-iz_- \cong (1 + A)\Gamma = \Gamma(- \to +) + \Gamma(+ \to -)$ describes the fast equilibration between the two sublevels via phonon-assisted processes $|+\rangle \leftrightarrow |-\rangle$; $-iz_+$ on the other hand reflects the comparatively slow phosphorescence decay of the two-level *quasiequilibrium* system; note that the effective phosphorescence lifetime $\bar{\gamma}_\kappa$, represents the "thermal average" of the rates γ_+ and γ_- according to the thermal population of the levels + and −.

The expressions of Eq. (39) apply to the population relaxation of nearby vibronic monomer levels, e.g., in PBQ (Ref. 16), provided that the temperature is sufficiently small to allow the neglect of guest→host detrapping processes. This is so, since there the spin-orbit relaxation between different spin levels is slow in comparison to the phosphorescence decay rate $\bar{\gamma}_\kappa$, Eq. (39).

In dimers, however, the situation is opposite, and consequently thermal equilibrium between the spin sublevels occurs faster than the optical decay. In this case there exists just *one* rather than three *phosphorescence lifetimes*, and this is shown in more detail in Appendix A.

We turn to the transition modes. The relevant SEM reads

$$\mathbf{L} = \begin{pmatrix} \omega_{-+} + i[\Gamma_{\rm PD} + \frac{1}{2}(1 + A)\Gamma] & -\frac{1}{2}i(1 + A)\Gamma \\ -\frac{1}{2}i(1 + A)\Gamma & -\omega_{-+} + i[\Gamma_{\rm PD} + \frac{1}{2}(1 + A)\Gamma] \end{pmatrix} . \tag{40}$$

The phosphorescence rates can be neglected here, and for convenience we have assumed that $\phi_{+-} = \phi_{-+}$. Hence, the eigenvalues of Eq. (40) read

$$z_{\uparrow,\downarrow} = i[\Gamma_{\rm PD} + \tfrac{1}{2}(1 + A)\Gamma] \pm \{\omega_{-+}^2 - [\tfrac{1}{2}(1 + A)\Gamma]^2\}^{1/2} . \tag{41}$$

As long as $\omega_{-+} > \frac{1}{2}(1 + A)\Gamma$ this yields oscillatory modes; in the opposite case the transition modes are overdamped.

We expect that the intrinsic temperature dependence of the rate $\Gamma = \Gamma(- \to +)$ (depopulation via phonon emission) is comparatively weak. For $\frac{1}{2}\Gamma < \omega_{-+} < \Gamma$, therefore, it can happen that the modes have finite effective transition frequencies at low temperatures T, but show a significant slowing down as T is increased and, at a specific T_c, become finally overdamped. This is because of the strong temperature dependence of the Arrhenius factor $A = A(T)$, Eq. (33). The slowing down of the transition frequency as described here is a purely dynamical effect, and it has no influence, therefore, on the activation energy $h\omega_{-+}$, which enters $A(T)$.

C. EPR modes

The dynamics of the EPR quartet of modes [see Table II (3)] is in many aspects similar to those of the quartet of orbital modes. This is, first, because the spin sublevel splitting $\omega_{ll}^{\lambda\kappa}$ $(\lambda \neq \kappa)$ is small in comparison with the orbital transition frequencies $\omega_{-+}^{\lambda\kappa}$, and, second, because the dynamic exciton–phonon coupling is large in comparison with the fine interaction: this allows the approximately valid identifications $D_{-+}^{\lambda\kappa} \approx D_{-+}^{\lambda\lambda} \approx D_{-+}^{\kappa\kappa} = D$ and $P_{+-}^{\kappa\lambda} \approx P_{+-}^{\lambda\lambda} \approx P_{+-}^{\kappa\kappa} = P$ $(D_{-+}^{\lambda\kappa} = \phi_{--}^{\lambda\lambda} - \phi_{++}^{\kappa\kappa})$.

The only significant difference between EPR and orbital modes occurs for the slowly decaying spin transition modes $N_{++}^{\lambda\kappa}$ versus slowly decaying population modes $N_{++}^{\kappa\kappa}$. We have shown in Sec. IV B that the relaxation constants of the slowly decaying population mode go to zero as the phosphorescence decay rates and intrinsic spin–orbit relaxation constants vanish. This is not so with the corresponding EPR modes, which still are dephased via hyperfine field fluctuations. Moreover, the dynamic coupling between spin transitions of different types is insignificant as long as the corresponding transition frequency differences are large in comparison with the intrinsic spin–orbit relaxation rates; this is in contrast to the sublevel population relaxation modes (see Appendix A).

In order to confirm the correspondence between spin–orbital modes and EPR modes, we consider, first of all, the generally valid expression for the off-diagonal relaxation elements $L_{klll}^{\kappa\lambda\kappa\lambda}$, $k \neq 1$ (the elements L_{lllk} are of corresponding form).

$$L^{\kappa\lambda\kappa\lambda}_{klll}=\tfrac{1}{2}i\langle D^{\kappa\lambda}_{kl}(\omega^{\kappa\kappa}_{lk})\,\phi^{\kappa\kappa}_{lk}\rangle_B+\tfrac{1}{2}i\langle D^{\kappa\lambda}_{ll}(0)\,\phi^{\kappa\kappa}_{kl}\rangle_B$$

$$+\frac{1}{2}\sum_{\alpha\neq k}[\gamma^{\alpha\kappa\alpha\kappa}_{kkkl}(\omega^{\kappa\kappa}_{lk})+\gamma^{\alpha\kappa\alpha\kappa}_{lkll}(\omega^{\kappa\alpha}_{ll})],$$

$$D^{\kappa\lambda}_{kl}=\phi^{\kappa\kappa}_{kk}-\phi^{\lambda\lambda}_{ll}\ . \qquad (42)$$

This first term on the right-hand side can be approximated by $\langle D(\omega_{lk})P>$; the other terms are negligible with respect to the first one for both orbital modes, $\kappa=\lambda$, as well as for EPR transitions $k\neq\lambda$.[7] Second, it can be shown that the elements of the 2×2 submatrix that is related to the combined spin–orbital transitions is essentially given by those of the matrix [Eq. (40)], which applies to orbital transition modes. The difference between those matrices has the magnitude of phosphorescence decay rates, intrinsic spin–orbit relaxation rates, and/or spin dephasing rates, which are negligible with respect to all elements of Eq. (40). We conclude, therefore, that the eigenvalues (and eigenvectors) of the combined spin–orbital modes are essentially identical to those of the pure orbital transition modes. Consequently, the results given in Eq. (41) apply also to the orbital–EPR transition modes.

The SEM of a pure $\lambda\to\kappa$ EPR mode doublet ($N^{\kappa\lambda}_{++}$ and $N^{\kappa\lambda}_{--}$) reads

$$\mathbf{L}=\begin{pmatrix} L^{(0)}_{+}+iA(T)\Gamma & -i\Gamma \\ -iA(T)\Gamma & L^{(0)}_{-}+i\Gamma \end{pmatrix}\ . \qquad (43)$$

We have neglected here the weak dependence of the orbital relaxation rates $\Gamma=\Gamma(-,\ \alpha\to +,\ \alpha)$ and of the Arrhenius factor $A(T)$ on the sublevel quantum numbers $\alpha=\kappa,\ \lambda$. The terms $L^{(0)}_{+}$ and $L^{(0)}_{-}$ contain the information about the spin transition frequencies $\omega^{\kappa\lambda}_{ll}$, ($l=+,\ -$), the spin pure dephasing rates $\Gamma_{\mathrm{PD}}\binom{\lambda\kappa}{ll}$, the spin–orbit decay rates $\gamma^{\lambda}_{l}=\sum_{a=\pm}\sum_{\alpha\neq\lambda}\Gamma(l,\ \lambda\to a,\ \alpha)$, the phosphorescence lifetimes $\gamma^{P}_{l\lambda}=\sum_{v}\Gamma(l,\ \lambda\to 0,\ v)$, and detrapping rates $\gamma^{B}_{l\lambda}=\Gamma(l,\ \lambda\to\text{band})$:

$$L^{(0)}_{\pm}=\omega^{\lambda\kappa}_{\pm\pm}+i\Gamma^{(0)}_{\pm}\ ,$$

$$\Gamma^{(0)}_{\pm}=\Gamma_{\mathrm{PD}}\binom{\lambda\kappa}{\pm\pm}+\tfrac{1}{2}(\gamma^{\lambda}_{\pm}+\gamma^{\kappa}_{\pm})+\tfrac{1}{2}(\gamma^{P}_{\pm\lambda}+\gamma^{P}_{\pm\kappa})+\tfrac{1}{2}(\gamma^{B}_{\pm\lambda}+\gamma^{B}_{\pm\kappa})\ . \qquad (44)$$

For the eigenvalues of the SEM [Eq. (43)] we find, in good approximation

$$z_1=L^{(0)}_{+}+\delta z\ ,$$

$$z_2=[1+A(T)]\Gamma+L^{(0)}_{-}-\delta z\ ,$$

$$\delta z=\frac{i[L^{(0)}_{-}-L^{(0)}_{+}]A(T)\Gamma}{\{(L^{(0)}_{-}-L^{(0)}_{+})+i[1+A(T)]\Gamma\}}\ . \qquad (45)$$

Corrections to these expressions are of the order $\delta z^2[(L^0_{-}-L^0_{+})+(1+A)\Gamma]^{-1}$.

We comment on this result as follows: at very low temperature the exchange term δz is negligible since the Arrhenius factor $A(T)\to 0$ as $T\to 0$. In this case, the EPR transition frequencies are given by $\omega^{\lambda\kappa}_{++}$ and $\omega^{\lambda\kappa}_{--}$, respectively. The linewidths of the slowly decaying EPR modes, $N^{\lambda\kappa}_{++}$ are equal to the sum of pure dephasing rate $\Gamma_{\mathrm{PD}}\binom{\lambda\kappa}{++}$ plus the arithmetic average $\frac{1}{2}(\gamma^{\lambda}_{+}+\gamma^{\lambda}_{-})+\frac{1}{2}(\gamma^{P}_{+\lambda}+\gamma^{P}_{-\lambda})$ of spin–orbit relaxation and phosphorescence decay rates (detrapping is negligible as $T\to 0$). For increasing temperature $k_BT\sim\hbar\omega_{-+}$, the exchange term δz becomes increasingly significant: it causes an EPR transition frequency shift and an additional line broadening, and both effects show a strong, i.e., exponential, dependence on temperature, via the Arrhenius factor $A(T)$, Eq. (33).

The exchange term [Eq. (45)] reads, in more explicit form

$$\delta z=A(T)[\delta\omega+i\delta\Gamma]\ ,$$

$$=\frac{A(T)\{\Delta\omega(1+A)\Gamma^2+i\Gamma[(\Delta\omega)^2+(\Delta\Gamma)^2+\Delta\Gamma(1+A)\Gamma]\}}{\{(\Delta\omega)^2+[\Delta\Gamma+(1+A)\Gamma]^2\}}\ . \qquad (46)$$

Here, we have made use of the abbreviations [cf. Eq. (44)]

$$\Delta\omega=\omega^{\lambda\kappa}_{--}-\omega^{\lambda\kappa}_{++}\ ;\quad \Delta\Gamma=\Gamma^{(0)}_{-}-\Gamma^{(0)}_{+}\ . \qquad (47)$$

For $|(L^{(0)}_{-}-L^{(0)}_{+})|\ll\Gamma$, Eq. (46) simplifies to

$$\delta z=A(T)\left[[1+A(T)]^{-1}\Delta\omega+i\left(\frac{(\Delta\omega)^2}{(1+A)^2\Gamma}+\frac{\Delta\Gamma}{1+A}\right)\right]\ . \qquad (48)$$

Equation (48) reduces to previous results by van't Hof[8] provided that: (i) the temperature is small to allow the neglect of terms of quadratic and higher order in $A(T)$; (ii) the difference between the diagonal damping terms is negligible. The second condition is not necessarily valid since spin–orbit depopulation and, at higher temperatures, detrapping rates may contribute to $\Delta\Gamma$; $\Delta\omega$, on the other hand, can be (almost) zero (accidentally, or systematically for translationally equivalent molecules). Hence, the product $\Delta\Gamma\cdot\Gamma$ can be comparable to or greater than $(\Delta\omega)^2$ [cf. Eqs. (46) and (48)].

V. RESULTS AND DISCUSSION

In the present paper we have developed a theory for the relaxation modes of triplet impurity states in host matrices. Particular attention has been paid to the dynamics of dimer triplet excitations. Systems of this kind have been subject to numerous experimental investigations.[1–7,12] One aim of the following discussion is a comparison of some of the experimental findings with results derived here.

Our approach is based on the quantum mechanical version of Redfield's relaxation theory.[15] Its application to dimer triplet states as performed in Secs. II–IV yields some significant generalization of previous theoretical work on the subject.[1,9–11] This is so, despite the various approximations that have been applied and already discussed in Secs. II–IV.

We will start the discussion with comments on the original model by Haken and Strobl,[10] then turn to its extension to EPR modes (Reineker *et al.*[11]), and finally focus on the exchange model by van't Hof and Schmidt, paying attention to their experimental observations on naphthalene.

A. Comparison with the Haken–Strobl model (Ref. 10)

The Haken–Strobl model in its version applicable to dimer triplet states represents an approach for the orbital modes (cf. Sec. IVB). Despite its merits and its conceptual simplicity, there are problems associated with it that must be recognized when applying it to experimental situations. The model implies three main approximations: first, it deals with a simplified Hamiltonian, $\mathcal{H}_{\mathrm{HS}}$ (49); second, it assumes white spectra for the coupling potential correlation functions $\langle \tilde{\phi}^{+}_{ab}(\omega)\tilde{\phi}_{cd}\rangle_B$ (Gaussian random fluctuations); third, it neglects cross correlation terms between these fluctuations [cf. Eq. (51)]. In the following, we are going to comment on the validity of these approximations.

The Haken–Strobl Hamiltonian (in site representation) is of the form

$$\begin{aligned}\mathcal{H}_{\mathrm{HS}} &= \mathcal{H}_{\mathrm{dimer}} + \delta\mathcal{H}_{\mathrm{orbit}} + \mathcal{H}_B \\ &= \sum_{a=1}^{2}(\hat{\epsilon}'_a + \delta\hat{\epsilon}_a)\hat{\mathbf{N}}_{aa} + (\hat{J}' + \delta\hat{J})(\hat{\mathbf{N}}_{12} + \hat{\mathbf{N}}_{21}) + \mathcal{H}_B\ , \qquad (49)\end{aligned}$$

[cf. Eqs. (21), (17), and (1)]. The eigenstates of $\mathcal{H}_{\mathrm{dimer}}$ are of the factorized type and spin relaxation processes are absent, because of the form of the coupling term $\mathcal{H}_{\mathrm{orbit}}$.[17] As to the orbital modes of the dimer triplet, the Haken–Strobl *Hamiltonian* implies only minor important approximations as long as the intrinsic spin-orbit relaxation processes and the phosphorescence decay can be considered as insignificantly slow.

The Redfield relaxation matrix **R** that results from the Haken–Strobl *Hamiltonian* [Eq. (49)] is shown in Table III, in dimer representation. The Haken–Strobl *model* relaxation matrix [which is the result of the approximation Eq. (51)] reads, on the other hand,

$$\hat{R}_{\mathrm{HS}} = \begin{array}{c} |11\rangle \\ |22\rangle \\ |12\rangle \\ |21\rangle \end{array}\begin{bmatrix} 2\gamma_1 & -2\gamma_1 & 0 & 0 \\ -2\gamma_1 & 2\gamma_1 & 0 & 0 \\ 0 & 0 & 2\gamma_0 + 2\gamma_1 & -2\gamma_1 \\ 0 & 0 & -2\gamma_1 & 2\gamma_0 + 2\gamma_1 \end{bmatrix}, \qquad (50)$$

and this refers to the *site* representation.

Here, γ_0 and γ_1, respectively, denote Gaussian-distributed, delta-correlated site-energy and exchange-integral fluctuations:

$$\begin{aligned}\langle \delta\hat{\epsilon}_a(t)\delta\hat{\epsilon}_a(t')\rangle_B &= 2\gamma_0\delta(t-t')\ ; \quad a = 1, 2\ , \\ \langle \delta\hat{J}(t)\delta\hat{J}(t')\rangle_B &= 2\gamma_1\delta(t-t')\ .\end{aligned} \qquad (51)$$

(Note the identities $\hat{\phi}_{aa} = \delta\hat{\epsilon}_a$, $\hat{\phi}_{ab} = \hat{\phi}_{ba} = \delta\hat{J}$, $a \neq b$). It is this approximation that yields the essential shortcomings of the Haken–Strobl approach.

First of all, the model is restricted to the infinite temperature limit, because of the spectral symmetry of the correlations [Eq. (51)] that violate the proper detailed balance relations at finite temperatures T. For that reason, the model implies an equilibrium equipartition of the two orbital levels; it is, in particular, inappropriate to predict the thermal activation of specific relaxation processes that yields the Arrhenius-type behavior of T [cf. Table III and Eqs. (39) and (41)]. This has already been pointed out in a recent publication by Rahman *et al.*[14]

Second, the model ignores cross-correlations between different site fluctuations $\delta\hat{\epsilon}_1$ and $\delta\hat{\epsilon}_2$ and also between site- and transfer-element fluctuations, $\delta\hat{\epsilon}_a$ and $\delta\hat{J}$. Since these fluctuating forces depend on the same phonon/librational and/or vibrational coordinates, there is no *a priori* justification for the neglect of their cross-correlations. As a consequence, the HS-model, even for $T \to \infty$, becomes invalid if the stationary site energy difference $\Delta = |\hat{\epsilon}_1 - \hat{\epsilon}_2|$ is comparable to the stationary transfer matrix element $\hat{J}$ (see Appendix B).

Third, the model does not take into account that the individual relaxation terms can depend sensitively on the magnitude of the mismatch frequencies that are involved in specific relaxation terms. At low temperatures, for instance, the spectral density available for quasielastic processes might be (almost) zero, except those (exothermic) population relaxation processes which are still finite. This is of particular relevance in relation to the cross-correlation terms ψ_0 and ψ_1 of the relaxation matrix $\bar{\Gamma}$ (Table III), and also in relation to Reineker's treatment of the EPR modes,[11] which is essentially based on the Haken–Strobl model (see Sec V B).

These invalidities can be concluded from the expressions given in Appendix B. There we have expressed the Redfield relaxation parameters of Table III in terms of the fluctuations in the site space so that they can be compared directly to the corresponding expressions from the Haken–Strobl model. [cf. Eqs. (B1) and (B3)].

According to these results, the Haken–Strobl model becomes only valid provided that (simultaneously):

(i) The temperature is large in comparison with the dimer energy separation ω_{-+}.

(ii) The *site* energy difference Δ is small in comparison with the stationary transfer matrix element.

(iii) The cross correlations ψ_1 and/or ψ_0, which show up in the general relaxation matrix $\bar{\Gamma}$ (Table III) are negligible for any reasons discussed in Sec. IVB (insignificant exchange coupling of transition and population variables).

(iv) Cross correlations between $\delta\hat{\epsilon}_1$ and $\delta\hat{\epsilon}_2$ are negligible, and $\langle \delta\hat{\epsilon}_1(t)\delta\hat{\epsilon}_1\rangle = \langle \delta\hat{\epsilon}_2(t)\delta\hat{\epsilon}_2\rangle$.

As an alternative to (ii), the model also applies if the site-energy spacing $\Delta = |\hat{\epsilon}_1 - \hat{\epsilon}_2|$ is large in comparison with $|\hat{J}|$. This is, of course, the trivial case in which the sites become stationary decoupled and in which site and dimer representation are essentially identical.

Only in these limiting situations is it possible *formally* to establish a one-to-one relation between the site correlations γ_0 and γ_1, on the one hand, and the dephasing and depopulation rates Γ_{PD} and Γ, on the other hand. The limit $T \to \infty$ and $\Delta \to 0$ yields

$$\Gamma = \gamma'_0\ , \quad \Gamma_{\mathrm{PD}} = 4\gamma'_1\ . \qquad (52)$$

[Since Γ and Γ_{PD} do not generally result from Gaussian random fluctuations, we have supplied γ'_0 and γ'_1 with a prime here in order to distinguish them from γ_0 and γ_1 defined in Eq. (51). We note that the exchange integral correlation term γ'_1 represents a quasielastic component in this case, which, at small temperatures is expected to vanish. This is not so with the site energy correlations, which correspond to (exothermic) inelastic processes at energy $h\omega_{-+}$.]

In the intermediate regime, $\Delta \sim |\hat{J}|$, even at infinite temperature, the dephasing and depopulation rates Γ_{PD} and Γ, respectively, contain contributions from the site cross-correlation terms between $\delta\hat{\epsilon}_1$, $\delta\hat{\epsilon}_2$, and $\delta\hat{J}$, which have been neglected in the HS model [cf. Eqs. (B3) and (B4)]. Correspondingly, the site self-correlations γ_0' and γ_1' contribute off-diagonal relaxation matrix elements in *dimer* representation, which are irrelevant as long as the exchange coupling between transition and population variables can be considered as insignificant [see Sec. IVB, cf. Eq. (B3)]. If this coupling mechanism is in fact irrelevant the orbital relaxation can be still characterized by only two rate constants (Γ and Γ_{PD}) which, in the general case, however, cannot be related to γ_0' and γ_1'.

In conclusion, we would like to emphasize that it can be insufficient to design relaxation models in site representation and we note that this might be of relevance concerning theoretical models for exciton transport in exciton bands, impurity bands, and/or disordered solids.

B. Reineker's treatment of EPR spectra (Ref. 11)

Reineker's treatment is essentially based on the HS model. Its only generalization refers to the stationary Hamiltonian, which includes (in addition to the HS Hamiltonian) first the Zeeman interaction with an external magnetic field and second the site dependent molecular fine structure tensors, which result from the different orientations of the translationally inequivalent molecules. Reineker's stationary Hamiltonian is of the form (cf. Sec. IIC)

$$\mathcal{H}_R = \mathcal{H}_{\text{orbit}} + \sum_{a=1}^{2} (\mathbf{S}\cdot\hat{\mathbf{F}}_{aa}\cdot\mathbf{S})\hat{\mathbf{N}}_{aa} + \mu_B \mathbf{H}_0\cdot\mathbf{S}\ . \tag{53}$$

The coupling Hamiltonian $\delta\mathcal{H}$ and the resulting relaxation terms are exactly approximated as in the HS model [cf. Eqs. (49) and (51)].

Since $\hat{\mathbf{F}}_{11} \neq \hat{\mathbf{F}}_{22}$ for inequivalent molecules the eigenstates of $\mathcal{H}_R$ are of the form given in Eq. (22) rather than of the (orbital–spin) factorized type, and it is the term $\frac{1}{2}\mathbf{S}\cdot(\hat{\mathbf{F}}_{11}-\hat{\mathbf{F}}_{22})\cdot\mathbf{S}(\hat{\mathbf{N}}_{11}-\hat{\mathbf{N}}_{22})$ that causes the stationary coupling of orbital and spin degrees of freedom. Hence, the effective coupling potential matrix elements [Eq. (23)] are not diagonal with respect to the sublevel quantum numbers, nor are diagonal elements with different sublevel index identical (finite sublevel dephasing terms $\phi_{\pm\pm}^{\alpha\alpha} - \phi_{\pm\pm}^{\beta\beta}$, finite sublevel transition terms $\phi_{\pm\pm}^{\alpha\beta}$, $\alpha \neq \beta$).

As a consequence, the sublevels show finite lifetimes, the EPR transitions finite dephasing times, and the EPR transition modes, in particular, can be dynamically coupled. According to Reineker's model, the significance of all these mechanisms depends on the magnitude of the two orbital relaxation parameters γ_0 and γ_1, Eq. (51), retained in the HS approach. This has been demonstrated in numerous investigations by Reineker, for fixed strength of the stationary spin interaction Hamiltonian. In a recent publication[11] dealing with the modes of naphthalene dimers, the 35-dimensional eigenvalue problem was solved numerically.

Despite this computational effort, the applicability of Reineker's model to experimental situations must be questioned. This is, of course, first because of the restricted validity of the HS approach, which was discussed in Sec. VA. Second, even an improved model that overcomes the objections drawn in Sec. VA would be, in our opinion, invalid to describe the EPR spectra at low temperatures. We maintain this objection particularly for systems in which the sublevel dephasing is *in fact* dominated by intrinsic spin–orbit relaxation mechanisms. Third, recent experimental studies on monomers[9] indicate it may be the hyperfine-field fluctuations rather than the ISOR that cause, at least at low temperatures, the temporal decay of the EPR transition modes.

In the remainder of this subsection, we shall substantiate our objections as follows.

(i) In systems like naphthalene the translationally inequivalent dimer molecules are subject to the condition $|\hat{\epsilon}_1 - \hat{\epsilon}_2| \ll |\hat{J}|$. One might expect therefore that the HS model becomes valid for $k_B T \gg |\tilde{\epsilon}_+ - \tilde{\epsilon}_-|$. This is, however, not necessarily so, since the temperature in the classical regime becomes comparable to the trap depth, ϵ_T. Detrapping and/or thermal activated processes to higher vibronic states are likely to occur and these may even favor spin lattice relaxation (e.g., via exciton band states[21]).

(ii) For $\epsilon_T \gg k_B T$ Reineker's treatment becomes invalid since $k_B T \lesssim |\tilde{\epsilon}_+ - \tilde{\epsilon}_-|$ in this regime. However, even if it were corrected to include the proper detailed balance relations it would be invalid to describe the orbitally induced sublevel relaxation (ISOR) in terms of the two rate constants γ_0' and γ_1', Eq. (52). As a matter of fact, *different* frequency components of the relevant coupling potential correlation functions contribute to the relaxation rates of the orbital modes and the EPR modes, respectively. In cases where the intrinsic spin–orbit coupling is small, the orbital depopulation rate $\Gamma(-, \alpha \to +, \alpha)$, e.g., is dominated by $\gamma_0' \approx \langle \delta\tilde{\phi}_{+-}^{\dagger}(\omega_{+-}^{\alpha\alpha})\delta\tilde{\phi}_{+-}\rangle_B$ [cf. Eq. (30)]. The main contribution to the sublevel transition rate $\Gamma(+, \alpha \to +, \beta)$, $\alpha \neq \beta$ on the other hand, is given by admixtures of the type $\langle \delta\tilde{\phi}_{+-}^{\dagger}(\omega_{++}^{\alpha\beta})\delta\tilde{\phi}_{+-}\rangle_B$. Since the frequencies $\omega_{+-}^{\alpha\alpha}$ and $\omega_{++}^{\alpha\beta}$ differ typically for one order of magnitude, we expect (in the low and intermediate temperature regime, at least) that the two spectral densities differ by at least two orders of magnitude. (A much stronger than quadratic dependence of the spectral density on the frequency is suggested by comparative studies on naphthalene dimers with different orbital transition frequencies.[6,7]) That is, the EPR relaxation parameters cannot be expressed in terms of only two constants, γ_0' and γ_1'.

(iii) In order to demonstrate the relevance of the intrinsic spin–orbit coupling to the EPR line shapes of naphthalene Reineker has varied the HS parameters that occur in his model, inserting values for γ_0, e.g., up to 5000 cm^{-1}.[11] This corresponds to an orbital relaxation time Γ^{-1} of the order of 10^{-15} s, which is far beyond the time scales of relevance in the lattice and incompatible with the underlying assumption of Markovian processes. The rate constant Γ has been determined previously from experiment and has a value corresponding to about 5×10^{-10} s. Moreover, recent experimental studies by van't Hof and Schmidt[9] show that hyperfine interaction-induced spectral diffusion (and thermally activated transitions between the two Davydov components), rather than the fine structure fluctuations, may be important in the EPR relaxation. Botter *et al.*[7] have applied a relaxation model developed by van't Hof[8] in order to interpret their data, and this (together with the experimental results themselves) will be discussed next.

C. Comparison with van't Hof's model (Ref. 8) and the experimental findings on naphthalene

Van't Hof's model represents an exchange theory for the EPR modes and is of the type developed by Anderson and Kubo.[13] The basic idea is that, in addition to the usual dephasing mechanism, random (spin diagonal) scattering processes between the two Davydov components occur. This causes a shift of the effective transition frequency (since the stationary EPR frequencies are slightly different) and an additional contribution to the effective linewidth. Both effects shown an Arrhenius-type temperature behavior since the mechanism requires an activation energy corresponding to the frequency difference of the Davydov components. The expression for the temperature dependent shift and linewidth contribution reads

$$\delta z_{\text{van't Hof}} = A(T)\frac{\Delta\omega\Gamma^2 + i(\Delta\omega)^2\Gamma}{(\Delta\omega)^2+\Gamma^2}\,, \qquad A(T)=\exp(-\beta\hbar\omega_{-+})\,. \tag{54}$$

Equation (54) can be directly compared to our result, Eq. (46). In case of naphthalene, the condition $\Gamma^2 \gg [\Delta\omega]^2$ and $\Delta\Gamma \ll \Gamma$ apply; thus the difference between Eqs. (54) and (46) reduces to terms nonlinear in the Arrhenius factors

$$\delta z - \delta z_{\text{van't Hof}} = -\frac{A^2}{1+A}\Delta\omega - i\frac{2A^2+A^3}{(1+A)^2}\cdot\frac{(\Delta\omega)^2}{\Gamma} + i\frac{A}{(1+A)^2}\Delta\Gamma\,. \tag{55}$$

provided that $\Delta\Gamma \ll (\Delta\omega)^2/\Gamma$. That is, only for low temperatures ($A \ll 1$), but not in the intermediate regime do these results agree. In fact, the experimental data on naphthalene show systematic deviations from van't Hof's expression which have the correct sign. A quantitative analysis of the experiment in terms of our results is difficult, however, because of the large scatter and the restricted regime of the data.

In a more recent study[9] van't Hof and Schmidt have demonstrated that the EPR dephasing of quinoline monomers at low temperatures may be dominated by hyperfine field fluctuations and that the corresponding decay times are of the order of 10 μs. From the theoretical point of view, it is therefore interesting to give a quantitative estimate on the significance of the intrinsic spin-orbit coupling mechanism as to the EPR line broadening in naphthalene dimers. Proceeding from Eq. (23), we have expressed the actual coupling parameters ϕ in terms of the fluctuating forces $\tilde{D}$ and $\tilde{P}$ (Table III), which occur in dimer representation, making use of the assumptions that Reineker's Hamiltonian applies [$\tilde{D}=\delta\tilde{J}$, $\tilde{P}=\delta\tilde{\epsilon}$, Eqs. (51) and (53)] and that the intrinsic spin-orbit coupling is small, $U^{\alpha\alpha}_{aa}\cong 1 \gg U^{\alpha\beta}_{ab}$, $\alpha\neq\beta$ and/or $a\neq b$. The result, which corresponds to second-order perturbation theory with respect to $\delta H_R - \delta H_{\text{dimer}}$ [Eqs. (53) and (21)] is shown in Table IV. For naphthalene, we estimate admixture parameters U which are smaller than 0.05. Thus, the rate constants for combined transitions for instance are reduced by at least two orders of magnitude with respect to Γ (pure orbital transition rate). For the pure sublevel transitions, an additional reduction of at least two orders of magnitude is expected according to mismatch frequency arguments as pointed out in Sec. VB (see also Sec. IIIB). The corresponding decay times are thus roughly estimated to be larger than 5×10^{-6} s, and this is the order of magnitude of the observed hyperfine field induced EPR dephasing times of quinoline monomers. If one assumes that the frequency dependence of the spectral density is stronger than quadratic, the ISOR can be considered as insignificant with respect to the EPR broadening (provided that the hyperfine-field fluctuations in the naphthalene system yield dephasing times of the order of some microseconds as in quinoline).

TABLE IV. The fluctuating forces ϕ in eigenstate representation are expressed in terms of the exciton–phonon dynamic interactions $\tilde{D}$ and $\tilde{P}$ (cf. Table III). The expressions shown here represent the leading terms of the canonical transformation [Eq. (23)] (first order with respect to the off-diagonal elements of U). This corresponds to second-order perturbation theory with respect to $\mathcal{H}_{\text{Ex}} - \mathcal{H}_{\text{dimer}}$ [Eqs. (15a) and (21)].

Orbital or spin-orbital pure dephasing	$\phi^{\alpha\alpha}_{--} - \phi^{\beta\beta}_{++} \cong \tilde{D}$
Pure sublevel dephasing	$\phi^{\alpha\alpha}_{++} - \phi^{\beta\beta}_{++} \cong 2(U^{\alpha\alpha}_{+-} - U^{\beta\beta}_{+-})\,\tilde{P}$
Sublevel transition	$\phi^{\alpha\beta}_{++} \cong U^{\alpha\beta}_{++}\tilde{D} + (U^{\alpha\beta}_{+-} + U^{\alpha\beta}_{+-})\,P$
Pure orbital transition	$\phi^{\alpha\alpha}_{+-} \cong \tilde{P}$
Combined transition	$\phi^{\alpha\beta}_{+-} \cong (U^{\alpha\beta}_{++} + U^{\alpha\beta}_{--})\,\tilde{P}$

$\tilde{D}=\tilde{\phi}_{++}-\tilde{\phi}_{--}\,,\qquad \tilde{P}=\tilde{\phi}_{-+}=\tilde{\phi}_{+-}$

This is eventually consistent with the experimental findings on naphthalene. In Ref. 7 van't Hof and Schmidt have reported experimental values for the frequency shift $\Delta\omega$ and the broadening parameters Imδz, Eq. (48). The former have been observed with ODMR techniques, and the latter were obtained from spin-echo measurements for various sublevel transitions. The authors interpreted the Arrhenius broadening in terms of $k_\infty = (\Delta\omega)^2/\Gamma$ [Eq. (48)], and this allowed them to determine Γ. A typical value for k_∞ is 3 μs. Unfortunately, it is not clear to us whether Γ was determined from more than just one EPR transition. If the values for $\Delta\omega$ and k_∞ from *different* EPR modes led to consistent values for the orbital relaxation rate Γ, this would provide a strong argument for the insignificant effect of the ISOR mechanism on the EPR dephasing. This is so, because at low temperatures the term $\Delta\Gamma$, which shows up in Eq. (48), *is* of the order of the ISOR rate constants; hence significant differences would be expected for $k_\infty/(\Delta\omega)^2$ from different EPR transitions if $\mathrm{Im}\,\delta z$ were dominated by $\Delta\Gamma$. In the opposite situation, however, in which $\Delta\Gamma$ were small with respect to $(\Delta\omega)^2/\Gamma$ (3 μs), then $k_\infty/(\Delta\omega)^2=\Gamma^{-1}$ and, since $\Delta\Gamma$ is due to ISOR, the residual spin dephasing time of ≈ 5 μs (at $T\approx 1$ K) must be due to hyperfine-field fluctuations [cf. Eq. (4.4) and Table IV]. Then the only evidence for ISOR would be the quasiequilibrium between the spin sublevels, which is reached before the phosphorescence decay is likely to occur (see Appendix A, Ref. 7). In the absence of more data, we are unable to rule out either mechanism (ISOR and hyperfine fluctuations) as the source of the decay of the EPR transition modes; further experiments are needed to resolve this.

We conclude this discussion with some final remark on the "coherence" properties of the dimer triplet excitation. According to Eq. (41), the orbital transition modes show an oscillatory behavior as long as the transition frequency ω_{-+} is greater than the depopulation rate $\Gamma=\Gamma(-\to+)$. In naphthalene dimers consisting of translational equivalent (inequivalent) molecules, the two site exciton shows "coherent" behavior since the transition frequencies and depopulation rates amount to 1.0 (2.5) cm^{-1} and 7×10^{-5} (0.01) cm^{-1}, respectively, at liquid He temperatures.

In an opposite situation $\Gamma>\omega_{-+}$ in which the orbital transition mode were overdamped (diffusive exciton transport), the EPR modes of the lower Davydov component would still show finite transition frequencies (at least at moderate magnetic fields) and comparatively small linewidths as long as $\omega_{-+}/k_BT\ll 1$ [cf. Eq. (45)].

APPENDIX A: PHOSPHORESCENCE IN PRESENCE OF FAST SPIN-ORBIT RELAXATION

We present an approximate evaluation of the population relaxation rates of excited dimers, on the assumption that there are three distinct time scales, namely, those of orbital relaxation (Γ^{-1}), spin relaxation (Γ_s^{-1}), and phosphorescence decay (γ_p^{-1}): $\Gamma\gg\Gamma_s\gg\gamma_p$.

The relaxation matrix R for the coupled rate equations is given by

$$\mathbf{R}=\begin{pmatrix}\mathbf{R}_{++} & \mathbf{R}_{+-}\\ \mathbf{R}_{-+} & \mathbf{R}_{--}\end{pmatrix}\ . \tag{A1}$$

The elements of the four block matrices are defined as

$$R_{ab}^{\alpha\beta}=\delta_{ab}\delta_{\alpha\beta}\left(\sum_{c,\gamma}\Gamma_{ac}^{\alpha\gamma}+\gamma_{a\alpha}^{p}\right)-\Gamma_{ba}^{\beta\alpha}\ ,$$
$$\Gamma_{ba}^{\beta\alpha}=\Gamma(b,\beta\to a,\alpha)\ . \tag{A1a}$$

The elements $\Gamma_{-+}^{\alpha\alpha}\cong\Gamma$ are fast orbital relaxation rates, $\Gamma_{ab}^{\alpha\beta}(\alpha\neq\beta)$ represents a spin relaxation rate (order Γ_s^{-1}), the phosphorescence rate from the level $|a,\alpha\rangle$ is given as $\gamma_{a\alpha}^{p}$, and detrapping processes are neglected.

We apply a similarity transformation according to

$$\mathbf{R}^s=\mathbf{S}^{-1}\mathbf{R}\mathbf{S}\ ,\quad \mathbf{S}=\begin{pmatrix}\mathbf{S}_{++} & \mathbf{S}_{+-}\\ \mathbf{S}_{-+} & \mathbf{S}_{--}\end{pmatrix}\ , \tag{A2}$$
$$\mathbf{S}_{++}=\mathbf{S}_{+-}=\mathbf{S}_{--}=\mathbf{1}\ ,\quad \mathbf{S}_{-+}^{\alpha\beta}=\delta_{\alpha\beta}A_{-+}^{\alpha\beta}\ .$$

$A_{ab}^{\alpha\beta}$ represents an Arrhenius factor

$$A_{ab}^{\alpha\beta}=\exp(-h\omega_{ab}^{\alpha\beta}/k_BT)\ . \tag{A3}$$

The transformed matrix $\mathbf{R}^s$ is approximately of block-diagonal form. $\mathbf{R}_{--}^s$ provides the rates of the three fast orbital modes, which, in zeroth order are given by

$$z_-^\alpha=(1+A)\Gamma+O(\Gamma_s)\ . \tag{A4}$$

The eigenvalues of $\mathbf{R}_{++}^s$, on the other hand, represent the phosphorescence decay rate γ_p and the two spin relaxation rates. (The coupling between $\mathbf{R}_{--}^s$ and $\mathbf{R}_{++}^s$ is of the order Γ_s/Γ).

The matrix $\mathbf{R}_{++}^s$ is of the form

$$R_{++}^s=\begin{pmatrix}A_2\Gamma_2+A_3\Gamma_3+\delta_1 & -\Gamma_3 & -\Gamma_2\\ -A_3\Gamma_3 & A_1\Gamma_1+\Gamma_3+\delta_2 & -\Gamma_1\\ -A_2\Gamma_2 & -A_1\Gamma_1 & \Gamma_1+\Gamma_2+\delta_3\end{pmatrix}\ . \tag{A5}$$

Here δ_α are the phosphorescence rates from the quasiequilibrium doublet $|+,\alpha\rangle$ and $|-,\alpha\rangle$:

$$\delta_\alpha=(\gamma_{+\alpha}^p+A_{-+}^{\alpha\alpha}\gamma_-^p)/(1+A_{-+}^{\alpha\alpha})\ ;\quad A_{-+}^{\alpha\alpha}\cong A\ . \tag{A6}$$

Γ_α represent combinations of spin relaxation rates

$$\Gamma_1=[\Gamma_{++}^{32}+A_{-+}^{23}\Gamma_{-+}^{23}+A(\Gamma_{-+}^{32}+\Gamma_{--}^{32})]/[1+A]\ ,$$
$$\Gamma_2=[\Gamma_{++}^{31}+A_{-+}^{13}\Gamma_{-+}^{13}+A(\Gamma_{-+}^{31}+\Gamma_{--}^{31})]/[1+A]\ , \tag{A7}$$
$$\Gamma_3=[\Gamma_{++}^{21}+A_{-+}^{12}\Gamma_{-+}^{12}+A(\Gamma_{-+}^{21}+\Gamma_{--}^{21})]/[1+A]\ ,$$

and A denotes the low energy Arrhenius factors

$$A_1=A_{++}^{32},\quad A_2=A_{++}^{31},\quad A_3=A_{++}^{21}\ . \tag{A8}$$

$A_{-+}^{\alpha\alpha}$ is approximated by A. In Eqs. (A6) and (A7) we have ordered the sublevels $(X,Y,Z)=(1,2,3)$ according to $\epsilon_a^1<\epsilon_a^2<\epsilon_a^3$, and this yields the cyclic asymmetry of the coefficients Γ_α and A_α.

If $\delta_1=\delta_2=\delta_3=0$, the matrix [Eq. (A5)] is singular, and the related characteristic polynomial $p_0^{(3)}(z)=zp_0^{(2)}(z)$ can be used to calculate the rate constants of the two spin relaxation modes (in zeroth order with respect to γ_p/Γ_s).

The third eigenvalue, z_p, is obtained from the Taylor expansion

$$p(z_p)=0\cong p(z_p^{(0)}=0)+p'(z_p^{(0)}=0)\times(z_p-0)\ . \tag{A9}$$

Here, we have made use of the fact that z_p is close to zero; this is so because $p(z)-p_0(z)=O(\delta_i)$ is a continuous function of δ_i. From $p(z)=z^3+az^2+bz+c$ and Eq. (A9) we obtain $z_p=-c/b$, and this yields to first order in γ_p/Γ_s:

$$z_p=[\delta_1X_1+\delta_2X_2+\delta_3X_3]/[X_1+X_2+X_3] \tag{A10}$$

$$X_1=A_1\Gamma_1\Gamma_2+\Gamma_2\Gamma_3+\Gamma_1\Gamma_3\ ,$$
$$X_2=A_2\Gamma_1\Gamma_2+A_3\Gamma_2\Gamma_3+A_3\Gamma_1\Gamma_3\ , \tag{A10a}$$
$$X_3=A_1A_2\Gamma_1\Gamma_2+A_2\Gamma_2\Gamma_3+A_2\Gamma_1\Gamma_3\ .$$

At very low temperatures (i.e., for $1 \gg A_1, A_2, A_3 \gg A_{-+}$, we may retain only A_1, A_2, and A_3 (A_2 in linear order) to obtain

$$z_p \cong \delta_1 + A^{21}_{++}(\delta_2 - \delta_1) + A^{31}_{++}(\delta_3 - \delta_1) + \frac{\Gamma^{32}_{++}\Gamma^{31}_{++}}{\Gamma^{21}_{++}(\Gamma^{32}_{++} + \Gamma^{31}_{++})} A^{32}_{++}(\delta_2 - \delta_1) \ . \tag{A11}$$

APPENDIX B: RELAXATION PARAMETERS IN SITE REPRESENTATION: COMPARISON WITH THE HAKEN-STROBL RESULTS

Making use of the Haken–Strobl (HS) assumptions (see Sec. V A), we find the following relaxation parameters (cf. Table III):

$$\begin{aligned} \tilde{\Gamma} &= s^2\gamma_0 + 2c^2\gamma_1 \ , \\ \tilde{\Gamma}_{\mathrm{PD}} &= 2c^2\gamma_0 + 4s^2\gamma_1 \ , \\ \tilde{\psi}(\omega_{-+}) &= \tilde{\psi}(0) = sc(\gamma_0 - 2\gamma_1) \ , \\ \tilde{A} &= 1 \ , \quad (\text{i.e., } \hbar\omega_{-+} \ll k_BT) \ . \end{aligned} \tag{B1}$$

The quantities on the left-hand side refer to the dimer representation, γ_0 and γ_1 are the site-energy and transfer-integral fluctuations defined in Eq. (51), and c and s contain the information about the stationary HS Hamiltonian [Eq. (49)].

$$\begin{aligned} &c = \cos\theta \ , \quad s = \sin\theta \ , \\ &\tan\theta = -2\hat{J}/(\hat{\epsilon}_2 - \hat{\epsilon}_1) \ , \quad \hat{\epsilon}_2 > \hat{\epsilon}_1 \ . \end{aligned} \tag{B2}$$

In order to compare the HS relaxation parameters [Eq. (B1)] with those obtained from the Redfield equations, we give the more general relations between Γ, Γ_{PD}, and ψ (Table III) and the fluctuations in site space.

$$\begin{aligned} \Gamma &= \tfrac{1}{2}s^2\gamma_{\epsilon\epsilon}(\omega_{-+}) + sc[\gamma_{\epsilon J}(\omega_{-+}) + \gamma_{J\epsilon}(\omega_{+-})] + 2c^2\gamma_{JJ}(\omega_{-+}) \ , \\ \Gamma_{\mathrm{PD}} &= c^2\gamma_{\epsilon\epsilon}(\omega = 0) - 2sc[\gamma_{\epsilon J}(\omega = 0) + \gamma_{J\epsilon}(\omega = 0)] \\ &\quad + 4s^2\gamma_{JJ}(\omega = 0) \ , \\ \psi(\omega) &= \tfrac{1}{2}sc\gamma_{\epsilon\epsilon}(\omega) - s^2\gamma_{\epsilon J}(\omega) + c^2\gamma_{J\epsilon}(\omega) - 2sc\gamma_{JJ}(\omega) \ , \\ A &= \exp(-\hbar\omega_{-+}/k_BT) \ . \end{aligned} \tag{B3}$$

The correlation function on the right-hand side is given by the Fourier transforms of

$$\begin{aligned} \gamma_{\epsilon\epsilon}(t) &= \tfrac{1}{2}\langle[\delta\hat{\epsilon}_2(t) - \delta\hat{\epsilon}_1(t)][\delta\hat{\epsilon}_2(0) - \delta\hat{\epsilon}_1(0)]\rangle_B \ , \\ \gamma_{\epsilon J}(t) &= \tfrac{1}{2}\langle[\delta\hat{\epsilon}_2(t) - \delta\hat{\epsilon}_1(t)]\delta J(0)\rangle_B \ , \\ \gamma_{J\epsilon}(t) &= \tfrac{1}{2}\langle\delta J(t)[\delta\hat{\epsilon}_2(0) - \delta\hat{\epsilon}_1(0)]\rangle_B \ , \\ \gamma_{JJ}(t) &= \tfrac{1}{2}\langle\delta J(t)\delta J(0)\rangle_B \ . \end{aligned} \tag{B4}$$

Comparison between Eq. (B1) and Eqs. (B3) and (B4) shows that the HS results do apply only if $\gamma(\omega_{-+}) = \gamma(\omega = 0)$, $\gamma_{\epsilon J} = \gamma_{J\epsilon} = 0$, and $h\omega_{-+} \ll k_BT$. In this case $\gamma_{\epsilon\epsilon}(\omega) \to 2\gamma_0$ and $\gamma_{JJ} \to \gamma_1$ [Eq. (51)].

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