PHYSICAL REVIEW B VOLUME 28, NUMBER 9 1 NOVEMBER 1983

Spin relaxation of triplet excitons in molecular crystals

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(Received 11 January 1982; revised manuscript received 3 June 1983)

The primary electronic spin relaxation mechanism for triplet excitons in many molecular crystals arises from hopping transport between two orientationally inequivalent sites and is the source of both EPR linewidth and level equilibration. A generalized stochastic theory of resonance linewidth due to Blume which was previously applied to this mechanism and shown in its random-phase approximation (RPA) to yield the exciton EPR linewidth spectrum is here shown to give a *complete* formulation of both linewidth and equilibration rate. The method employs the averaged time-development superoperator of Blume's theory in the RPA in order to construct an equation of motion for the appropriately averaged spin-density matrix from which these two can be extracted. We show associations between this work and related studies by Kubo and Suna. Comparison is made between rates calculated for anthracene and values of T_1 deduced by Haarer and Wolf from a Bloch analysis of their EPR saturation measurements.

I. INTRODUCTION

This paper presents a general quantum-mechanical formulation which describes spin-relaxation processes of triplet excitons in molecular crystals. The analysis derives from Blume's stochastic theory of magnetic resonance linewidth[1] and applies to the class of lattices that have two orientationally inequivalent sites in the unit cell (e.g., such organic solids as the familiar aromatic hydrocarbons). While the theory was shown recently to account for the EPR linewidth spectrum of triplet excitons in the dimer lattice at room temperature,[2] we will show here that it is also conceptually broad enough to provide the basis for a more general treatment of exciton spin dynamics. The results are suited to obtaining directly resonance linewidths and the rates of spin relaxation that leads to equilibrium of the spin levels.

To appreciate the applicability of the Blume theory it is helpful to have a qualitative picture of the manner in which spin relaxation of triplet excitons is related to the nature of the transport. The primary fact is that propagation in organic molecular solids at room temperature is diffusive (incoherent transport) and thus approximated by a hopping model. Since all molecular sites of a given orientation excited to the triplet state define a single molecular spin Hamiltonian, the random hopping between the two subsets of differently oriented molecules induces a stochastic time dependence in the *exciton* spin Hamiltonian[3] which is then the relaxation perturbation. This description underlies the use of a purely stochastic theory, such as Blume's, in treating the hopping regime. Thus in the stochastic formalism the effective "hopping rate" between stochastic states (orientations) is introduced *a priori* as a phenomenological system parameter without any reference to a specific dynamical model. This means, incidentally, that the details of the transport will not be apparent in experiments that solely reflect the relaxation process, a fact which was discussed in our earlier application of the formalism.[2] We should point out here also that, while the primary theory was developed by Blume, it was later specialized by Dattagupta and Blume[4] to a random-phase approximation (RPA) which turns out to be the appropriate form for the exciton system.[2]

The process we have sketched provides a relaxation to equilibrium as well as a mechanism for homogeneous line broadening. This result is an automatic consequence of our analysis which is not apparent from the original linewidth formalism. The presence of a common mechanism for linewidth and relaxation is not to be understood, however, as implying a lifetime broadening of the resonance. Also, although other mechanisms may be present which do not fix both linewidth and relaxation simultaneously, the EPR linewidth studies in anthracene,[5-7] naphthalene,[5,8] pyrene,[2] and tetracene[9] show that the hopping mechanism is the dominant one in the lattices investigated so far.

Before turning to the theoretical development we should like to describe the context of this paper as it relates to other theories and to a number of experimental observations. As far as theory is concerned, although other authors have treated either the problem of relaxation or linewidth for these lattices, the inherent relationship between the two, as we shall demonstrate it, has not been an express concern in any previous work. Reineker's investigations of linewidth[10] do not include an explicit treatment of relaxation. Suna, on the other hand, developed a theory of relaxation for his analysis of the magnetic field dependence of delayed fluorescence from molecular crystals[11] but was not concerned with the problem of EPR linewidth.[12] With regard to experiment, although the EPR linewidth of triplet excitons in several aromatic lattices mentioned have already been explained, there is a specific need for relaxation rates since they figure in the analysis of several recent investigations. These include the field dependence of fluorescence from crystalline tetracene[13] and naphthalene,[14] the spin polarization in the EPR spectrum of triplet excitons in tetracene,[15] and the analysis of anthracene in an optical method for the direct measurement of rates.[16] The only published experiments devoted to a direct determination of relaxation in the aromatics at room temperature are the EPR saturation measurements of Haarer and Wolf on anthracene and naphthalene.[5] We shall compare their conclusions with a theoretical prediction in the last section.

In Appendix A we show the equivalence between the Blume and Kubo formulations of the stochastic model, while in Appendix B we discuss the relationship between the stochastic methods of this paper and Suna's theory of spin relaxation.

II. THEORY

Blume's theory treats a class of problems in which the Hamiltonian undergoes random transitions among a set of noncommuting operators that represent different stochastic states. These conditions are satisfied in the case of triplet excitons in the systems we discuss, since spin Hamiltonians associated with differently oriented molecular sites are noncommuting. In essence the theory addresses the basic problem of diagonalizing a Hamiltonian in which quantum-mechanical and classical (stochastic) degrees of freedom are strongly coupled. Blume's approach is to consider the time-development operator of the system rather than particular quantities that are closer to observation but more specialized or intricate in structure. The value of the theory lies in this methodology and for the purpose of evaluating a general linewidth expression, Blume has shown how to obtain an averaged time-development operator when the stochastic transitions are governed by a stationary Markov process. We shall adopt this basic strategy but recast the formalism and its development, the goal being the derivation of an asymptotic equation of motion for the density matrix of the system from which both relaxation rates and linewidth may be extracted.[17] In the process certain results from the original theory will be recovered but in a form that facilitates our generalization. Since we are concerned with the particular application to triplet excitons, the analysis does not require the primary Blume theory but invokes at an early stage the RPA which is incorporated naturally in our reformulation.

We turn first to the problem of determining the averaged time-development operator induced by a generalized Blume Hamiltonian that we write as

$$H(t)=V_{\xi(t)}\ , \tag{1}$$

where $\xi(t)$ represents a random process over a set of indices $\{\xi_i\}$ that are chosen to label the given stochastic manifold. Following Blume we exploit the advantages of a superoperator formalism and thus note that (1) generates the time-development superoperator

$$U_\pm(t)=\exp\left[\pm i\int_0^t H^x(t')dt'\right]\ , \tag{2}$$

where the Liouville operator H^x is defined by $H^xA\equiv[H,A]$ for any operator A. The double sign appears in (2) for the purposes of generality. That is, while the Heisenberg representation $(+)$ would be invoked for dynamical variables, we shall ultimately be concerned with the time dependence of the density matrix, thus requiring the Schrödinger representation $(-)$. We will maintain the double sign until this point is reached. In using superoperators we adopt the standard notational conventions underlying the formalism.[18,19] Ordinary operators are assigned to a Hilbert space, $A\rightarrow|A)$, with inner product $(B\,|A)\equiv\mathrm{Tr}(B^\dagger A)$ and represented in any orthonormal basis as

$$|A)=\sum_{m,n}\langle m\,|A\,|\,n\rangle\,|\,m,n)\ ,$$

where $|\,m,n)\equiv|\,m\rangle\langle n\,|$ and $\{\,|\,n\rangle\}$ is a complete set of states. With this notation our defining identity above for the Liouville operators is completed as

$$H^xA\rightarrow H^x\,|A)\ .$$

Our goal can now be stated: to obtain for the general operator A the time dependence given by

$$\langle A(t)\rangle=\langle U_\pm(t)\rangle A\equiv\bar U_\pm(t)\,|A)\ , \tag{3}$$

where the angular bracket $\langle\ \rangle$ denotes the average over stochastic processes in the interval $(0,t)$. The latter is defined in general as a term-by-term average of the time-ordered development of (2). That is

$$\bar U_\pm(t)=1+\sum_{n=1}^{\infty}(\pm i)^n\int_0^t dt_n\cdots\int_0^{t_2}dt_1\sum_{\xi}\sum_{\xi_n}\cdots\sum_{\xi_0}P_{n+2}(\xi,t;\xi_n,t_n;\ldots;\xi_1,t_1;\xi_0,0)V^x_{\xi_n}\cdots V^x_{\xi_1}\ , \tag{4}$$

where V_{ξ_i} is the value of $H(t)$ at $t=t_i$, and where all relevant information about the process $\xi(t)$ is contained in the hierarchy of joint probabilities $P_n(\xi_n,t_n;\ldots;\xi_1,t_1)$ of the values $\xi(t_n)=\xi_n,\ldots,\xi(t_1)=\xi_1$ at epochs $t_n\geq t_{n-1}\geq\cdots\geq t_1$ for $n=1,2,3,\ldots$. For a stationary process, $P_1(\xi_1,t_1)=P(\xi_1)\equiv p_\xi$ where p_ξ is identified with the *a priori* or equilibrium probability of finding the system in stochastic state ξ. For the particular case of a stationary, first-order Markov process, which we assume here, the joint probabilities are decomposed into products of conditional probabilities according to

$$P_{n+2}(\xi,t;\xi_nt_n;\ldots;\xi_1,t_1;\xi_0,0)=P(\xi,t\,|\,\xi_n,t_n)\cdots P(\xi_1,t_1\,|\,\xi_0,0)p_{\xi_0}\ , \tag{5}$$

where $P(\xi_i,t_i\,|\,\xi_{i-1},t_{i-1})$ is the probability that $\xi(t)=\xi_i$ at $t=t_i$ given that $\xi(t)=\xi_{i-1}$ occurred at the earlier time $t=t_{i-1}$. The right-hand side of (4) is then immediately resummed as

$$\bar{U}_{\pm}(t)=\sum_{\xi}\sum_{\xi_0}\langle U_{\pm}(t)\,|\,\xi(t)=\xi,\xi(0)=\xi_0\rangle p_{\xi_0}\ , \tag{6}$$

where the conditional average on the right satisfies

$$\langle U_{\pm}(t)\,|\,\xi(t)=\xi,\xi(0)=\xi_0\rangle=P(\xi,t\,|\,\xi_0,0)\pm i\int_0^t dt_1\sum_{\xi_1}P(\xi,t\,|\,\xi_1,t_1)V^x_{\xi_1}\langle U_{\pm}(t_1)\,|\,\xi(t_1)=\xi_1,\xi(0)=\xi_0\rangle\ . \tag{7}$$

The evolution of the conditional probabilities is determined by a master equation

$$\partial_t P(\xi,t\,|\,\xi'',0)=\sum_{\xi'}W(\xi,\xi')P(\xi',t\,|\,\xi'',0)\ , \tag{8}$$

in which the transition matrix $W(\xi,\xi')$ now incorporates all model-dependent information and fulfills the conditions

$$\begin{aligned}&W(\xi,\xi')p_{\xi'}=W(\xi',\xi)p_{\xi},\quad \xi\neq\xi'\\&\sum_{\xi}W(\xi,\xi')=0\ ,\end{aligned} \tag{9}$$

for detailed balance and conservation of probability, respectively. For the special case of the RPA (strong-collision limit) developed by Dattagupta and Blume,[4] the transition matrix has the form

$$W^{\mathrm{RPA}}(\xi,\xi')=\lambda p_{\xi}(1-\delta_{\xi\xi'})-\lambda(1-p_{\xi})\delta_{\xi'\xi}\ , \tag{10}$$

where λ is the single rate parameter of the model. In particular, for $\xi\neq\xi'$, we have $W(\xi,\xi')=\lambda p_{\xi}$, independent of the initial stochastic state ξ' (recall that here temporal ordering is to the left). Using (10), the RPA solution of (8) is readily found to be

$$P^{\mathrm{RPA}}(\xi,t\,|\,\xi_0,0)=p_{\xi}+(\delta_{\xi\xi_0}-p_{\xi})e^{-\lambda t}\ . \tag{11}$$

The RPA result for $\bar{U}_{\pm}(t)$, which is obtained by combining (6), (7), and (11), is expressed simply in terms of the Laplace transform, using the notational convention $f[p]\equiv\int_0^{\infty}dt\,e^{-pt}f(t)\equiv\mathscr{L}(f(t))$:

$$\bar{U}^{\mathrm{RPA}}_{\pm}[p]=\bar{U}^{0}_{\pm}[p+\lambda]\{1-\lambda\bar{U}^{0}_{\pm}[p+\lambda]\}^{-1}\ , \tag{12}$$

where

$$\bar{U}^{0}_{\pm}[p+\lambda]=\sum_{\xi}p_{\xi}[(p+\lambda)1\mp iV^x_{\xi}]^{-1}\ . \tag{13}$$

[The result for general $W(\xi,\xi')$ is found in Eq. (21) of Ref. 1 which we also exhibit in Appendix B.]

Following Ref. 4 we introduce the average Hamiltonian

$$\bar{V}=\sum_{\xi}p_{\xi}V_{\xi} \tag{14}$$

and the associated deviation

$$\Delta_{\xi}=V_{\xi}-\bar{V}\ . \tag{15}$$

Then the inverse of $\bar{U}^{0}_{\pm}[p+\lambda]$ may be expanded in powers of the deviation superoperator Δ^x_{ξ}. To second order one has (we drop the explicit RPA designation)

$$\bar{U}_{\pm}[p]=\{p\mp i\mathscr{P}_{\pm}[p]\}^{-1}\ , \tag{16}$$

where

$$\mathscr{P}_{\pm}[p]=\bar{V}^x\pm i\Gamma_{\pm}[p] \tag{17}$$

and

$$\Gamma_{\pm}[p]=\sum_{\xi}p_{\xi}\Delta^x_{\xi}[(p+\lambda)1\mp i\bar{V}^x]^{-1}\Delta^x_{\xi}\ , \tag{18}$$

which becomes exact for $\lambda\gg|\Delta^x_{\xi}|^2$. This completes the construction of the averaged time-development operator and we turn now to the primary goal of determining the asymptotic form of the averaged density matrix.

The density matrix evolves in general according to

$$|\rho(t))=U_{-}(t)\,|\rho(0))\ . \tag{19}$$

Because the longtime behavior of the system is independent of its initial specification we may however take $|\rho(0))=|\bar{\rho}(0))$ without loss of generality (i.e., complete ignorance of the initial stochastic state). Thus we will analyze

$$|\bar{\rho}(t))=\bar{U}_{-}(t)\,|\bar{\rho}(0))\ . \tag{20}$$

In order to incorporate the results (16)—(18) into (20) we note that

$$\begin{aligned}\mathscr{L}\partial_t\,|\bar{\rho}(t))&=(p\bar{U}_{-}[p]-1)\,|\bar{\rho}(0))\\&=-i(\bar{V}^x-i\Gamma_{-}[p])\,|\rho[p])\ ,\end{aligned} \tag{21}$$

so that with the aid of the convolution theorem

$$\partial_t\,|\bar{\rho}(t))=-i\bar{V}^x\,|\bar{\rho}(t))-\int_0^t d\tau\sum_{\xi}p_{\xi}\Delta^x_{\xi}e^{-(\lambda+i\bar{V}^x)\tau}\Delta^x_{\xi}\,|\bar{\rho}(t-\tau))\ . \tag{22}$$

Then with the transformation

$$|\rho(t))=e^{-i\bar{V}^x t}\,|\sigma(t)) \tag{23}$$

we obtain from (22)

$$\partial_t(n,m\,|\,\sigma(t))=-\sum_{l,l'}\sum_{n',m'}\int_0^t d\tau\,e^{-(\lambda+iE_{ll'}-iE_{nm})\tau}\sum_{\xi}p_{\xi}(n,m\,|\,\Delta^x_{\xi}\,|\,l,l')(l,l'\,|\,\Delta^x_{\xi}\,|\,n',m')\times e^{i(E_{nm}-E_{n'm'})(t-\tau)}(n',m'\,|\,\sigma(t-\tau)) \tag{24}$$

in the eigenbases $|n,m)$ of $\bar{V}^x$, i.e., where

$$\bar{V}^x\,|n,m)=(E_n-E_m)\,|n,m)=E_{nm}\,|n,m)\ . \tag{25}$$

The asymptotic analysis of (24) has two components. First, only those states $|n',m')$ which minimize the second exponent in (24) contribute to $|\sigma(t))$ as $t\to\infty$, regardless of the value of λ. Thus for $n\neq m$ we retain $|n',m')=|n,m)$ only, since then $E_{nm}-E_{n'm'}=0$. We neglect the influence of *degenerate* pairs $|n',m')\neq|n,m)$, which in the triplet spin resonance problem corresponds to the coincidence of the two transitions at isolated values of magnetic field. (There is no evidence that degeneracy effects have an observable consequence even within the region of overlap of transitions in the EPR spectra of triplet excitons in anthracene,[5,6] pyrene,[2] tetracene[15,20] or naphthalene.[5]) For the case $n=m$ we require $n'=m'$ without further restrictions since $E_{nn}=0$ automatically.

The terms that are retained in (24) imply that in the asymptotic regime the off-diagonal matrix elements of $|\bar{\rho}(t))$ evolve independently of each other and also become decoupled from the evolution of the diagonal matrix elements. The neglect of the degeneracies just described affects the first of these behaviors only; the decoupling of diagonal from off-diagonal evolution is accomplished quite generally by the ansatz which isolates contributions that make $E_{nm}-E_{n'm'}$ vanish. (We ignore the possibility that $E_{nm}=0$ for $n\neq m$, which is of no interest in the usual resonance context.)

The second component of the analysis takes account of the value of λ. Since the first exponential in (24) provides the integrand with a natural cutoff $\tau=O(\lambda^{-1})$, for $t\gg\lambda^{-1}$ one may extract $|\sigma(t-\tau))$ from the integral as $|\sigma(t))$. The combination of these procedures produces the result

$$\partial_t(n,m\,|\bar{\rho}(t))=-iE_{nm}(n,m\,|\bar{\rho}(t))-(1-\delta_{nm})K_{nm;nm}(\lambda-iE_{nm})(n,m\,|\bar{\rho}(t))-\delta_{nm}\sum_{n'}K_{nn;n'n'}(\lambda)(n',n'\,|\bar{\rho}(t))\ , \tag{26}$$

where we have also inverted (23) using (25) and defined the tetradic

$$K_{nm;n'm'}(\lambda)=\sum_{l,l'}\sum_{\xi}p_{\xi}\frac{(n,m\,|\Delta_{\xi}^{x}|\,l,l')(l,l'\,|\Delta_{\xi}^{x}|\,n',m')}{\lambda+iE_{ll'}} \tag{27}$$

which satisfies the sum rule

$$\sum_{n'}K_{nn;n'n'}(\lambda)=0\ . \tag{28}$$

In order to express (27) in terms of the ordinary operators Δ_ξ we use the decomposition

$$(n,m\,|\Delta_{\xi}^{x}|\,n',m')=\langle n\,|\Delta_{\xi}|\,n'\rangle\delta_{mm'}-\langle m'\,|\Delta_{\xi}|\,m\rangle\delta_{nn'} \tag{29}$$

and obtain

$$K_{nn;n'n'}(\lambda)=\frac{-2\lambda\sum_{\xi}p_{\xi}\,|\langle n\,|\Delta_{\xi}|\,n'\rangle|^2}{\lambda^2+(E_n-E_{n'})^2}\quad\text{for } n'\neq n\ , \tag{30}$$

while for $n\neq m$

$$K_{nm;nm}(\lambda-iE_{nm})=\sum_{\xi}p_{\xi}\left[\frac{1}{\lambda}(|\langle n\,|\Delta_{\xi}|\,n\rangle|^2+|\langle m\,|\Delta_{\xi}|\,m\rangle|^2-2\langle n\,|\Delta_{\xi}|\,n\rangle\langle m\,|\Delta_{\xi}|\,m\rangle)\right.$$
$$\left.+\frac{2|\langle n\,|\Delta_{\xi}|\,m\rangle|^2}{\lambda-i(E_n-E_m)}+\sum_{l\neq(n,m)}\left[\frac{|\langle n\,|\Delta_{\xi}|\,l\rangle|^2}{\lambda-i(E_n-E_l)}+\frac{|\langle m\,|\Delta_{\xi}|\,l\rangle|^2}{\lambda-i(E_m-E_l)}\right]\right]\ . \tag{31}$$

One sees from (26) that dissipation (relaxation, line broadening) is incorporated into the real parts of the tetradics. Isolating these contributions we have (asymptotically)

$$\begin{aligned}\partial_t(n,m\,|\bar{\rho}(t))\,|_{\text{diss}}\sim&-(1-\delta_{nm})R_{nm;nm}\,(n,m\,|\bar{\rho}(t))\\&+\delta_{nm}\sum_{n'\neq n}R_{nn;n'n'}[(n',n'\,|\bar{\rho}(t))\\&-(n,n\,|\bar{\rho}(t))]\ ,\end{aligned} \tag{32}$$

where

$$R_{nm;nm}=\operatorname{Re}K_{nm;nm}(\lambda-iE_{nm}) \tag{33}$$

as obtained from (31), and where

$$R_{nn;n'n'}=-K_{nn;n'n'}(\lambda),\quad n\neq n' \tag{34}$$

from (30), defining $R_{nn;nn}\equiv0$. According to the remarks following (18) and (24), (32) becomes exact if $\lambda\gg\max|\langle n\,|\Delta_{\xi}|\,n\rangle|^2$ and $t\gg\lambda^{-1}$. In actual practice the description in (32) is likely to be valid in many typical experimental situations, even when the above conditions are not strictly met. (The EPR spectrum of triplet excitons in pyrene[2] offers a good example of a case in which the nominal perturbation condition on λ is not met strongly, but the theory provides an accurate description of the observable linewidths.)

With Eq. (32) we complete the formal development from the Blume theory in the RPA of the required equation for the density matrix.[17] The identification of the parameters in (32) follows at once from its form. The $R_{nn,n'n'}$ determine the rate of equilibration of the level populations $N_n(t)=(n,n\,|\bar{\rho}(t))=\langle n\,|\bar{\rho}(t)\,|\,n\rangle$ and are thus identified with the spin relaxation rates. [Strictly speaking, the stochastic theory corresponds to the limit of infinite temperature, in which the equilibrium level population is distributed uniformly; this condition is satisfied in room-temperature triplet exciton resonance studies. If required, Boltzmann factors may be introduced into the definition of the infinite time limit $(n,n\,|\bar{\rho}(t))$ according to $(nn\,|\bar{\rho}(t))\rightarrow e^{\beta E_n}(n,n\,|\rho_\beta)$ where ρ_β is the canonical distribution.] The $R_{nm;nm}$ give the resonance linewidths as we can see in the following way. Note first that in either the Heisenberg or Schrödinger representations the absorption intensity for the linear response regime (no saturation) is proportional to the real part of

$$F[\pm i\omega]=(S_y\,|\,\bar{U}_\pm[\pm i\omega]\,|\,S_y) \tag{35}$$

with $(n,n\,|\,S_y)=0$. Under the conditions leading to (32) only the elements $(n,m\,|\,\bar{U}_\pm[p]\,|\,n,m)$ occur in (35), and thus (32) predicts

$$(n,m\,|\,\bar{U}_\pm(t)\,|\,n,m)\sim e^{(\pm iE_{nm}-R_{nm;nm})t}\,. \tag{36}$$

It follows that

$$\mathrm{Re}(F[\pm i\omega])=\sum_{n,m\neq n}\frac{|(n\,|\,S_y\,|\,m)\,|^2R_{nm;nm}}{(\omega-E_{nm})^2+R_{nm;nm}^2}\,, \tag{37}$$

which describes a set of Lorentzian lines having widths $R_{nm;nm}$. [We have ignored in (36) the shift of the spectrum E_{nm} that results from $\mathrm{Im}K_{nm;nm}(\lambda-iE_{nm})$.]

It is thus clear that in the stochastic formulation based on Blume's theory there is no mechanistic distinction between relaxation and homogeneous broadening. Both manifestations of dissipation have the same source in the temporal fluctuations of the model Hamiltonian.

III. EXAMINATION OF EPR SATURATION MEASUREMENTS

It is a straightforward exercise to calculate relaxation rates from Eqs. (30) and (34) (the matrix elements have been evaluated for a general crystal system in the Appendix of Ref. 2) and such values have already been used in the analyses of Refs. 13, 15, and 16 mentioned above. For our present discussion the EPR saturation measurements of Haarer and Wolf[5] on anthracene and naphthalene at room temperature offer data which probe the relaxation rates in these molecular crystals. The results have been interpreted by the authors as obeying the Bloch equations and therefore the analysis yields a relaxation time T_1 rather than the rates we have been discussing.[21] It is possible however to relate the two quantities if one accepts the applicability of the standard relationship for a three-level system[22,5] given by

$$\frac{1}{T_1}=W_1+2W_2\,, \tag{38}$$

where W_1 and W_2 are the rates for the $\Delta M=1$ and 2 transitions, respectively. We have calculated the right-hand side of (38) from (34) for anthracene to compare with the values of T_1 deduced from the experiments. Anthracene was chosen because its EPR spectrum is more fully characterized and understood,[6,23] including the effect of orientational disorder[7] on the crystals used by Haarer and Wolf. Since the disorder caused an excess contribution to the linewidth in the original experiments, thereby distorting the values of T_1 calculated from the Bloch equations, we have corrected these values to conform to the known homogeneous widths. The final comparison is shown in Fig. 1 for the magnetic field in the ac plane of anthracene.

From the figure it is obvious that the saturation analysis based on the Bloch equations is inconsistent with the calculated rates in the comparison made through Eq. (38). In view of the limited applicability of the Bloch model, the result is not surprising.

ACKNOWLEDGMENT

One of the authors (J.R.) acknowledges partial support from the Radiation and Solid State Laboratory of New York University, through a grant from the U. S. Department of Energy, Contract No. E[11-1]2386.

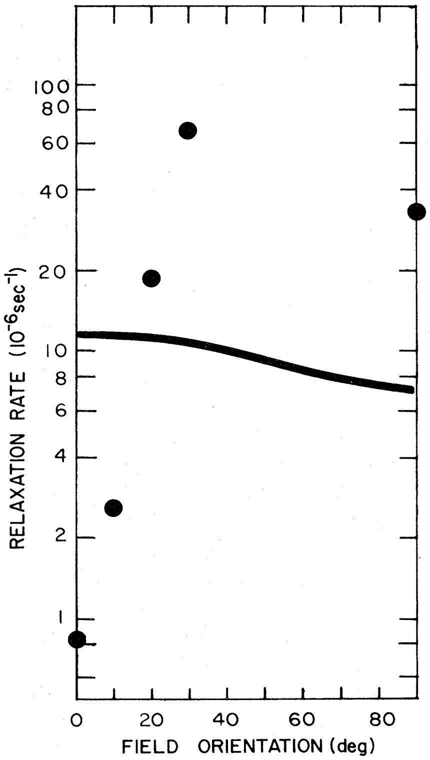

FIG. 1. Comparison between values of T_1 given by Haarer and Wolf (Ref. 5) for field variation in the a-c plane of anthracene at room temperature and relaxation rates calculated with a hopping rate $\Gamma_1=3200$ G (Ref. 6). The solid curve is W_1+2W_2 as in Eq. (38) and closed circles are from Ref. 5 after correction for disorder broadening as discussed in text. 0° marks the y^* (principal) axis of the excitonic fine-structure tensor.

APPENDIX A: EQUIVALENCE OF BLUME AND KUBO FORMULATIONS OF THE STOCHASTIC MODEL

Equation (3) of the text can be rewritten as

$$\langle A(t)\rangle=\sum_{\xi}A(\xi,t)\;, \tag{A1}$$

where

$$A(\xi,t)=\langle U_+(t)\,|\,\xi(t)=\xi\rangle A \tag{A2}$$

and

$$\langle U_+(t)\,|\,\xi(t)=\xi\rangle=\sum_{\xi_0}\langle U_+(t)\,|\,\xi(t)=\xi,\xi(0)=\xi_0\rangle p_{\xi_0}\;. \tag{A3}$$

From (7) one finds that the conditionally averaged operator $A(\xi,t)$ satisfies

$$A(\xi,t)=p_{\xi}A+i\int_0^t dt_1\sum_{\xi_1}P(\xi,t\,|\,\xi_1,t_1)V^x_{\xi_1}A(\xi_1,t_1) \tag{A4}$$

so that

$$\partial_t A(\xi,t)=iV^x_{\xi}A(\xi,t)+i\sum_{\xi'}W(\xi,\xi')A(\xi',t)\;. \tag{A5}$$

In obtaining (A5) from (A4) we have used the fact that $P(\xi,t\,|\,\xi_1,t)=\delta_{\xi\xi_1}$. Equation (A5) was first derived by Kubo[24] using an argument that makes explicit use of the property

$$\sum_{\xi'}W(\xi,\xi')p_{\xi'}=0\;. \tag{A6}$$

This condition is implied by the two conditions in (9). Thus the formulations of the stochastic model developed independently by Blume and Kubo are equivalent.

APPENDIX B: RELATION OF THIS STUDY TO SUNA'S THEORY OF SPIN RELAXATION OF TRIPLET EXCITONS

In a paper concerned with the kinematics of exciton-exciton annihilation in molecular crystals and its role in explaining the magnetic field dependence of delayed fluorescence, Suna (Appendix D of Ref. 11) developed a theory of triplet exciton spin relaxation which is equivalent to the one presented here. Specifically, $\zeta^{(1)}_{nn'}=R_{nn;n'n'}$, $\zeta^{(2)}_{nm}=R_{nm;nm}$, and $f(\frac{1}{2}G)=\lambda$, where the symbols on the left of each equality are Suna's. The physical significance of the rate parameter $\zeta^{(2)}_{nm}$ was not addressed, however, and it does not appear to be generally recognized that Suna's formula anticipated Reineker's equivalent expression for triplet exciton EPR linewidth which, as we have noted, was derived starting from the Haken-Strobl formalism. Since we have already discussed elsewhere[2] the relationship between Reineker's theory and Blume's formalism, we use this opportunity to establish the connection between Suna's approach and the stochastic method of Dattagupta and Blume.[4]

Suna begins his development with the stochastic Liouville equation [(D2) of Ref. 11]

$$\partial_t\rho(\vec{R}_i)=-iH^x(\vec{R}_i)\rho(\vec{R}_i)-\sum_j D_{ii,jj}\rho(\vec{R}_j)\;, \tag{B1}$$

where

$$D_{ii;jj}=\Psi\delta_{ij}-\Psi(\vec{R}_j-\vec{R}_i)\;. \tag{B2}$$

In (B1) $\rho(\vec{R}_i)$ and $H(R_i)$ are the density matrix and spin Hamiltonian, respectively, of an exciton at site $\vec{R}_i$, and in (B2) $\Psi(\vec{R})$ is the hopping rate between sites separated by $\vec{R}$;

$$\Psi=\sum_{\vec{R}\neq 0}\Psi(\vec{R}) \tag{B3}$$

is the total rate of hopping from any one site to all the others. We consider crystals composed of two sublattices A and B which define the stochastic states of the system. While the spin Hamiltonian takes on only two distinct values

$$H(\vec{R}_i)=V_q,\quad q=A,B \tag{B4}$$

depending on which of the two sublattices the site $\vec{R}$ resides, the lattice diffusion portion of (B1) includes "irrelevant" transport that does *not* induce transitions between them. We thus average out this intralattice hopping by introducing the quantities

$$\rho(q)=\sum_{i(q)}\rho(\vec{R}_i),\quad q=A,B \tag{B5}$$

where the indices $i(A)$ and $i(B)$ refer only to sites on the indicated sublattices. Then combining (B1)—(B5) and after some algebraic manipulation, we have

$$\partial_t\rho(q)=-iV^x_q\rho(q)+\sum_{q'}W(q,q')\rho(q')\;, \tag{B6}$$

where

$$W(q,q')=(1-2\delta_{q,q'})\Psi_{AB} \tag{B7}$$

and

$$\begin{aligned}\Psi_{AB}&=-\sum_{i(A)}D_{i(A)i(A);j(B)j(B)}\\&=\sum_{i(A)}D_{i(A)i(A);j(A)j(A)}\end{aligned} \tag{B8}$$

is the total hopping rate from any site to all sites of the other sublattice. In terms of Blume's convention of writing stochastic functions in explicit matrix form (denoted by a tilde) (B6) is

$$\partial_t\tilde{\rho}(t)=\left[-i\sum_q V^x_q\tilde{F}_q+\tilde{W}\right]\tilde{\rho}(t)\;, \tag{B9}$$

where $\tilde{F}$ is the projector into the stochastic state having label q. This immediately produces

$$\tilde{\rho}(t)=\tilde{U}_-(t)\tilde{\rho}(0)\;, \tag{B10}$$

where

$$\tilde{U}_-(t)=\exp\left[\left[-i\sum_q V_q^x\tilde{F}_q+\tilde{W}\right]t\right]$$

is identified with the conditional average $\langle U_-(t)\,|\,\xi(t)=\xi,\xi(0)=\xi_0\rangle$ of (6) since in (B10) stochastic states are specified at times $t=t$ and $t=0$. Thus

$$\tilde{U}_-[p]=\left[p\,1-\tilde{W}+i\sum_q V_q^x\tilde{F}_q\right]^{-1}, \qquad \text{(B11)}$$

which is the form of the general solution of (7) with $\tilde{W}$ at once in the form specified in the RPA, since (B7) may be recast as (10) with $p_A=p_B=\frac{1}{2}$ and

$$\lambda=2\psi_{AB}=8\Psi_d\ ,$$

where $\Psi_d=\Psi[\frac{1}{2}(\vec{a}+\vec{b})]$ as in Ref. 11.

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