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# Are the homogeneous linewidths of spin resonance (ODMR) and optical transitions related?

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This paper examines two problems that are central to the question raised in the title. First, we describe formally the origin of homogeneous broadening of ODMR and optical transitions in the presence and absence of spin-orbital couplings between the lowest triplet and other triplet or singlet states. Second, we deduce expressions that relate the spin-to-orbital widths to the rates of *orbital* and *spin* scatterings in the singlet and triplet states. In the absence spin-orbital coupling, it is found that the optical width caused by *pure* dephasing has a much different origin than the ODMR width. In the presence of spin-orbital coupling, on the other hand, the two widths are *related* and depend on the phonon-induced scattering cross section of the ground electronic state and the other spin sublevel that is involved in the ODMR transition and is not perturbed by spin-orbital interactions. Throughout the paper the coupling of only one triplet sublevel to the singlet was chosen to sufficiently represent the effect of spin-orbital coupling on ODMR and optical widths. Finally, using these theoretical findings we compare the results with some available data on aromatics ( $\pi\pi^*$  states) and azines and carbonyls ( $n\pi^*$  states) and also conjecture on possible future experiments.

## I. INTRODUCTION

In this paper, we address the question of why the line-width of a spin resonance transition may or may not differ from the homogeneous width of an optical transition taking place between these spin sublevels and the ground state of the system. The question is relevant to the problem of triplet exciton transport in crystals and to the origin of relaxations of a guest molecule imbedded in a host lattice.

The triplet state of the crystal or the impurity molecule is usually excited either indirectly through the singlet to obtain the ESR of the triplet, or directly to the triplet to obtain the optical line shape. Under these circumstances, the spin resonance width can be determined by direct zero-field ESR measurement using the methods of Hutchison *et al.*<sup>1</sup> or by using the technique of ODMR (optical detection of magnetic resonance) developed recently by several groups.<sup>2</sup> Similar to the ODMR transition, the optical transition obtained from the direct singlet-triplet absorption may or may not be homogeneously broadened. Typically, the ODMR inhomogeneous width is  $\sim 1-10$  MHz while that of the optical is  $\sim 1-10$  cm<sup>-1</sup>. The homogeneous width in both cases could be lifetime limited, i.e., Hz to kHz for sec to msec decay times.

Questions about the origin of the difference in the homogeneous width between ODMR and optical transitions were first raised after Harris and co-workers<sup>3</sup> had determined the coherence properties of triplet excitons and dimers from ODMR line shape analysis. Francis-Harris and Zewail-Harris experiments<sup>3</sup> provided a coherence time for the triplet exciton of  $\sim 10^{-7}$  sec. Knox's group<sup>4</sup> have argued that to obtain the coherence or dephasing time [i.e., the time related to the homogeneous width  $\Delta\nu_H$  by the uncertainty relation-

ship  $(\pi T_2)^{-1} = \Delta\nu_H$ ] of optical transitions, it is not sufficient to use the ODMR width alone. In a model calculation, they computed the ODMR linewidth of the dimer using Haken *et al.*<sup>5</sup> theory of line shape as applied to 1, 2, 4, 5-tetrachlorobenzene systems. Furthermore, they obtained "reasonable" values for the spin-orbital coupling matrix element in tetrachlorobenzene and phenazine<sup>6</sup> using this model and assuming that the optical transition width of the singlet ( $\sim 3$  cm<sup>-1</sup>) is "homogeneous." This assumption is a crucial one since optical transitions with 7 MHz real homogeneous width, and not the  $\sim 3$  cm<sup>-1</sup> apparent (inhomogeneous) width, have recently been reported.<sup>7</sup> So the question is as follows: *In general, are the homogeneous linewidths of spin resonance and optical transitions related?*

In this work, we start first by defining the system and present formal theoretical expressions for homogeneous broadening in solids. We then relate these expressions to ODMR and optical transitions whose states are coupled or not coupled by spin-orbital interactions. We restrict ourselves to intramolecular effects and consider intermolecular coupling effects in dimers and excitons elsewhere. Finally, we apply the results to present data of  $n\pi^*$  and  $\pi\pi^*$  state systems and conjecture on possible future experiments.

## II. SPIN-ORBITAL BORN-OPPENHEIMER STATES AND THE SYSTEM

We shall consider the following simple case of a ground singlet, excited singlet, and triplet states that are coupled by spin-orbital interactions. It is assumed that only one spin state is coupled to the excited singlet, although one can extend the treatment to more than one channel coupling (see Fig. 1). Also, the electronic part of the vibronic Born-Oppenheimer wave functions is considered without showing the effect of vibrational quantum number on the width. The latter is a separate issue and is treated elsewhere.<sup>8</sup>

The wave function for the spin-orbital triplet state

<sup>a)</sup> Alfred P. Sloan Fellow.

<sup>b)</sup> Contribution No. 5913.

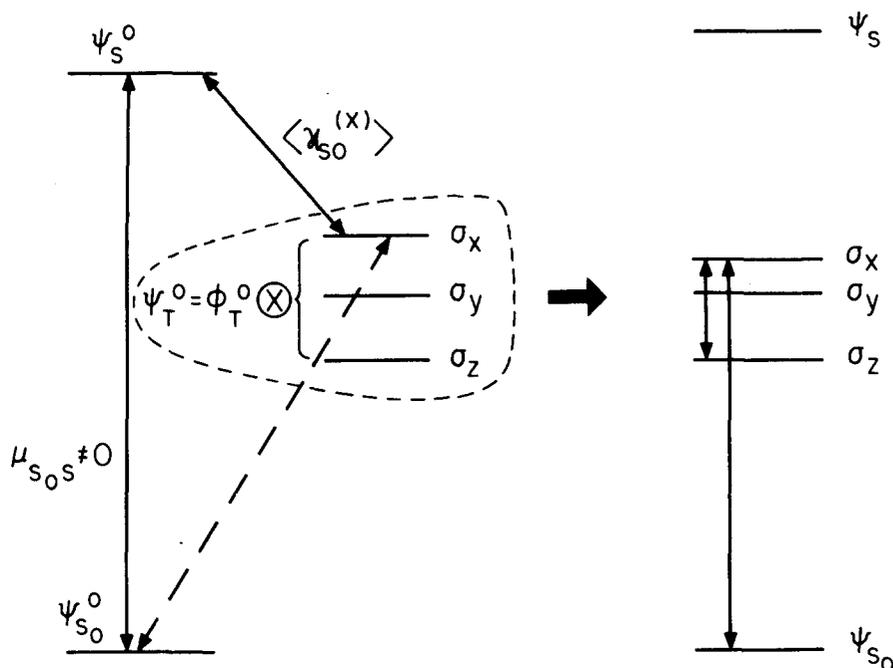


FIG. 1. A schematic for a one-channel spin-orbital coupling in molecules. The drawing on the left is for unperturbed singlets and triplet states while that on the right is after SOC is turned on.

can be written as

$$\psi_T(\sigma_i) = a\psi_T^0 + b\psi_S^0, \quad (\text{II. 1})$$

where  $a$  and  $b$  are the mixing coefficients and  $\sigma_i$  is the  $i$ th spin function of the first triplet state in zero magnetic field. The superscript zero is to indicate that the singlet and triplet functions are zeroth order. If the spin-orbital Hamiltonian  $\mathcal{H}_{SO}$  mixes  $\sigma_x$  with the excited singlet, then

$$\psi_T^{(x)} = a\phi_T^0\sigma_x + b\phi_S^0\sigma_s, \quad (\text{II. 2})$$

where (to second order)

$$|b|^2 = 1 - |a|^2 = \left| \langle \phi_T^0\sigma_x | \mathcal{H}_{SO}^{(x)} | \phi_S^0\sigma_s \rangle \right|^2 \Delta E_{s,t}^{-2}. \quad (\text{II. 3})$$

The zero order singlet-triplet splitting is denoted by  $\Delta E_{s,t}$ . For coupling with more singlets and/or triplets of the appropriate symmetry, the second term in Eq. (II. 2) becomes a sum over all these states. Note that only for two electron (not more than two) systems can we write the wave function as a product of  $\phi^0$  and  $\sigma$  when SOC is zero.

The states of Eq. (II. 2) are the spin-orbital states which make the singlet-triplet transition probability nonzero. The intensity of the optical transition in this case thus becomes

$$I_{op} = I_{s_0-T}^{(x)} = \left| \langle \psi_{s_0} | \mu | \psi_T^{(x)} \rangle \cdot \epsilon \right|^2 = b b^* \left| \mu_{s_0s} \cdot \epsilon \right|^2, \quad (\text{II. 4})$$

while

$$I_{s_0-T}^{(y)} = I_{s_0-T}^{(z)} = 0. \quad (\text{II. 5})$$

The angular dependence of the transition intensity depends on the dot product of the optical transition moment  $\mu$  and the applied (light) field amplitude  $\epsilon$ . Constants before the matrix elements are ignored.

For the spin case, the transition is between the spin sublevels of the first triplet state. These sublevels are

described by the *zero field* spin functions  $\sigma_i$  which are quantized along the molecular symmetry axes  $x$ ,  $y$ , and  $z$  (e.g.,  $C_{2v}$  point group) and defined by the following relationship:

$$S_i \sigma_i = 0 \quad (i = x, y, z). \quad (\text{II. 6})$$

Thus, the  $x$  sublevel has a  $yz$ -quantization plane defined according to Eq. (II. 6) since  $S_x \sigma_x = 0$ ;  $S_x$  is the total spin angular momentum for the two electrons. Different from the optical transition, the intensity of the spin transition between  $\sigma_x$  and  $\sigma_z$  is

$$I_{sp1n} = a a^* \left| \langle \sigma_x | \mathbf{M} | \sigma_z \rangle \cdot \mathbf{H} \right|^2, \quad (\text{II. 7})$$

where  $\mathbf{M}$  is the magnetic dipole operator which transforms like the irreducible representation of the  $R_x$ ,  $R_y$ ,  $R_z$  vectors of the point group symmetry.  $\mathbf{H}$  is the magnetic field of the applied microwaves. For generalization to mixed electric and magnetic dipole transitions, see the paper by El-Sayed.<sup>9</sup>

The above equations provide us with expressions for the intensity but not the linewidth or shape. Because we ignored the spin-orbital mixing to all  $\sigma_i \neq \sigma_x$ , the optical transition will not suffer from inhomogeneous broadening due to the zero-field splittings. In other words, if all spin states are allowed to the ground state [like Eq. (II. 4) and not Eq. (II. 5)], then three homogeneous transitions should be observed. We now turn to the problem of expressing the line shape function in terms of orbital and spin scattering parameters for both transitions (spin and optical) in order to separate the different effects of interest.

### III. THE WIDTH OF TWO-LEVEL TRANSITIONS IN A SOLID

The absorption line shape (or cross section) as a function of frequency can be expressed as the Fourier trans-

form of a correlation function

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mu(0) \cdot \mu(t) \rangle e^{-i\omega t} dt, \quad (\text{III. 1})$$

where  $\langle \dots \rangle$  is an ensemble average given by the trace of the product of the appropriate equilibrium density operator  $\hat{\rho}$  and  $\hat{\mu}(0) \cdot \hat{\mu}(t)$ , i. e.,

$$\langle \mu(0) \cdot \mu(t) \rangle = \text{Tr} \{ \hat{\rho} \hat{\mu}(0) \cdot \hat{\mu}(t) \}. \quad (\text{III. 2})$$

It is usually assumed that the correlation function<sup>10</sup> decays exponentially according to

$$\langle \mu(0) \cdot \mu(t) \rangle = \langle \mu(0) \cdot \mu(0) \rangle \exp[i(\omega_0 + \delta\omega)t - \Gamma t], \quad (\text{III. 3})$$

where  $\delta\omega$  is the shift and  $\Gamma$  is the decay constant. Substituting Eq. (III. 3) in (III. 1) and carrying out the integration yields

$$I(\omega) = C [(\omega - \omega_0 - \delta\omega)^2 + \Gamma^2]^{-1}, \quad (\text{III. 4})$$

where  $C$  is a constant that can be determined from the normalization condition of Eq. (III. 4). The result of Eq. (III. 4) is expected, of course, since we have already assumed that the two levels under consideration couple weakly to the "environment" (radiation field continuum and/or the phonon bath continuum). Furthermore, the result of Eq. (III. 4) assumes that the line is *homogeneously* broadened, and that the dependence of the linewidth or shift on temperature is contained in  $\Gamma$  and  $\delta\omega$ , respectively.

Formally, in solids,  $\Gamma$  can be written as

$$\Gamma = \frac{1}{T_2} = \frac{1}{2} (\gamma_i + \gamma_f) + \gamma_{if}, \quad (\text{III. 5})$$

where  $\gamma_i$  and  $\gamma_f$  are, respectively, the decay rates of the initial and final states and  $\gamma_{if}$  is given by<sup>11</sup>

$$\gamma_{if} = \frac{\pi}{\hbar} \sum_{p,p'} W_p |\langle ip' | \mathbf{T} | ip \rangle - \langle fp' | \mathbf{T} | fp \rangle|^2 \delta(E_p - E_{p'}). \quad (\text{III. 6})$$

In the above expression,  $p$  and  $p'$  denote the phonon states of the solid and the  $\delta$  function ensures that the scattering of state  $i$  and  $f$  through the "scattering" transition operator  $T$  is conserving energy (elastic processes). The other terms  $\gamma_i$  and  $\gamma_f$ , on the other hand, are inelastic and can be written explicitly using the golden rule with  $T$  being the operator. Finally,  $W_p$  is the thermal distribution function that will be discussed later.

The term  $\gamma_{if}$  is what might be called the *pure* dephasing rate  $(T_2')^{-1}$ , and  $\gamma_i$  and  $\gamma_f$  are the  $T_1$ -type terms. Specifically, we can now write

$$\Gamma = \frac{1}{2}(T_{1i}^{-1} + T_{1f}^{-1}) + (T_2')^{-1}. \quad (\text{III. 7})$$

The FWHH of the Lorentzian in Eq. (III. 4) is simply  $2\Gamma$ , and we therefore have the following relationship for the homogeneous width of the transition:

$$\frac{1}{\pi T_2} = \Delta\nu_H (\text{in sec}^{-1}) = \frac{2\Gamma (\text{in rad sec}^{-1})}{2\pi}. \quad (\text{III. 8})$$

This is the width that we shall deal with for the optical and spin transitions under consideration. Note that, from Eq. (III. 3),  $2\Gamma$  is the decay rate for the squared

amplitude of the correlation function while  $\Gamma$  is simply the decay rate of the correlation function itself. Thus,  $(2\Gamma)^{-1} = T_2/2$  is what is known as the dephasing time only if one is measuring a quantity that is proportional to the square of the correlation function as in the case of some picosecond dephasing experiments.<sup>12</sup>

From Eqs. (III. 5) and (III. 6), we can now divide the problem under consideration, namely, the origin of spin and optical dephasing, into two problems: the effect of temperature on the width and shift and the nature of molecular scattering matrix elements which explicitly depends on the wave function (spin or orbital). The former has been dealt with before<sup>13,14</sup> in solids and liquids using Eq. (III. 6) and we shall not focus attention to it here. Thus, in the coming sections, when treating the latter case, it should be kept in mind that the comparison between the spin and the optical case is done at the same temperature; the temperature dependence function ( $T^4$ ,  $T^7$ , etc.) contained in  $\sum_{p,p'}$  is the same but the cross section (matrix elements for scattering) is different.<sup>15</sup>

#### IV. SPIN VS OPTICAL MOLECULAR LINEWIDTH

For a triplet state at low temperatures, it is known that the spin-lattice relaxation is usually slow relative to the lifetime of the state. This means that the  $T_1$  process between the two spin sublevels  $\sigma_x$  and  $\sigma_y$  is inefficient and will contribute a homogeneous width on the order Hz since  $T_1$  is  $\sim 1$  sec. The  $T_1$  for the singlet-triplet optical transition determined by the lifetime of the triplet state is again sec to msec, thus giving a homogeneous width on the order of Hz–kHz. It appears, therefore, that the elastic term  $\gamma_{if}$  may be important in contributing to the observed homogeneous width (MHz–GHz) of the transitions especially at relatively high temperatures. In this section, we treat  $\gamma_{if}$  for the different cases of interest.

##### A. No spin-orbital coupling

Rewriting Eq. (III. 6) as

$$\begin{aligned} \gamma_{if} &= \frac{\pi}{\hbar} \sum_{p,p'} W_p |\langle ip' | \langle i | \mathbf{T} | i \rangle - \langle f | \mathbf{T} | f \rangle | p \rangle|^2 \delta(E_p - E_{p'}) \\ &= \frac{\pi}{\hbar} \sum_{p,p'} W_p |\langle ip' | \Delta \mathbf{T} | p \rangle|^2 \delta(E_p - E_{p'}) \end{aligned} \quad (\text{IV. 1})$$

allows us to deal with the matrix elements separately<sup>13</sup> from the temperature affecting terms. The transition matrix  $\mathbf{T}$  can be expanded using the Dyson equation:

$$\mathbf{T} = \mathbf{V} + \mathbf{V} G_0 \mathbf{V} + \dots, \quad (\text{IV. 2})$$

where  $V$  is the interaction potential causing the initial and final states either to decay or to get "blurred" by elastic collisions.  $G_0$  is the free propagator or Green operator. Replacing  $\mathbf{T}$  by  $\mathbf{V}$  is the lowest order approximation that simplifies the problem considerably and allows one to carry out some model calculations. It should be kept in mind, however, that, because of  $G_0$  in Eq. (IV. 2),  $\mathbf{T}$  is frequency dependent, and if  $\mathbf{T}$  is used instead of  $\mathbf{V}$ , one may evaluate the dephasing rate at a particular frequency, say the transition frequency.

Replacing  $\mathbf{T}$  by  $\mathbf{V}$  eliminates the dependence of  $\mathbf{T}$  on frequency via  $G_0$ .

The operator  $\mathbf{V}$  for the spin and orbital scattering may be written as<sup>16</sup>

$$\mathbf{V} = \mathbf{V}_{\text{or}} + \mathbf{V}_{\text{spin}}, \quad (\text{IV. 3})$$

thus yielding<sup>17</sup>

$$\Delta\mathbf{V} = \Delta\mathbf{V}_{\text{or}} + \Delta\mathbf{V}_{\text{spin}}. \quad (\text{IV. 4})$$

The wave function for the triplet state in the absence of spin-orbital coupling is simply given by Eq. (II. 1) with  $a = 1$ .

For the ODMR transition,  $\Delta\mathbf{T}_{\text{or}}$  and  $\Delta\mathbf{T}_{\text{spin}}$  become

$$\begin{aligned} \Delta\mathbf{T}_{\text{or}} &= \langle \phi_T^0 | \mathbf{T}_{\text{or}} | \phi_T^0 \rangle \langle \sigma_x | \sigma_x \rangle - \langle \phi_T^0 | \mathbf{T}_{\text{or}} | \phi_T^0 \rangle \langle \sigma_z | \sigma_z \rangle \\ &= 0 \end{aligned} \quad (\text{IV. 5})$$

and

$$\begin{aligned} \Delta\mathbf{T}_{\text{spin}} &= \langle \sigma_x | \mathbf{T}_{\text{spin}} | \sigma_x \rangle \langle \phi_T^0 | \phi_T^0 \rangle - \langle \sigma_z | \mathbf{T}_{\text{spin}} | \sigma_z \rangle \langle \phi_T^0 | \phi_T^0 \rangle \\ &= \langle \mathbf{T}_{\text{spin}} \rangle_{xx}^0 - \langle \mathbf{T}_{\text{spin}} \rangle_{zz}^0 \equiv \Delta\mathbf{T}, \end{aligned} \quad (\text{IV. 6})$$

where the 0 on the matrix element denotes the absence of spin-orbital coupling. The width of the transition from the  $\gamma_{if}(z-x)$  term is *only* given by difference in the spin scattering matrix elements. Thus, if the spin sublevels  $\sigma_x$  and  $\sigma_z$  elastically dephase by the same rate, then the width of the transition is entirely determined by the lifetime broadenings.

For the optical transition, similarly we have

$$\Delta\mathbf{T} = \langle \langle \mathbf{T}_{\text{or}} \rangle_{s_0 s_0}^0 - \langle \mathbf{T}_{\text{or}} \rangle_{T T}^0 \rangle + \langle \langle \mathbf{T}_{\text{spin}} \rangle_{s_0 s_0}^0 - \langle \mathbf{T}_{\text{spin}} \rangle_{xx}^0 \rangle. \quad (\text{IV. 7})$$

We can now draw the following important conclusions: (a) the width of the two transitions must be different since the matrix elements in Eqs. (IV. 6) and (IV. 7) are different; (b) the orbital portion of the scattering cancels for the ODMR transition not because the scattering amplitude of each level is zero; (c) the two transitions (ODMR and optical) have the same width from the pure dephasing events, if the low-energy level in both cases is *not* scattering by the reservoir. This can be easily seen from Eqs. (IV. 6) and (IV. 7); in both bases,  $\Delta\mathbf{T}$  becomes

$$\Delta\mathbf{T} \text{ (ODMR or optical)} = \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle. \quad (\text{IV. 8})$$

Thus, in the absence of SOC, optical and spin transitions will have the same width (by pure dephasing) if the common level is the only perturbed level by phonon scatterings. It should be remembered, however, that in the absence of SOC, the optical transition from the ground state to  $\sigma_x$  is forbidden because of spin orthogonality and only in higher order can the two levels be connected (see Sec. II).

## B. Spin-orbital coupling effects

The effect of SOC is to mix the triplet with the singlet, thus lifting the cancellation of the orbital part in Eq. (IV. 5). This is because the mixing brings into play another electronic state which has different orbital distribution. We shall now consider the case of spin and

optical transitions separately for cases where  $\langle \mathcal{H}_{SO}^x \rangle \neq 0$  and  $\langle \mathcal{H}_{SO}^y \rangle = \langle \mathcal{H}_{SO}^z \rangle = 0$ .

### 1. ODMR transitions

In this case, the wave function for the  $x$  spin level is given by Eq. (II. 2). Thus,

$$\Delta\mathbf{T}_{\text{or}} = b^* b [\langle \mathbf{T}_{\text{or}} \rangle_{ss}^0 - \langle \mathbf{T}_{\text{or}} \rangle_{TT}^0] \quad (\text{IV. 9})$$

and

$$\begin{aligned} \Delta\mathbf{T}_{\text{spin}} &= \langle \langle \mathbf{T}_{\text{spin}} \rangle_{xx}^0 - \langle \mathbf{T}_{\text{spin}} \rangle_{zz}^0 \rangle \\ &+ b^* b \langle \langle \mathbf{T}_{\text{spin}} \rangle_{ss}^0 - \langle \mathbf{T}_{\text{spin}} \rangle_{xx}^0 \rangle. \end{aligned} \quad (\text{IV. 10})$$

By comparing Eq. (IV. 5) with (IV. 9) and Eq. (IV. 6) with (IV. 10), we can see that, as a result of SOC, we have gained additional terms for line broadening that are proportional to  $|b|^2$  of Eq. (II. 3). To find the value of  $\Delta\mathbf{T}$ , we just simply add  $\Delta\mathbf{T}_{\text{or}}$  and  $\Delta\mathbf{T}_{\text{spin}}$ :

$$\begin{aligned} \Delta\mathbf{T}(\text{ODMR})|_{\text{SOC} \neq 0} &= |b|^2 \{ \langle \phi_s^0 \sigma_s | \mathbf{T} | \phi_s^0 \sigma_s \rangle - \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle \} \\ &+ \{ \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle - \langle \phi_T^0 \sigma_z | \mathbf{T} | \phi_T^0 \sigma_z \rangle \}. \end{aligned} \quad (\text{IV. 11})$$

Subtracting Eq. (IV. 6) from (IV. 11), we obtain

$$\begin{aligned} (\Delta\mathbf{T})_{\text{SOC} \neq 0} - (\Delta\mathbf{T})_{\text{SOC} = 0} &= |\langle \mathcal{H}_{SO}^x \rangle|^2 \Delta E_{s,t}^{-2} \\ &\times \{ \langle \phi_s^0 \sigma_s | \mathbf{T} | \phi_s^0 \sigma_s \rangle - \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle \}. \end{aligned} \quad (\text{IV. 12})$$

The following may therefore be concluded: First, if the singlet and triplet states purely scatter to the same extent, there will be no difference in the homogeneous width of ODMR transitions even if the spin-orbital mixing between the singlet and the triplet is very large. Second, the singlet state dephasing rate contributes to the homogeneous width of the triplet ODMR transition in a way that is reminiscent of vibronic coupling mechanisms in molecules. In other words, as a result of SOC, the ODMR transition "steals" a width from the singlet. Third, as expected when  $\langle \mathcal{H}_{SO}^x \rangle = 0$ ,  $\Delta\mathbf{T}$  is unchanged. Finally, the difference between  $\Delta\mathbf{T}$  of ODMR transitions when  $\text{SOC} \neq 0$  and  $\text{SOC} = 0$  is directly proportional to  $|\langle \mathcal{H}_{SO} \rangle|^2$  and inversely proportional to  $|\Delta E_{s,t}|^2$ , the square of the energy separation between the singlet and triplet state. We shall later estimate these differences numerically and calculate the actual width by substituting Eq. (IV. 12) in Eq. (IV. 1), which yields the *quartic* dependence of  $\gamma_{if}$  on both  $\langle \mathcal{H}_{SO} \rangle$  and  $\Delta E_{s,t}$ .

### 2. Optical transitions

According to Eq. (II. 4), only the  $\sigma_x$  sublevel is active in the optical transition from the ground state. Similar to the above treatment, the width of the resonance can be calculated if we know  $\Delta\mathbf{T}_{\text{or}}$  and  $\Delta\mathbf{T}_{\text{spin}}$ . Thus, the total  $\Delta\mathbf{T}$  (optical) is

$$\begin{aligned} \Delta\mathbf{T} \text{ (optical)}|_{\text{SOC} \neq 0} &= |b|^2 \{ \langle \phi_s^0 \sigma_s | \mathbf{T} | \phi_s^0 \sigma_s \rangle - \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle \} \\ &+ \{ \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle - \langle \phi_{s_0}^0 \sigma_{s_0}^0 | \mathbf{T} | \phi_{s_0}^0 \sigma_{s_0}^0 \rangle \}. \end{aligned} \quad (\text{IV. 13})$$

Comparing the above results with those obtained for ODMR transitions [Eq. (IV. 11)], we see that the first term in both equations is identical and that the second term reflects the effects before the SOC was turned on. For the ODMR case, this is clear [Eq. (IV. 11)], but

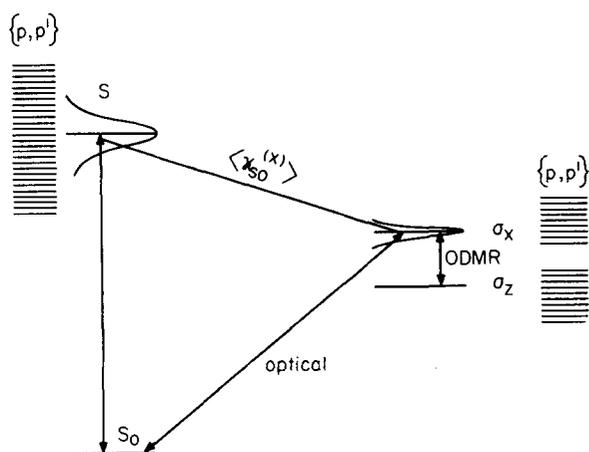


FIG. 2. The optical and ODMR transitions considered in this paper, together with their phonon reservoir  $p$  and  $p'$ .

for the optical case, one has to be careful about the resulting effects in the absence of SOC simply because the transition is not electric dipole allowed. [The second term in Eq. (IV. 13) appears because we are dealing with the case where SOC is nonzero.] It is interesting to note that, in both the ODMR and the optical case, when SOC is nonzero, the pure dephasing process is analogous to the vibronic coupling scheme known in molecules. Equation (IV. 13) reads as follows: The total  $\Delta T$  is given by  $\Delta T$  of the triplet-ground singlet plus  $|b|^2$  times  $\Delta T$  of the excited singlet-triplet states!

A useful equation can now be derived from Eqs. (IV. 11) and (IV. 13), which give the difference in  $\Delta T$ :

$$\Delta T (\text{optical})|_{\text{SOC} \neq 0} - \Delta T (\text{ODMR})|_{\text{SOC} \neq 0} = \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle - \langle \phi_{s_0}^0 \sigma_{s_0} | \mathbf{T} | \phi_{s_0}^0 \sigma_{s_0} \rangle. \quad (\text{IV. 14})$$

The above results indicate that, in the presence of SOC, the difference in  $\Delta T$  of the optical transition and the ODMR transition depends on the difference in scattering amplitude of the triplet  $z$  sublevel (i.e., *not* the common level) and the ground state, for the same amount of SOC parameter  $|b|$ . Physically, this means that the role of  $\sigma_x$  is brought about because it influences the width of ODMR transitions. If  $|\phi_T^0 \sigma_x\rangle$  purely scatters as the ground state, then  $\Delta T$  for both the ODMR and the optical are equal. If both  $\langle T \rangle_{xx}$  and  $\langle T \rangle_{s_0 s_0}$  are zero, then the same results will be obtained. So, if the ground state is not dephasing and if the  $|\phi_T^0 \sigma_x\rangle$  level is also not dephasing, we expect the pure width of the ODMR and the optical transition to be the same under the above mentioned conditions. The effect of SOC in the latter case does not play a direct role because of "cancellation" due the presence of only one common spin-orbital level (see Figs. 2 and 3). Looking back at Eqs. (IV. 13) and (IV. 11) and involving the previous condition that the ground and  $|\phi_T^0 \sigma_x\rangle$  do not dephase, we see that the observed absolute width of the ODMR and the optical transitions depend on the mixing of the  $x$  sublevel to the excited singlet through SOC.

Rewriting Eq. (IV. 13) for the case where the ground state is not purely dephasing (e.g., 0 °K limit), we obtain the following expression for the  $\Delta T$  of the optical

transition into the  $\sigma_x$  sublevel:

$$\Delta T (\text{optical})|_{\text{SOC} \neq 0} = aa^* \langle \phi_T^0 \sigma_x | \mathbf{T} | \phi_T^0 \sigma_x \rangle + bb^* \langle \phi_s^0 \sigma_s | \mathbf{T} | \phi_s^0 \sigma_s \rangle. \quad (\text{IV. 15})$$

Using this equation [which also holds for  $\Delta T (\text{ODMR})|_{\text{SOC} \neq 0}$  when the  $z$  sublevel is not purely dephasing], we can now obtain the homogeneous width in terms of  $|a|^2$  and  $|b|^2$ , and numerically calculate the pure width as we shall see later.

In general, the ratio  $R$  of the  $\Delta T$  [which is related to the width by Eq. (IV. 1)] for the optical-to-the-ODMR transition can be written using Eqs. (IV. 13) and (IV. 11) as

$$R_{o/s} = \frac{|a|^2 \langle T \rangle_{T\sigma_x} + |b|^2 \langle T \rangle_{s\sigma_s} - \langle T \rangle_{s_0}}{|a|^2 \langle T \rangle_{T\sigma_x} + |b|^2 \langle T \rangle_{s\sigma_s} - \langle T \rangle_{T\sigma_x}}, \quad (\text{IV. 16})$$

yielding the results of Eq. (IV. 15) in the appropriate limit; the ground state is not purely dephasing. The implications of the equation are straightforward and will not be dwelt upon here. The important conclusion is that, when the ground state and the other spin-orbitally uncoupled levels are not purely dephasing, the pure scattering which leads into the width of both the optical and the ODMR transitions is the same. *This width, however, is directly dependent on the singlet state width because of the spin-orbital stealing mechanism.*

## V. COMPARISON WITH EXPERIMENTAL RESULTS AND QUALITATIVE PREDICTIONS

### A. ODMR linewidth of $\pi\pi^*$ and $\pi\pi^*$ systems

In order to illustrate the effect of SOC on the observed width, we shall confine the treatment of this section to a specific case of an isolated molecule interacting with a reservoir ( $p, p'$ ) of known density of states. As an example, we shall consider a Debye model for the density of states. For this case, at temperatures below the Debye temperature, Eq. (IV. 1) becomes<sup>13</sup> (no  $T_1$

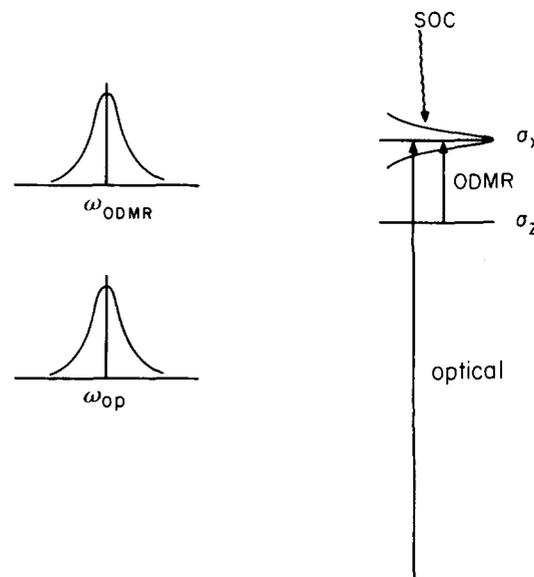


FIG. 3. A schematic for a special case where the width of optical and ODMR transitions are the same.

terms)

$$\gamma_{if} = \eta T^7 |\langle f | V_2 | f \rangle - \langle i | V_2 | i \rangle|^2, \quad (\text{V.1})$$

where  $\eta$  is a constant and  $T^7$  is the temperature term characteristic of acoustic phonon scattering processes.  $V_2$  is the second order term in the expansion of the molecule-lattice interaction  $V$  in powers of the local strain tensor around the molecule. Note that a *linear* strain term is directly given in terms of the creation and annihilation operators of the phonons (i.e., absorption and emission), while a *quadratic* strain term will have terms that conserve energy. As mentioned previously, the above temperature dependent terms will be assumed the same for the singlet and triplet states so we may benefit from the oversimplified physics of the problem. Extension to other cases can be done to higher orders if sufficient experimental data are available.

Combining Eq. (V.1) and Eq. (IV.11) and (IV.6), we can now write an expression for the ratio of the homogeneous width (by pure dephasing) of an ODMR transition in the presence of SOC to that in its absence since  $V_2$  is an operator which depends only on the molecular degrees of freedom. The result is

$$\frac{\gamma_{if}(\text{ODMR; SOC})}{\gamma_{if}(\text{ODMR; no SOC})} = \left| 1 + \left| \frac{\langle \mathcal{K}_{\text{SO}}^{(x)} \rangle}{\Delta E_{s,t}} \right|^2 \times \frac{\langle V_2 \rangle_{s\sigma_s} - \langle V_2 \rangle_{T\sigma_x}}{\langle V_2 \rangle_{T\sigma_x} - \langle V_2 \rangle_{T\sigma_s}} \right|^2. \quad (\text{V.2})$$

Several conclusions can be drawn from this equation. First, if the matrix elements  $\langle V_2 \rangle$  for singlet and the spin-orbitally coupled triplet level ( $\sigma_x$ ) are the same, then there is no effect for SOC on the linewidth of the ODMR transition. Second, the effect of SOC matrix element is to cause extra broadening or narrowing [if  $\langle V_2 \rangle_{s\sigma_s} = \langle V_2 \rangle_{T\sigma_x} = 0$ , the latter case will be at hand and Eq. (V.2) becomes simply  $|1 - |b|^2|^2$ ]. As the energy difference between the singlet and triplet states gets larger, the width of the ODMR resonance gets smaller, reaching the zero SOC limit when  $\Delta E_{s,t}$  is very large compared to  $\langle \mathcal{K}_{\text{SO}} \rangle$ . Finally, as the two spin sublevels gets closer in width, the ratio of Eq. (V.2) gets larger. The singularity in Eq. (V.2) when  $\langle V_2 \rangle_{T\sigma_x} = \langle V_2 \rangle_{T\sigma_s}$  simply reflects that any broadening of an ODMR resonance starting from the  $\delta$  function width represent an infinite change in the width. An interesting limit is the case where  $|T\sigma_s\rangle$  does not scatter. Under this condition, and assuming that  $\langle V_2 \rangle_{s\sigma_s} \times \langle V_2 \rangle_{T\sigma_x}^{-1} \gg 1$ , then

$$\frac{\gamma_{if}(\text{ODMR; SOC})}{\gamma_{if}(\text{ODMR; no SOC})} = \left| 1 + \left| \frac{\langle \mathcal{K}_{\text{SO}}^{(x)} \rangle}{\Delta E_{s,t}} \right|^2 \frac{\langle V_2 \rangle_{s\sigma_s}}{\langle V_2 \rangle_{T\sigma_x}} \right|^2. \quad (\text{V.3})$$

The  $\pi\pi^*$  states of aromatic hydrocarbons such as naphthalene has a SOC matrix element on the order of  $1 \text{ cm}^{-1}$  and  $\Delta E_{s,t}$  on the order of  $10^4 \text{ cm}^{-1}$ . Therefore, the second term in the equation is on the order of  $10^{-5}$  even if the ratio of singlet to triplet scattering matrix element is  $\sim 10^3$ . Thus, the homogeneous width of the ODMR will approach the zero SOC limit.

Hutchison *et al.*<sup>18</sup> have carefully examined the width of the EPR absorption lines for the naphthalene- $h_8$  triplet state molecules in a single diphenyl- $h_{10}$  crystal in zero external magnetic field at  $\sim 83 \text{ }^\circ\text{K}$ . The lines

are inhomogeneously broadened by hyperfine splittings due to the protons on the molecule. Hutchison *et al.* had calculated the absorption frequencies and intensities at exactly zero external magnetic field including all the protons for the  $D+E$ ,  $D-E$ , and  $2E$  transitions. The "resolution" of their calculation is 100 kHz. If this width is close to the homogeneous width, then  $\gamma_{if}$  is given by this width at  $80 \text{ }^\circ\text{K}$  and the pure dephasing must be orders of magnitude larger than the  $T_1$ -type broadening (assuming  $T_1$  is on the order of seconds).

For  $n\pi^*$  states in azines and carbonyls, the situation is different. Benzophenone,<sup>19</sup> which is known to have the  $n\pi^*$  excitation essentially localized on the  $c=0$  fragment and all of the spin activity essentially in the  $z$  sublevel (carbonyl axis), has a nearby  $\pi\pi^*$  state that is only  $\sim 2000 \text{ cm}^{-1}$ . When considering the one-center spin-orbital term on oxygen, a value of  $28.5 \text{ cm}^{-1}$  was computed for the spin-orbital matrix element using  $\lambda(\text{oxygen}) = 147 \text{ cm}^{-1}$ .<sup>20</sup> Thus, a finite temperature broadening of these  $n\pi^*$  systems of 1–5 MHz (compared to the naphthalene case) will indicate that  $\langle V_2 \rangle_{s\sigma_s} / \langle V_2 \rangle_{T\sigma_x} \approx 10^5$ , or that the high energy state must scatter enormously larger than the lowest triplet. It is interesting that the ODMR width of benzenone in 4, 4'-dibromodiphenyl-ether is 4.1 MHz. Of course, this width might not be homogeneous, although the proton hyperfine effect is not that large<sup>19</sup> in this case when compared with naphthalene, where the triplet electrons are delocalized over the entire molecule. Also, the effect of oxygen isotope hyperfine effects seems to be small.<sup>19,21</sup> The point here is that SOC may broaden ODMR lines homogeneously! The above estimates are very qualitative, but perhaps useful. It will be interesting to test some of these ideas especially on systems with very close-lying states like those found by Depres and Migirdicyan.<sup>22</sup>

## B. Optical linewidth of $n\pi^*$ and $\pi\pi^*$ systems

Similar to the above treatment and by using Eqs. (IV.15) and (IV.1), we arrive at the following relation for the pure width of the optical transition:

$$\gamma_{if}(\text{optical}) \approx |1 + \beta |b|^2|^2 \gamma_{if}(\phi_T^0 \sigma), \quad \beta \gg 1, \quad (\text{V.4})$$

where  $\beta$  is the ratio of  $\langle V_2 \rangle_{s\sigma_s}$  to  $\langle V_2 \rangle_{T\sigma_x}$ . Again, if this ratio is  $\sim 10^4$ , an enhancement of about 9 is expected for the pure width as a result of SOC in benzophenone-type systems. For naphthalene, on the other hand, even if  $\beta \sim 10^4$ , the pure width is essentially  $\gamma_{if}(\phi_T^0 \sigma_x)$ , as Eq. (V.4) predicts.

## C. Optical vs ODMR pure broadening

In this section, we shall describe the effect of ground state and  $|T\sigma_x\rangle$  dephasing processes on the ratio of ODMR width to the optical width. Equation (IV.16) can be written in the following form:

$$|R_{s/o}|^2 = \frac{| |a|^2 + \beta |b|^2 - \gamma|^2}{| |a|^2 + \beta |b|^2 - \alpha|^2} = \frac{\gamma_s}{\gamma_o}, \quad (\text{V.5})$$

where  $\alpha = \langle V_2 \rangle_{s\sigma_s} \langle V_2 \rangle_{T\sigma_x}^{-1}$  and  $\gamma = \langle V_2 \rangle_{T\sigma_x} \langle V_2 \rangle_{T\sigma_x}^{-1}$ .

Figure 4 shows the behavior of this function in different limits. The trivial case mentioned earlier is when

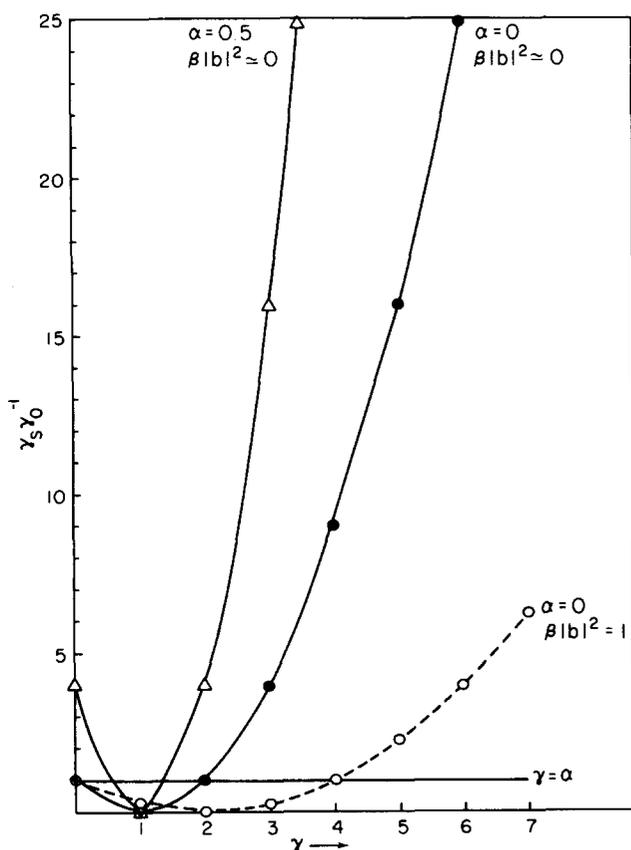


FIG. 4. The variation of the ratio of pure spin-optical widths as a function of  $\gamma$  for different values of  $\beta|b|^2$  and  $\alpha$ .

$\gamma = \alpha$ , shown in the figure as a straight line (optical = ODMR). If  $\alpha = 0$  (i.e., the ground state matrix element is zero) and the SOC parameter times  $\beta$  is very small ( $\approx 0$ ), then the ODMR width is continuously increasing (above  $\gamma = \alpha$  region) as a function  $\gamma$  except in the region below which the two spin sublevels invert their behavior. The effect of ground state scattering in this case is to make the rise more steep and to also enhance the effect below the  $\gamma = 1$  region. Increasing the SOC and the scattering of the singlet makes the rise go slower. It is interesting to note the behavior in the region below the  $\gamma = \alpha$  line. In this region, the pure optical width picks up broadening more than the ODMR, but the functionality of this broadening on  $\gamma$  crucially depends on the ground singlet and excited singlet scattering matrix elements as well as the magnitude of SOC.

If we now apply these ideas to aromatic hydrocarbons, azines, and carbonyls that have only *one* active spin sublevel, we can conjecture on the relative pure width of optical and ODMR transitions. For example, if  $\gamma = 3$ , then we expect the ODMR pure width to be larger than the optical by a factor of 4 for aromatic-type systems. If, however, the SOC and the singlet scattering is large (as may be the case in some carbonyls or azines), then the optical will exceed the ODMR width by a factor of 4. Note that when  $\gamma = 1$ , the function in Fig. 4 gives zero value. This is simply because the pure width of the ODMR transition at this point is zero (the relative optical width will "appear" mathematically infinite) since the two spin sublevels are scattering to the same extent.

#### D. On the effect of SOC on the $T_1$ contribution to the linewidth

From Eq. (V.1), we see that the pure dephasing rate for a Raman type process is expected to go to zero at  $0^\circ\text{K}$  under the above mentioned approximations. The only contribution to the width of the optical resonance is then from  $T_1$  processes. These processes may be radiative or nonradiative. The radiative part again scales by the SOC according to Eq. (II.4). This means that the lifetime of the triplet is directly related to that of the singlet by  $|b|^{-2}$ . For 10 nsec lifetime and  $|b| = 10^{-4}$ , the triplet lifetime is  $\sim 1$  sec, giving rise to a width of 1 Hz. The long lifetime is typical of aromatic hydrocarbons like naphthalene. For benzophenone, the example used in calculating  $\gamma_{if}$ ,  $|b|^2 \approx 2 \times 10^{-4}$ , thus giving a width of  $\approx 1$ –10 kHz.

The nonradiative  $T_1$  time of the triplet cannot be calculated without detailed knowledge of the vibronic structure in molecules like naphthalene and benzophenone, and which is beyond the scope of this work. In any event, the  $T_1$  contribution should be added to Eq. (V.4), satisfying Eq. (III.5), if one is performing an exact calculation. Note that although the radiative  $T_1$  of the lowest singlet state may determine the homogeneous width of the singlet (as, for example, in pentacene/*p*-terphenyl systems)<sup>7</sup> at  $\sim 1^\circ\text{K}$ , it may play a relatively small role in the triplet broadening. One reason is that higher energy singlets or triplets may couple by SOC to the lowest triplet. The  $\beta$  value for these higher energy states may be very large, and hence the triplet broadening may become very large. Also, as emphasized before, at higher temperatures, 3 K or above, pure dephasing is expected to overcome the  $T_1$  contribution.

#### VI. CONCLUDING REMARKS

- (1) Spin-orbital coupling between singlet and triplet or triplet and triplet states in molecules influences the homogeneous broadening of optical and spin resonance (ODMR) transitions.
- (2) The correlation time for scattering by the phonon bath may be the same but the molecular matrix elements are different for optical and ODMR transitions. In the present work, we have taken the correlation time of the bath to be very short at both resonance frequencies. This assumption needs further testing.
- (3) In the theory described here, the optical and ODMR homogeneous widths are *related*. The relationship depends on the extent to which the excited singlet states, the ground state, and the spin-orbitally uncoupled spin level are dephasing by the phonon bath. The coupling is reminiscent of the well-known vibronic-intensity-stealing mechanism in molecules.
- (4) Carbonyl and azines with  $n\pi^* - \pi\pi^*$  coupling are expected to show homogeneous broadenings different from naphthalene-type (assumed to possess one active level) systems.
- (5) For the *pure* homogeneous width of optical and ODMR transitions to be much different from those tran-

sitions with  $SOC=0$ , the singlet state dephasing rates and/or SOC must be very large. Only the radiative part of  $T_1$  mechanisms is addressed here. These  $T_1$ -type broadenings may dominate the  $T_2'$ -type broadening [Eq. (III. 7)] mechanisms discussed here, especially as  $T \rightarrow 0$ .

(6) Even though the two spin levels, which have a small energy splitting, are imbedded in the phonon "continuum," high energy phonons can make the  $T_2'$  processes very efficient, e.g., Raman scatterings.

(7) High-energy singlets and/or triplets could have a much larger dephasing cross section and in turn broaden the lowest triplet, causing its homogeneous broadening to be much different from the lowest singlet.

(8) The formal treatment of linewidth presented in this paper can be extended to systems with more than one active spin state. The assumption we made of using only one active spin level is to illustrate the importance of the new findings. This extension together with the treatment of dimers and excitons will be published in a forthcoming paper.

(9) Measurements of optical and spin dephasing on the same system (e.g., naphthalene) will be of interest as it may provide means of confirming or excluding some of our conjectures. Whether this treatment has general validity will only become clear when more (quantitative) experimental results are available.

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<sup>15</sup>It is assumed that the phonon bath has the same structure in all the states under consideration. Thus, only the matrix elements for coupling are considered here. Perhaps this is a reasonable assumption at low temperature and may break down at high temperatures, where the optical phonon (having different frequencies in the different electronic states) get involved in the scattering processes. Also, the bath correlation time may be different.

<sup>16</sup>In the model considered here, we assume that the different states of the system couple to their own phonon reservoirs through the operator  $V$ . In the absence of SOC, the wave functions of the singlet and triplet states (two electron approximation) can be written as products of spin and orbital functions. Under this condition, one may write the total potential as the sum of the orbital and spin scattering potentials since the projectile (phonons) and the target (impurity molecule) are different, and because in the absence of SOC, the spin and the orbital parts are uncorrelated. Adding the SOC to the total Hamiltonian of the system ( $\mathcal{H}_{\text{singlet}} + \mathcal{H}_{\text{triplet}} + \mathcal{H}_{\text{ground}} + \sum V$ ) mixes the states of the impurity molecule, thus modifying the influence of  $V$ . Now, the "orbital scattering" is no longer decoupled from the spin scattering since the molecular states are mixed. The potential  $V$  did not cause scattering between the excited singlet and triplet states because (a) as the model dictates, the states independently couple to the reservoir, and (b) such scattering effects are most likely to be  $T_1$ -type matrix elements which do not conserve the phonon energy. Finally, the separation made for  $V$  will not necessarily apply for  $T$ . This can be seen if we substitute Eq. (IV.3) in (IV.2). (It was mentioned to me by Professor V. McKoy that the separation of  $V$  done here is analogous to the inclusion of SOC in electron-atom scattering where the SOC is confined to the target states.)

<sup>17</sup>As pointed out in Ref. 16, the separation of  $V$  does not guarantee the same separation for  $T$  because of the cross terms in Dyson's equation. Throughout most of the paper, we shall use  $T$  not to imply the ignoring of the cross terms but rather to use the notation of Eq. (III.6). In the section where we compute the  $T_2'$ -type terms, we simply use  $V$ .

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