AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **75**, 5630 (1981); doi: 10.1063/1.442002 View online: http://dx.doi.org/10.1063/1.442002 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v75/i12 Published by the American Institute of Physics.

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Absorption and circular dichroism line shapes of a molecular dimer in the strong electronic coupling limit^{a)}

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We have derived approximate analytical expressions for the absorption and circular dichroism line shapes of a molecular dimer composed of two identical molecules (each with a single excited electronic state and single vibrational mode) in the strong electronic coupling limit. These are compared with numerical results and yield excellent agreement. We compare our approach to other theories and discuss experimental applications and possible extensions of this work.

I. INTRODUCTION

There have been many theories which allow calculations of the optical line shape of a molecular dimer which use a variety of methods: simple exciton theory, ¹ classical polarizability theory (or equivalently time-dependent Hartree theory with a decorrelation approximation),² quantum mechanical approaches which explicitly include vibrational states, ^{3-5,23} and treatment of the excitonphonon or vibronic coupling as a stochastic process.⁶ Despite these efforts, the number of quantiative analyses of experimental results is vanishingly small.

In another paper⁷ we discussed the general validity of the above approaches, and suggested an alternative program: analytic (but approximate) solution of the molecular vibrations coupled to the optical excitation, followed by inclusion of medium effects either as inhomogeneous broadening (for slow modes), or as vibronic perturbations to be treated stochastically or directly via a mean field approximation.⁹ We expect in this manner to be able to include most important effects in a real system, with a calculation simple enough to analyze experimental results with curve fitting.

In this paper, we derive analytic expressions for the optical absorption and circular dichroism line shapes for a dimer composed of two identical monomers in the strong electronic coupling limit $(2J > \omega)$. Each monomer excited state is linearly coupled to a single vibrational mode. We include inhomogeneous broadening as a shift in the monomer electronic energy separation $\Delta E = (E_{\text{excited}} - E_{\text{ground}})$, which we assume is the same for each monomer in the dimer. That is, ΔE varies from dimer to dimer, but not in a dimer. We determine the dependence of the spectrum on this parameter as well as the temperature T, the electronic exchange coupling J, and the exciton-phonon coupling parameter g. We discuss the qualitative features of the spectrum and compare to other approaches.

In conclusion, we discuss the theoretical extensions and possible applications of this work. Of particular interest are dimers in photosynthetic systems, which we believe will be especially suited for study with our approach.

II. THEORY

A. Absorption line shape

The Hamiltonian for our dimer system is $(\hbar = 1)$

$$H = J(A_1^*A_2 + A_2^*A_1) + \omega(B_1^*B_1 + B_2^*B_2) + \Delta E$$

+ $g[A_1^*A_1(B_1 + B_1^*) + A_2^*A_2(B_2 + B_2^*)],$ (2.1)

where $A_i(A_i^*)$, $B_i(B_i^*)$ are the usual annihilation (creation) operators for excitons and phonons, respectively, for site *i*.

In a previous paper,⁸ we have approximately diagonalized this Hamiltonian. We will consider an inhomogeneous distribution of such dimers, with the distribution function given as

$$D(\Delta E) = (1/\pi^{1/2} \Delta) \exp - (\Delta E)^2 / \Delta^2 . \qquad (2.2)$$

Reference 7 has a complete discussion of this idea.

After transforming H as in Ref. 8, including $n_* - 1/2g^2\omega$ in the excitation energy ΔE where n_* is the number of phonons of + symmetry, and expressing all energies in units of ω , we find

$$H = J(A_*^*A_- - A_*^*A_-) + B^*B + \Delta E + \frac{g}{\sqrt{2}}(A_*^*A_- + A_*^*A_+)(B + B^*),$$
(2.3)

where $|\pm\rangle = (1/\sqrt{2})(|1\rangle \pm |2\rangle)$ and B, B^{*} refer to the (-) vibrational mode.

We will only be concerned with the strong electronic coupling limit 2J > 1 (remember that the unit of energy is now ω). In this limit, we have found that the eigenvalues and eigenfunctions of H are well represented by $\Delta E + E_{\pi\alpha}$, where

$$E_{n\alpha} \simeq n \pm \{J^2 + g^2(n+1/2)\}^{1/2} \equiv n \pm \Gamma_n , \qquad (2.4a)$$

$$\psi_{n\alpha} = \left| + \right\rangle \chi_{n\alpha}^{(*)} + \left| - \right\rangle \chi_{n\alpha}^{(-)} . \tag{2.4b}$$

Here $\alpha = 1$ denotes the (+) sign in Eq. (2.4a), while $\alpha = 2$ denotes the (-) sign. We will need a number of other results from previous work, which we collect here

$$\langle \chi_{n\alpha}^{(+)} | \chi_{n\alpha}^{(+)} \rangle - \langle \chi_{n\alpha}^{(-)} | \chi_{n\alpha}^{(-)} \rangle \approx \frac{\partial E_{n\alpha}}{\partial J} \approx \pm \frac{J}{\Gamma_n} , \qquad (2.5)$$

$$\langle \chi_{n\alpha}^{(+)} | Q | \chi_{n\alpha}^{(-)} \rangle = \frac{1}{2} \frac{\partial E_{n\alpha}}{\partial g} = \pm (n + \frac{1}{2}) g / (2\Gamma_n) , \qquad (2.6)$$

$$\langle \chi_{n\alpha}^{(*)} | \chi_{n\alpha}^{(-)} \rangle = 0 , \qquad (2.7)$$

0021-9606/81/245630-10\$01.00

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^{a)}Supported in part by a grant from the NSF (CHE 78-07515) and by a NIH postdoctoral fellowship to RAF.

$$\left\langle \chi_{n\alpha}^{(*)} \middle| \chi_{n\alpha}^{(*)} \right\rangle = \frac{1}{2} \left[1 \pm J / \Gamma_n \right], \qquad (2.8)$$

$$\left\langle \chi_{n\alpha}^{(-)} \middle| \chi_{n\alpha}^{(-)} \right\rangle = \frac{1}{2} [1 \mp J / \Gamma_n] . \qquad (2.9)$$

The choice of signs on the right-hand side of Eqs. (2,5)-(2,9) again refer to the index α , with the upper sign corresponding to $\alpha = 1$.

Last, for reference we give the equations satisfied by $\chi_{n\alpha}^{(-)}$ and $\chi_{n\alpha}^{(+)}$:

$$(B^*B + J - E_{n\alpha})\chi_{n\alpha}^{(*)} = -gQ\chi_{n\alpha}^{(-)}, \qquad (2.10a)$$

$$(B^*B - J - E_{n\alpha})\chi_{n\alpha}^{(-)} = -gQ\chi_{n\alpha}^{(+)}, \qquad (2.10b)$$

where

 $Q = 1/\sqrt{2}(B + B^*)$.

The absorption line shape is⁷

$$I(E) = \int D(\Delta E) I(\Delta E, E) d(\Delta E) = \frac{1}{N} \int d(\Delta E) D(\Delta E)$$

$$\times \sum_{n,\alpha} \sum_{m=0}^{\infty} e^{-m\beta} |\langle \psi_{n\alpha} | \mu | 0m \rangle|^2 \delta(E - \Delta E - E_{n\alpha} + m)$$

$$= \frac{1}{N} \sum_{m} \sum_{n,\alpha} e^{-m\beta} \exp[-(E - E_{n\alpha} + m)^2 / \Delta^2] |\langle \psi_{n\alpha} | \mu | 0m \rangle|^2,$$
(2.11)

where

$$N = \pi^{1/2} \Delta (1 - e^{-\beta})^{-1}; \quad \beta = (k_B T)^{-1}$$
 (2.12)

and the sum over \pm is understood. The dipole moment operator is given by

$$\mu = \mu_1 (A_1 + A_1^*) + \mu_2 (A_2 + A_2^*)$$

= $\mu_1 (A_1 + A_1^*) + \mu_2 (A_2 + A_2^*)$, (2.13)

where μ_i is the transition moment for monomer *i* and $\mu_{+}(\mu_{-})$ is the transition moment for the state + (-):

$$\mu_{\pm} = \frac{1}{\sqrt{2}} \left(\mu_1 \pm \mu_2 \right) \,. \tag{2.14}$$

The notation $|0m\rangle$ refers to the ground electronic state and the m phonon vibrational state of the dimer.

Using the fact that $|0m\rangle$ is an eigenstate of $h_0 = B^*B$, we can rewrite Eq. (2.11) as

$$I(E) = \frac{1}{N} \sum_{n \alpha m} \sum_{n \alpha m} \langle \psi_{n \alpha} | \mu e^{-\beta h_0}$$

$$\times \exp\left[-(E - E_{n \alpha} + h_0)^2 / \Delta^2\right] |0m\rangle \cdot \langle 0m | \mu | \psi_{n \alpha} \rangle$$

$$= \frac{1}{N} \sum_{n, \alpha} \langle \psi_{n \alpha} | \mu e^{-\beta h_0} \exp\left[-(E - E_{n \alpha} + h_0)^2 / \Delta^2\right] \cdot \mu | \psi_{n \alpha} \rangle .$$
(2.15)

Now, we substitute Eq. (2.4b) into Eq. (2.15) to obtain

$$I(E) = \frac{1}{N} \sum_{n,\alpha} \left\langle \left\{ \mu_{+} \chi_{n\alpha}^{(*)} + \mu_{-} \chi_{n\alpha}^{(-)} \right\} e^{-\beta h_{0}} \right.$$

$$\times \exp\left[- \left(E - E_{n\alpha} + h_{0} \right)^{2} / \Delta^{2} \right] \cdot \left\{ \mu_{+} \chi_{n\alpha}^{(*)} + \mu_{-} \chi_{n\alpha}^{(-)} \right\} \right\rangle, \quad (2.16)$$

$$I(E) = \frac{1}{N} \sum_{n,\alpha} \left\{ \left| \mu_{+} \right|^{2} \left\langle \chi_{n\alpha}^{(*)} \right| \hat{O}_{n\alpha} \left| \chi_{n\alpha}^{(*)} \right\rangle + \left| \mu_{-} \right|^{2} \left\langle \chi_{n\alpha}^{(-)} \right| \hat{O}_{n\alpha} \left| \chi_{n\alpha}^{(-)} \right\rangle \right\}.$$

$$(2.17)$$

Since $\mu_* \cdot \mu_- = 0$, and

$$\hat{O}_{n\alpha} = \exp\left\{-\beta h_0 - (E - E_{n\alpha} + h_0)^2 / \Delta^2\right\}.$$
 (2.18)

We shall now compute the sums in Eq. (2, 17) in an approximate manner. First we will examine the integral

$$\langle \chi_{n\alpha}^{(+)} | \hat{O}_{n\alpha} | \chi_{n\alpha}^{(+)} \rangle$$

appearing in Eq. (2.17). We will approximate the integral by the first order cumulant:

$$\langle \chi_{n\alpha}^{(+)} | \hat{O}_{n\alpha} | \chi_{n\alpha}^{(+)} \rangle = \langle \chi_{n\alpha}^{(+)} | \chi_{n\alpha}^{(+)} \rangle \exp - \{ \langle \overline{\chi}_{n\alpha}^{(+)} | \beta h_0 + (E - E_{n\alpha} + h_0)^2 / \Delta^2 | \overline{\chi}_{n\alpha}^{(+)} \rangle \} ,$$

$$(2.19)$$

where

$$\left|\tilde{\chi}_{n\alpha'}^{(+)}\right\rangle = \left|\chi_{n\alpha}^{(+)}\right\rangle \left\{\left\langle\chi_{n\alpha}^{(+)} | \chi_{n\alpha}^{(+)}\right\rangle\right\}^{-1/2} .$$
(2.20)

This will certainly be valid for large Δ and small β . The actual limits of validity are investigated in more detail in the results section. First, note that by using Eq. (2.10), we find

$$\langle \tilde{\chi}_{n\alpha}^{(+)} | h_0 | \tilde{\chi}_{n\alpha}^{(+)} \rangle = E_{n\alpha} - J - g \frac{\langle \chi^{(+)} | Q | \chi_{n\alpha}^{(+)} \rangle}{\langle \chi_{n\alpha}^{(+)} | \chi_{n\alpha}^{(+)} \rangle}, \qquad (2.21)$$

$$\langle \tilde{\chi}_{n\alpha} | h_0 | \tilde{\chi}_{n\alpha} \rangle = E_{n\alpha} + J - g \frac{\langle \chi^{(-)} | Q | \chi_{n\alpha}^{(-)} \rangle}{\langle \chi^{(-)} | \chi_{n\alpha}^{(-)} \rangle} .$$
 (2.22)

Substituting Eqs. (2.4a), (2.6), (2.8), and (2.9) we find

$$\langle \tilde{\chi}_{n\alpha}^{(*)} | h_0 | \tilde{\chi}_{n\alpha}^{(*)} \rangle \cong n \pm \Gamma_n - J - \frac{(-1)^{\alpha} (n + \frac{1}{2}) (g^2/2)}{\frac{1}{2} [\Gamma_n + (-1)^{\alpha} J]}$$

= n (2.23)

and

$$\langle \tilde{\chi}_{n\alpha}^{(-)} | h_0 | \tilde{\chi}_{n\alpha}^{(-)} \rangle = n , \qquad (2.24)$$

so that

$$\langle \chi_{n\alpha}^{(+)} | \hat{O}_{nd} \chi_{n\alpha}^{(+)} \rangle = \langle \chi_{n\alpha}^{(+)} | \chi_{n\alpha}^{(+)} \rangle \exp\{-\beta n - (E - E_{n\alpha} + n)^2 / \Delta^2\},$$
(2.25)

where we have replaced, ²¹ e.g., $\langle \tilde{\chi}_{n\alpha}^{(+)} | h_0^2 | \tilde{\chi}_{n\alpha}^{(+)} \rangle$ by n^2 .

We now split I(E) into a sum over states with $\alpha = 1$ and $\alpha = 2;$

$$I(E) = I_{1}(E) + I_{2}(E)$$

$$I_{\alpha}(E) = \frac{1}{N} \sum_{n} \left\{ \left| \mu_{*} \right|^{2} \langle \chi_{n\alpha}^{(*)} \right| \chi_{n\alpha}^{(*)} \rangle \exp\{-\beta n - (E - E_{n\alpha} + n)^{2} / \Delta^{2}\} + \left| \mu_{*} \right|^{2} \langle \chi_{n\alpha}^{(*)} \right| \chi_{n\alpha}^{(*)} \rangle \exp\{-\beta n - (E - E_{n\alpha} + n)^{2} / \Delta^{2}\}.$$
(2.26)

Using Eqs. (2.8) and (2.9) yields

$$I_{1}(E) = \frac{1}{2N} \sum_{n} \left(\left| \mu_{+} \right|^{2} + \left| \mu_{-} \right|^{2} \right) \exp\{-\beta n - (E - \Gamma_{n})^{2} / \Delta^{2} \}.$$

+ $\frac{1}{N} \sum_{n} \frac{J}{2\Gamma_{n}} \left(\left| \mu_{+} \right|^{2} - \left| \mu_{-} \right|^{2} \right) \exp\{-\beta n - (E - \Gamma_{n})^{2} / \Delta^{2} \}$
Define (2.27)

$$F_1 = \frac{1}{2N} \sum_n e^{-\beta n} \exp[-(E - \Gamma_n)^2 / \Delta^2] , \qquad (2.28a)$$

$$G_{1} = \frac{1}{N} \sum_{n} e^{-\beta n} \exp[-(E - \Gamma_{n})^{2} / \Delta^{2}] (J/2 \Gamma_{n}) , \qquad (2.28b)$$

then

$$I_1(E) = (|\mu_+|^2 + |\mu_-|^2)F_1 + (|\mu_+|^2 - |\mu_-|^2)G_1. \quad (2.29)$$

Similarly,

J. Chem. Phys., Vol. 75, No. 12, 15 December 1981

$$I_2 = (|\mu_+|^2 + |\mu_-|^2)F_2 - (|\mu_+|^2 - |\mu_-|^2)G_2 . \qquad (2.30) \quad \text{wf}$$

So that

$$I = (|\mu_{\star}|^{2} + |\mu_{-}|^{2})(F_{1} + F_{2}) + (|\mu_{\star}|^{2} - |\mu_{-}|^{2})(G_{1} - G_{2}),$$
(2.31)

where

$$F_2 = \frac{1}{2N} \sum_n e^{-8n} \exp[-(E + \Gamma_n)^2 / \Delta^2] , \qquad (2.32a)$$

$$G_2 = \frac{1}{N} \sum_{n} e^{-\beta n} \exp[-(E + \Gamma_n)^2 / \Delta^2] \frac{J}{2\Gamma_n} \quad . \tag{2.32b}$$

In order to fine a convenient analytic form for I(E), we convert the sums over n in Eqs. (2.28) and (2.32) to integrals. These integrals are evaluated in the Appendix; the final result is

$$I(E) = \frac{1}{N} \frac{1}{\alpha^{1/2} g^2} \left\{ \left| \mu_{+} \right|^2 + \left| \mu_{-} \right|^2 \right\} \exp\left[-(E - \Gamma_0)^2 / \Delta^2 \right] \left\{ \frac{1}{2\alpha^{1/2}} + \frac{E}{\alpha \Delta^2} \cdot y \left(\alpha^{1/2} \Gamma_0 - \frac{E}{\alpha^{1/2} \Delta^2} \right) \right\} + \exp\left[-(E + \Gamma_0)^2 / \Delta^2 \right] \left\{ \frac{1}{2\alpha^{1/2}} - \frac{E}{\alpha \Delta^2} y \left(\alpha^{1/2} \Gamma_0 + \frac{E}{\alpha^{1/2} \Delta^2} \right) \right\} + \frac{J}{N\alpha^{1/2} g^2} \left\{ \left| \mu_{+} \right|^2 - \left| \mu_{-} \right|^2 \right\} \exp\left[-(E - \Gamma_0)^2 / \Delta^2 \right] y (\alpha^{1/2} \Gamma_0 - E / \alpha^{1/2} \Delta^2) - \exp\left[-(E + \Gamma_0)^2 / \Delta^2 \right] y (\alpha^{1/2} \Gamma_0 + E / \alpha^{1/2} \Delta^2) \right],$$

$$(2.33)$$

where

$$y(x) = e^{x^2} \operatorname{erfc}(x)$$
.

B. Circular dichroism

We shall be concerned here only with the exciton contribution to the circular dichroism (CD); the monomer CD, proportional to $\mu_{monomer} \cdot m_{monomer}$ (where m is the monomer magnetic moment operator) will be assumed zero. We also neglect small correction terms due to perturbation of the ground state.⁹ Then the ellipticity as a function of energy can be written as

$$\theta(E) = K(\mathbf{R}_{12} \cdot \boldsymbol{\mu}_1 \, x \, \boldsymbol{\mu}_2) \sum_{n_r \, \alpha} \left\langle \Psi_{n\alpha} \left| \left(A_{\star}^* A_{\star} - A_{\star}^* A_{\star} \right) \right. \right. \\ \left. \left. \left. \left. \left. \left(E_{n\alpha} - h_0 - E \right)^2 / \Delta^2 \right] \right| \Psi_{n\alpha} \right\rangle \right\rangle,$$

$$(2.34)$$

where K is a constant for a given absorption band, ${}^{10} R_{12}$ is the center-to-center distance of the two dimer molecules, and all other symbols are as defined in Sec. II A. Proceeding along the lines of Sec. II A, we obtain

$$\theta(E) = R \sum_{n\alpha} \sum_{m} e^{-\beta m} \exp[-(E_n - m - E)^2 / \Delta^2]$$
$$\times \left[\left| \langle \chi_{n\alpha}^{(+)} | m \rangle \right|^2 - \left| \langle \chi_{n\alpha}^{(-)} | m \rangle \right|^2 \right] , \qquad (2.35)$$

where $R = K(\mathbf{R}_{12} \cdot \boldsymbol{\mu}_1 \boldsymbol{x} \boldsymbol{\mu}_2)$ is the rotational strength.

This can be manipulated to yield

$$\theta(E) = R(G_1 - G_2)$$
, (2.36)

where G_1 , G_2 are given Eqs. (2.28b) and (2.32b). This expression is antisymmetric about E = 0 as is expected for the CD of a dimer.

III. RESULTS

A. Comparison of the approximate theory with numerical calculations

We investigate the validity of our approximations for the absorption and CD by comparing Eqs. (2.33) and (2.26) with results generated from direct diagonalization of Hamiltonian (2.3). In all cases a 100×100 matrix (50 vibrational states for each electronic state) was diagonalized, and the absorption and CD computed numerically from Eqs. (2.11) and (2.34). A sufficient number of vibrational basis states were included so that, for the highest temperature ($\beta = 0.1$) and exciton-phonon coupling strength ($g/\sqrt{2} = 0.5$) that we discuss here, all relevant excited states are accurately given by the matrix diagonalization of the truncated basis set.

For absorption we set $|\mu_{+}|^{2}=1$, $|\mu_{-}|^{2}=0$ for convenience; the term proportional to $|\mu_{-}|^{2}$ would be a mirror image of the spectrum presented here, reflected through E=0. For the actual choice, the main peak is at high energy (E > 0) with the low energy peak due to the vibronic coupling of the $|+\rangle$ and $|-\rangle$ states. The absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$.

In the circular dichroism calculation, we set the constant R in Eq. (2.36) equal to 1; $\theta(E)$ is then expressed in these (arbitrary) units. Here the absolute intensity is relevant and represents a real measure of the magnitude of the observed signal as a function of J, g, β , and Δ , given that R is fixed. The energy is, as above, in units of $\hbar\omega$.

In Fig. 1, we fix J, g, and β at reasonable values (strong electronic coupling, high temperature) and determine the effect in the absorption spectrum of varying Δ . As expected, for large Δ ($\Delta = 5.0$) agreement is essentially quantitative in all regions of the spectrum. As Δ decreases, agreement remains quantitative in the high energy region, but the details of the low-energy tail are to some extent incorrect in the approximate calculation. This is undoubtedly due to the use of the first order cumulant expansion, and could perhaps be improved by including higher order terms. However, the actual results are probably sufficient for analyzing experiments in practice, where the detailed shape of the tail will be obscured by background noise, other transitions and the peak proportional to $|\mu_-|^2$.



FIG. 1. Comparison of exact and approximate absorption line shapes for various values of Δ . Absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$.

J. Chem. Phys., Vol. 75, No. 12, 15 December 1981



FIG. 2. Comparison of exact and approximate absorption line shapes for various values of β . Absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$.

In Fig. 2 we fix J, g, and Δ , and vary β . Agreement of the absorption spectrum is good throughout the entire temperature range, although worst for the low energy tail at low temperature. Thus for moderate excitonphonon coupling (g < 1) the cumulant expansion of $e^{-\beta h_0}$ introduces little error even for large β ; this is because the lowest excited states yield intensity primarily at E = +J, so that vibronic exchange is of minimal importance in this region.

Finally, Fig. 3 shows that for weak electronic cou-

pling $(J \ll 1)$ the approximate theory of this paper is incorrect; in particular, the shift of the main peak to high energy is greatly overestimated. We will discuss the reasons for this in another publication.¹¹

The circular dichroism calculation produces quantitative agreement in all cases we have investigated; apparently the functions G_1 and G_2 are more accurate representations of their exact analogs for small Δ and β than F_1 and F_2 . In Fig. 4 we present a comparison of two typical exact and approximate CD line shapes.



FIG. 3. Comparison of exact and approximate absorption line shapes for weak electronic coupling. Absorption is normalized to 1 and in dimensionless units; energy is in units of $\hbar\omega$.

B. Characterization of the absorption and CD spectra

Qualitatively, our calculations are in agreement with what one would predict from a simple, stochastic two state exchange model¹² [the |+) and |-) states at energies +J and -J are coupled by a vibronic perturbation ~ $(A_*^*A_+ A_*^*A_*)$]; as temperature increases $(\beta \to 0)$ intensity is transferred to low energy in a peak (small Δ) or a broad, structureless tail (large Δ); at the same time, the maximum of the main peak moves to higher energy. In this way the first moment sum rule

$$M^{(1)} = \int_{-\infty}^{+\infty} I(E) E dE = J(|\mu_{+}|^{2} - |\mu_{-}|^{2})$$
(3.1)

is satisfied. Transfer is more efficient at high temperature because the value of the vibronic matrix element $\langle +n | Q | - (n+1) \rangle \propto \sqrt{n}$ is larger for high *n* states, which are increasingly populated as $T - \infty$.

In addition, exchange is suppressed by increasing J (this corresponds in the \pm representation, to increasing the energy separation of the two level system) or de-

creasing g. These features are illustrated in Table I, where the shift from E = J of the main peak, main peak amplitude, and integrated intensity of I(E) for E < 0 are presented as a function of g, J, and Δ . These numbers are calculated using the approximate expressions (2.33) and (2.36).

For the circular dichroism, increasing exchange has the effect of decreasing the signal amplitude. This is because the $|+\rangle$ and $|-\rangle$ states have equal and opposite rotational strengths; if transitions at all energy have large $|+\rangle$ and $|-\rangle$ contributions, they will cancel and the CD amplitude will be correspondingly reduced. Table I presents the integrated intensity R_{\star} of the high energy CD peak. (The low energy peak is simply an inversion of this through the origin.) The CD maximum is in all cases coincident with the absorption maximum in Table I.

Our calculations show that the approximate theory predicts the above specific features of the dimer optical spectra quite well. Other effects, like the narrowing of



FIG. 4. Comparison of exact and approximate circular dichroism line shapes. Ellipticity is in arbitrary units (see text); energy is in units of $\hbar \omega$. Only the E > 0 peaks is shown; the E < 0 peak is a mirror image of this reflected through the origin.

J. Chem. Phys., Vol. 75, No. 12, 15 December 1981

TABLE I. Characterization of the absorption and circular dichroism spectra for various values of J, g, and β . E_{\max} is the absorption maximum, $A(E_{\max})$ the absorption amplitude at this energy, LET is the integrated absorption intensity for E < 0, and $R^{(*)}$ is the integrated intensity of the CD for E > 0. J, g, and E are in units of $\hbar \omega$; β is in units of $(\hbar \omega)^{-1}$.

(a) $\beta = 0.1, \Delta = 2.0$					
2.0	0.1	2.1	0,278	0.079	0.83
2.0	0.2	2.2	0.269	0.095	0.80
2.0	0.3	2.4	0.254	0.116	0.76
2.0	0.4	2.6	0.237	0.141	0.71
2.0	0.5	2.8	0.218	0.165	0.67
			(b)		
1.0	0.5	2.1	0.182	0,299	0.39
2.0	0.5	2.8	0.218	0.165	0.67
3.0	0.5	3.6	0.239	0.094	0.81
4.0	0.5	4.5	0.252	0.060	0.88
5.0	0.5	5.4	0.260	0.042	0.91
			(c)		
		β =	$0.5, \Delta = 2.0$		
2.0	0.1	2.0	0.281	0,092	0.82
2.0	0.2	2.0	0.278	0.095	0.81
2.0	0.3	2.1	0.275	0.100	0.80
2.0	0.4	2.2	0.269	0.107	0.79
2.0	0.5	2.3	0,263	0.115	0.77
			(d)		
1.0	0.5	1.5	0.294	0.25	0.48
2.0	0.5	2.3	0.263	0.115	0.77
3.0	0.5	3.2	0.272	0.04	0.92
4.0	0.5	4.1	0.276	0.02	0.96
5.0	0.5	5.1	0.277	0.01	0.98

the main peak relative to the monomer, are also correctly predicted; note that in our model, this depends on the relative degree of homogeneous and inhomogeneous broadening. The narrowing will be most pronounced for large exchange (high temperature, large g).

IV. COMPARISON WITH OTHER METHODS

Optical line shapes of dimers contain information about the geometry and interactions of the molecular pair. The objective in fitting a theoretical expression to experimental data is to extract as much of this information as possible. The validity of a parametrized fit will depend on two aspects of the method used to derive the line shape function:

(1) Initial inclusion of various interactions in the Hamiltonian; (2) mathematical approximations leading to the final result.

Analytical approximation methods are usually able to include more terms in the Hamiltonian, but make more serious mathematical approximations than direct numerical techniques. In the remainder of this section, we will contrast our approach with currently available methods of both types. For the Hamiltonian we have chosen here, calculations can be performed via direct diagonalization of a truncated basis set (e.g., the "exact" results of Sec. III). If a calculation were to be made with a single, known set of parameters $(g, J, \omega, \Delta, R, \beta, |\mu_+|^2, |\mu_-|^2)$, this would be the preferred approach. However, in actual systems many of these quantities are not known and must be determined by curve fitting. This fit may not be unique; it is important to explore the entire region of parameters pace and determine the acceptable range of parameters. This procedure will be most useful if several spectra (e.g., at different temperatures) can be fit simultaneously.

To carry out the program described above numerically would require large amounts of computer time. The analytic theory of this paper, on the other hand, uses a negligible amount of computer time per spectrum; in addition, nonlinear least squares curve-fitting methods can be conveniently used to find the best-fitting parameter regions. Simultaneous fits can easily be made and specific features of the spectrum (involving moments higher than the second) investigated. Reasonable agreement with a single spectrum is usually simple enough to generate; the exhaustive study needed to generate meaningful parameters is greatly facilitated by relatively simple analytic expressions.

We now compare our formalism with other approximate analytical theories. Polarizability theory (or time-dependent Hartree theory) has been shown to give incorrect answers in the strong coupling limit (3, 13). We therefore focus the discussion on Hemenger's DGS (Degenerate Ground State) theory.³⁻⁵

We shall not investigate the details of the approximations made in deriving the DGS line shapes for absorption [Eq. (38), Ref. 3], or circular dichroism [Eq. (22), Ref. 4], although it is clear that these are more drastic than those in this paper. Rather, we will point out the fundamental assumptions in the DGS approach, and show that the systems which may be so described form a small subset of those given by Eq. (2.1).

First, we note that the DGS assumption of a single phonon frequency is equivalent, for a *dimer*, to a one phonon per molecule model; a canonical transformation can be made in which only one mode is coupled to the electronic degrees of freedom. Then, the DGS model is at best equivalent to Hamiltonian (2.1).

Secondly, the DGS theory is a zero-temperature theory [Eq. (11) of Ref. 3 is valid only at zero temperature] and so is incapable of describing the temperature dependence of the line shape. This is a serious restriction on the utility of this formalism for actual calculations.

Finally, DGS theory does not include the effects of inhomogeneous broadening. This point is discussed in more detail in Ref. 7, where it is shown that a single monomer spectrum can generate quite different dimer spectra (with the geometry and electronic exchange interactions fixed) depending on the relative proportions of vibronic and inhomogeneous broadening. Thus, DGS theory can only be applicable where inhomogeneous broadening is negligible. In contrast, Eqs. (2.33) and (2.36) contain an explicit dependence upon this quantity which reproduces its effect in numerical calculations.

To conclude this section, we briefly comment on the stochastic approach. The stochastic Hamiltonian is valid in the limit that the phonon bandwidth is large compared to the electronic exchange interaction. As Eq. (2.1) has no phonon dispersion, it is inappropriate to compare our present results with stochastic theory.

V. CONCLUSION

The results of the previous section suggest that our analytical expressions, Eqs. (2.33) and (2.36) are potentially useful for any system in which individual vibronic lines are not resolved, assuming $2J > \omega$ and $g \leq 1$. (We have not investigated g > 1, as this is not likely for a molecular system.) Even at relatively small Δ and large β , agreement is quite reasonable.

The applicability of the physical model (one primary molecular vibration, inhomogeneous broadening) remains to be investigated. There are certainly some limits (slow medium motion, e.g.), for which it is a good approximation. We will discuss this point in detail in a forthcoming publication, ¹⁴ where we will analyze the effects of a finite phonon bandwidth and compare various theoretical approaches. At the very least, however, the results in this paper are a necessary prelude to the more complicated multiphonon case, which we will analyze in a similar method using a Hartree or mean field approximation.

The advantage of using our equations to analyze experimental data is that they can be fit to experimental curves, varying the parameters J, $|\mu_{+}|^{2}$, Δ , and R, and determining g from the monomer spectrum. Ideally, one would be able to investigate a significant temperature range, but this may not always be possible. This serching of a four-dimensional parameter space would be an extremely lengthy task if done via numerical matrix diagonalization and could produce incorrect answers if other, less accurate analytical theories were used.

In this way one could extract three significant parameters of the dimer; J, $|\mu_{+}|^{2}$, and R. These quantities are simply related to the dimer geometry; analysis of two well-separated transitions would provide enough equations to determine the six parameters needed to specify the dimer geometry. One suitable system for such calculations is a chlorophyll protein with two chlorophyll molecules per protein, which can be isolated from the antenna of R-26 mutants of the photosynthetic bacterium Rps. spheroides. Many experimental measurements have been performed on this system, ¹⁵ and we plan to analyze the data as described above in the future.

Another interesting set of systems are two-sited mixed-valence ionic complexes.¹⁶ These systems can be described by a vibronic Hamiltonian equivalent to Eq. (2.1).¹⁷ One particular complex (of the Creutze – Taube ion) has been studied in detail experimentally and theoretical interpretations of the absorption spectrum, using numerical diagonalization of a vibronic¹⁹ or adiabatic^{17,18} set of basis states, have been performed. A different set of parameters was obtained by each group, due principally to assumptions of differing contributions of the equivalent of inhomogeneous broadening.²² By applying the methods of this paper, it should be possible to analyze the parameter space exhaustively and obtain more reliable results.

The theory of Sec. II can easily be modified to generate an approximate Green's function G(E) for the ensemble of dimers. From this, one could calculate not only the absorption and CD [these are just particular combinations of matrix elements of G(E)] but also other optical properties, e.g., fluorescence, fluorescence polarization, and linear dichroism. Expressions analogous to Eqs. (2.33) and (2.36) will be produced, which can quantitatively be compared to experimental results.

We have also extended our results to a generalized two-level system, which will be treated in another publication. Thus, the methods described here can be used not only to analyze dimer spectra, but also to investigate any system in which two excited states interact via linear vibronic coupling.

The theory presented here possesses definite advantages over previous theories; inclusion of inhomogeneous broadening, quantitative agreement for a strong coupling, explicit dependence on temperature and microscopic monomer parameters, and tractability for computational purposes. When multiphonon effects have been included, it should be capable of accurately modeling a wide range of real experimental systems.

APPENDIX: EVALUATION OF INTEGRALS IN LINE SHAPE FORMULAS

We want to evaluate, for example,

$$F_{1} = \int dn \, e^{-\beta n} \, \exp[-(E - \Gamma_{n})^{2}/\Delta^{2}] \, .$$

We set
$$z = \Gamma_{n} = \{J^{2} + g^{2}(n + 1/2)\}^{1/2} \, ,$$
$$\frac{dz}{dn} = \frac{1}{2} g^{2}/z \, ,$$
$$n = (z^{2} - J^{2})/g^{2} - 1/2 = (z^{2} - \Gamma_{0}^{2})/g^{2} \, .$$

then

J. Chem. Phys., Vol. 75, No. 12, 15 December 1981

(A1)

$$F_{1} = \int_{\Gamma_{0}}^{\infty} dz \frac{2z}{g^{2}} \exp\left[-(E-z)^{2}/\Delta^{2}\right] e^{-\beta z^{2}/z^{2}} e^{\beta \Gamma_{0}/z^{2}} = \frac{z e^{-E^{2}/\Delta^{2}} e^{\beta \Gamma_{0}/z^{2}}}{g^{2}} \int_{\Gamma_{0}}^{\infty} dz \, z \, \exp\left\{-z^{2} \left(\frac{\beta}{g^{2}} + \frac{1}{\Delta^{2}}\right) + \frac{2zE}{\Delta^{2}}\right\} ,$$
Let

$$\alpha = \left(\frac{\beta}{g^2} + \frac{1}{\Delta^2}\right) ,$$

$$z = \left(\frac{\beta}{g^2} + \frac{1}{\Delta^2}\right)^{-1/2} y + \frac{E}{\Delta^2} \left(\frac{\beta}{g^2} + \frac{1}{\Delta^2}\right)^{-1} = \alpha^{-1/2} y + \frac{E}{\alpha \Delta^2} ,$$

then

$$F_{1} = \frac{2}{\alpha^{1/2}g^{2}} e^{-E^{2}/\Delta^{2}} e^{\beta\Gamma_{0}/t^{2}} e^{\frac{E^{2}}{\alpha}\Delta^{4}} \int_{\alpha^{1/2}\Gamma_{0}-E/\alpha^{1/2}\Delta^{2}}^{\infty} dy \ e^{-y^{2}} [\alpha^{-1/2} \ y + E/\Delta^{2}\alpha]$$

$$= \frac{2}{\alpha^{1/2}g^{2}} \exp\left(-\frac{E^{2}}{\Delta^{2}} + \frac{\beta\Gamma_{0}}{g^{2}} + \frac{E^{2}}{\alpha\Delta^{4}}\right) \left\{ \frac{\alpha^{-1/2}}{2} \exp\left[-(\alpha^{1/2}\Gamma_{0} - E/\Delta^{2}\alpha^{1/2}]^{2} + \exp\left(E/\alpha\Delta^{2}\right) \operatorname{erfc}\left[\alpha^{1/2}\Gamma_{0} - E/(\alpha^{1/2}\Delta^{2})\right] \right\}$$

$$= (\alpha g^{2})^{-1} \exp\left[-(E - \Gamma_{0})^{2}/\Delta^{2}\right] + 2E(\alpha^{3/2}g^{2}\Delta^{2})^{-1} \exp\left[-(E - \Gamma_{0})^{2}/\Delta^{2}\right] \exp\left[\alpha^{1/2}\Gamma_{0} - E/(\Delta^{2}\alpha^{1/2})^{-1}\right]^{2} \operatorname{erfc}\left[\alpha^{1/2}\Gamma_{0} - E/(\alpha^{1/2}\Delta)\right].$$

Another integral we need is

$$G_{1} = \int dn \ e^{-\beta n} \frac{1}{\Gamma_{n}} \exp\left[-(E - \Gamma_{n})^{2}/\Delta^{2}\right]$$

= $\frac{2}{g^{2}} \exp\left(\Gamma_{0} \beta/g^{2} - E^{2}/\Delta^{2}\right) \int_{\Gamma_{0}}^{\infty} dz \ \exp\left\{-z^{2}\left(\frac{1}{\Delta^{2}} + \frac{\beta}{g^{2}}\right) + \frac{2Ez}{\Delta^{2}}\right\}$
= $2(\alpha^{1/2}g^{2})^{-1} \exp\left[-(E - \Gamma_{0})^{2}/\Delta^{2}\right] \exp\left[\alpha^{1/2}\Gamma_{0} - E/\alpha^{1/2}\Delta^{2}\right]^{2} \operatorname{erfc}\left[\alpha^{1/2}\Gamma_{0} - E/\alpha^{1/2}\Delta^{2}\right].$

We also need integrals for the part of I(E) where $\alpha = 2$. These are

$$\begin{split} F_{2} &= \int dn \, e^{-\beta n} \, \exp[-(E+\Gamma_{n})^{2}/\Delta^{2}] \\ &= \frac{2}{g^{2}} \, \exp\!\left(\frac{\beta \, \Gamma_{0}^{2}}{g^{2}} - \frac{E^{2}}{\Delta^{2}}\right) \! \int_{\Gamma_{0}}^{\infty} \, dz \, z \, e^{-\beta s^{2}/s^{2}} \, e^{-zEst/\Delta^{2}} \\ &= \frac{2}{\alpha g^{2}} \, \exp\!\left[-(E+\Gamma_{0})^{2}/\Delta^{2}\right] - \frac{2E}{\alpha^{3/2} g^{2} \Delta^{2}} \, \exp\!\left[-(E+\Gamma_{0})^{2}/\Delta^{2}\right] \, \exp\!\left[\alpha^{1/2} \Gamma_{0} + \frac{E}{\Delta^{2} \alpha^{1/2}}\right]^{2} \, \operatorname{erfc}\left(\alpha^{1/2} \Gamma_{0} + \frac{E}{\Delta^{2} \alpha^{1/2}}\right) \, . \end{split}$$

Analogously,

$$G_{2} = \int dn \, e^{-\beta n} \, \frac{1}{\Gamma_{n}} \, \exp\left[-(E + \Gamma_{n})^{2} / \Delta^{2}\right]$$

= $2(\alpha^{1/2}g^{2})^{-1} \exp\left[-(E + \Gamma_{0})^{2} / \Delta^{2}\right] \exp\left(\alpha^{1/2}\Gamma_{0} + \frac{E}{\alpha^{1/2}\Delta^{2}}\right)^{2} \operatorname{erfc}\left(\alpha^{1/2}\Gamma_{0} + \frac{E}{\alpha^{1/2}\Delta^{2}}\right)$

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- ²⁰In addition to inhomogeneous broadening, we also have to include broadening due to the (+) phonons which have been decoupled in Eq. (2.3). These will generate a vibronic envelope which will be identical for each transition $|0m_{-}\rangle \rightarrow \psi_{n}(Q_{-})$. This is isomorphic to the model of inhomogeneous broadening in Ref. 7; we can therefore incorporate this effect in the broadening function $D(\Delta E)$, so that D is now understood to be a convolution of the (+) vibronic envelope with an inhomogeneous width. This means that Δ in Eq. (2, 2) should be temperature dependent; we ignore this in the calculations

which follow but it should be included in analysis of the temperature dependence of the line shape. ²¹This can be justified more rigorously by writing

$$\langle \chi_{n\alpha}^{+} | \hat{0}_{n\alpha}(E) | \chi_{n\alpha}^{+} \rangle = \int D(\Delta E) d(\Delta E)$$

$$\times \int e^{iBt} dt \langle \chi^{*}_{n\alpha} | \hat{0}_{n\alpha} (\Delta E, t) | \chi^{*}_{n\alpha} \rangle ,$$

where

 $\hat{0}_{n\alpha}(\Delta E, t) = e^{it(\Delta B - E_{n\alpha} + h_0)} e^{-\beta h_0} .$

The cumulant expansion is made before performing the time integration, directly yielding Eq. (2.25) without further ap-

proximation. ²²In Refs. 17 and 18, broadening is assumed to arise from vibrational modes of the complex which are uniformly coupled to both singly excited electronic configurations. These are equivalent to the (+) phonons of Eq. (2.3) and can be treated as described in Ref. 20.

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