SPIN ABSORPTION IN TRIPLET EXCITON SYSTEMS

Thesis by

Joel I. Krugler

In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1965
(Submitted September 30, 1964)

Acknowledgments

I am indebted to Professor H. M. McConnell, who supervised my research, for suggesting the problems treated, and for many helpful discussions. Thanks are also due to C. G. Montgomery for many useful suggestions.

TABLE OF CONTENTS

Abstract

A theoretical study of the low-temperature paramagnetic resonance lines of linear-chain organic free-radical crystals characterized by triplet excitons is made by means of a generalized moment method. Techniques which permit the determination of the moments of absorption lines at all temperatures, and to any desired order in interaction parameters, are developed. The necessity for the usual truncation of the hamiltonian is avoided with the aid of the absorption operator expansions of Cheng.

The method is used to calculate the zeroth through fifth moments of the g=2 doublet absorption lines of crystals of Wurster's blue perchlorate. The hamiltonian for the system includes exchange and anisotropic spin interactions, and coupling to a strong external magnetic field. It is shown that exciton creation, annihilation, and transfer processes have negligibly small effect on the absorption. The calculated exciton density, ρ, and the line width, W, have temperature dependence given by

$$\rho \sim e^{-J/kT}$$

$$W \sim e^{-J/2kT}.$$

The inclusion of phonon coupling, through distance-dependent exchange integrals, is shown, by means of a canonical linear transformation, to produce an effective exciton-exciton repulsion; this repulsion decays exponentially with distance.

Inclusion of this phonon interaction in the moment calculation leads to exciton density and line width varying like

$$\rho \sim e^{-\bar{J}/kT}$$

$$W \sim e^{-(\bar{J} + \Delta E)/2kT}$$

The activation energy, ΔE, can account for the "anomalous" line broadening observed in many triplet systems.

1. Introduction

The low temperature paramagnetic properties of many organic free-radical crystals can be most easily interpreted as resulting from the presence of triplet excitons. For present purposes, a triplet exciton may be defined as any collective crystal excitation of spin 1. A dimerized system of spin $\frac{1}{2}$ molecules, with spin pairing in the singlet ($S=0$) configuration energetically favorable, will be characterized by such spin excitations. The excited $S=1$ multiplet of a dimer of a system of this sort can propagate through the crystal by means of such mechanisms as exchange and dipole interactions, and phonon coupling.

The experimentally significant properties of a triplet exciton system include:

(1) a characteristic splitting of spin states, due to spin-spin dipole interactions and the influence of an external magnetic field;

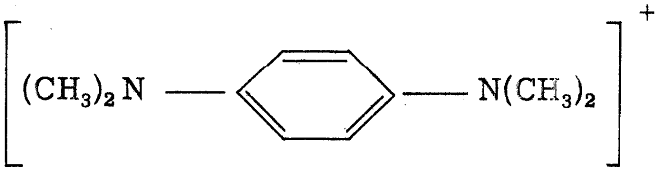
(2) a broadening of the spin resonance line, as compared with the line width for an undimerized system;

(3) low spin concentration (and paramagnetic susceptibility), resulting from the singlet-triplet energy gap to the paramagnetic states of the system.

The <u>cooperative</u> nature of these elementary excitations manifests itself in the disappearance of proton hyperfine structure in the absorption spectrum. That is, the fact that a triplet exciton is not localized, but is distributed over many molecules, results in an averaged hyperfine structure that is small compared to that associated with isolated molecules.

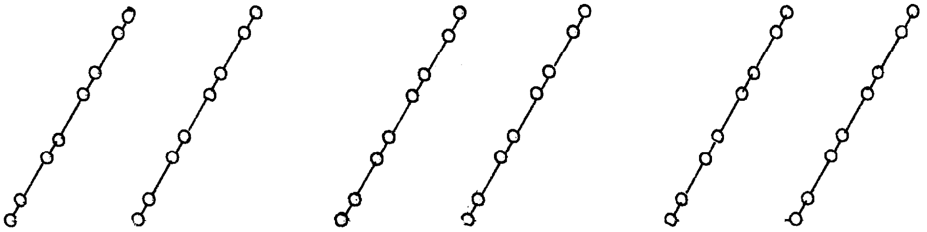
We shall be concerned primarily with a study of the absorption spectra of organic crystals that are composed of essentially independent, topologically linear chains. That is, the molecules of these systems are assumed to interact strongly with at most two nearest neighbors. Systems exhibiting triplet exciton paramagnetic resonance in which exciton motion is principally along linear free radical chains include a number of salts based on the acceptor TCNQ[1-4], the ionic crystal of Wurster's blue perchlorate (WBP)[5, 6], and others. For definiteness, we shall consider specifically WBP; our results, however, should be indicative of the behavior of many other linear triplet systems.

In WBP, linear chains of N, N, N', N'-tetramethyl-p-phenylene diamine cations ($s=\frac{1}{2}$), (shown schematically below) are insulated from one another by perchlorate groups.



The WB Cation

At room temperature, the WB ions are equally spaced [7], and the absorption spectrum shows a sharp exchange-narrowed resonance line. (A projection of the orthorhombic structure of room temperature WBP onto the $a_o c_o$ plane is shown in Fig. 1 .) Below 186°K, the molecules dimerize to a configuration in which the intermolecular WB distances alternate[5, 6]. Such a dimerized chain can be represented schematically as:



Chain of Dimerized WB Cations

The instability of strictly linear chains of spin $\frac{1}{2}$ molecules to distortions of this sort has been described theoretically by a number of authors [8-11], and is a quite general property for strictly linear chains.

Experimental and theoretical studies of the paramagnetic resonance of Wurster's blue perchlorate at low temperatures have been reported in the literature in some detail. Thomas, Keller and McConnell [6] (TKM) show, from single crystal measurements in the 20° - 70° K temperature range, that the elementary triplet excitation energy is 246 cm^{-1} , and find an absence of hyperfine structure which indicates exciton motion. Using the fact that different linear WB chains of the crystal are not magnetically equivalent for an arbitrary direction of the external magnetic field, they are able to estimate the rate of exciton chain jumping. Their conclusion is that exciton motion is indeed primarily along single chains, and the jumping rate is greater than 50 Mc/sec but probably less than 10^3 - 10^4 Mc/sec. For a magnetic field directed along the chain axes, however, all chains are magnetically equivalent, and chain jumping has no effect on the fine structure splitting of the resonance lines.

TKM also observe an "anomalous" broadening of the resonance lines with increasing temperature, an effect also observed in a number of the TCNQ free-radical salts [2,3]. McConnell and Soos[12] suggest that an exiton-phonon coupling can lead to an activation energy for spin-exchange line broadening that could account for this effect. The present work includes a detailed calculation of such an interaction, the results of which confirm that this may be so if the coupling parameter is sufficiently large.

Calculations of triplet exciton band structure, magnetic susceptibility of an exciton gas, fine structure splitting and similar properties have been performed on the basis of a number of simplified models.[11,13-16] It has been shown that the statistical properties of these excitons may be approximated by Fermi[13,15] or Bose[11] statistics, although the true commutation relations obeyed by triplet exciton creation and annihilation operators are more complicated than either of these. In general, any predictions made by these methods about the shapes of the absorption lines tend to be qualitative, and based on a simplified truncated version of the hamiltonian of the system.

The present calculation is based on a moment method. The moments of the resonance line(at g=2), of WBP will be calculated quantitatively using an untruncated model hamiltonian which should yield a reasonable representation of the magnetic properties of many linear triplet systems.

The method of moments, originally developed by Broer, Van Vleck, and others[17-19], is a powerful tool for studying the absorption lines of paramagnetic systems subject to a strong constant magnetic field and simultaneously to a weak oscillating field. The basis of this method is the expression of the moments of a (narrow) absorption peak in terms of traces of known operators. Since a trace is invariant with respect to representation, any convenient complete set of states can be used in the calculation. The eigenstates and eigenvalues of the hamiltonian of the system need not be known explicitly.

In its original formulation, the moment method was subject to two fundamental approximations. The first is a restriction to high temperatures, so that the relative population of excited states of the system depends only linearly on the energy difference between them. (That is, it was assumed that $e^{-\mathcal{H}/kT}$ could be approximated reasonably by

$1 - \mathcal{H}/kT$.) The second approximation is a result of a truncation of the hamiltonian in order to eliminate terms which can introduce contributions to the moments from secondary lines that are far removed from the line of interest. A truncation of this sort will, of course, in general also discard terms that affect the shape of the primary line in some higher order.

The restriction to high temperatures has been relaxed by Kambe and Usui[20], and McMillan and Opechowski[21], who present general temperature-dependent expressions for line moments. Since there are many equivalent forms for these expressions, we shall present in Section 2 a brief independent derivation that yields the form most convenient for the present calculation.

The necessity for truncating the hamiltonian has been removed by Hung Cheng[22], who has developed a method for generating absorption operators to all orders. These operators are functions of frequency; they are peaked in the region of the frequency of the absorption line of interest, and fall rapidly to zero outside this reagion. Alternatively, they can be looked upon as projecting out those parts of the hamiltonian that give rise to absorption in the vicinity of the frequency of the primary absorption line. Using the truncated form of the spin hamiltonian, as in earlier treatments, is equivalent to using the zeroth-order absorption operators of Hung Cheng.

It should be noted that in <u>any</u> calculation of this sort there are certain inherent limitations. In order to calculate the properties of a single absorption peak, we must assume that individual resonance lines are clearly defined. For lines proportional to the magnetic field for example, this condition is satisfied if the external field is sufficiently large; such splittings may be obtained in low field as a result of anisotropic spin-spin coupling. A second assumption made here is that saturation of the spin system does not occur. That is, we assume that the power in the perturbing oscillatory field is sufficiently low so that first order perturbation theory is an adequate description of the transition probabilities. Experimentally, this condition is readily satisfied.

The present work combines the previous advances in the theory of line moments, and presents a general method for determining the moments of the absorption lines of a broad class of systems, to any order in interaction parameters, and for a wide range of temperatures. It will be seen that problems not hitherto encountered are met in the present method. The techniques developed to handle these problems should find applications elsewhere in the general field of statistical physics, where quantities expressed in similar forms are often encountered.

In Section 2 we develop general expressions for the moments of resonance lines in terms of traces of absorption operators, and present a brief re-derivation of Hung Cheng's prescriptions for obtaining these operators. Section 3 is concerned with the application of such expressions to the calculation of the absorption spectrum of WBP. In this section we neglect phonon coupling. This restriction is relaxed in Section 4. For a model of the low-temperature spin structure of WBP, we use a hamiltonian that includes nearest-neighbor exchange interactions, an anisotropic spin-spin dipole term, and coupling to a (moderately strong) external magnetic field. As we shall see, a hamiltonian of this form contains components that create and annihilate triplet excitons both singly and in pairs, and other components that correspond to excitation transfer. Terms of this sort are often neglected in earlier theoretical examinations of the properties of triplet system. We shall see that this assumption is reasonable, in that creation, annihilation and transfer terms do not affect the shape of resonance lines until negligibly small terms of high order in interaction parameters are considered.

Also in Section 3, we treat the special problems that arise in the present method. These include a discussion of the convergence of the various expansions used, the elimination of a spurious N-dependence of the quantities calculated, and a presentation of the general techniques for taking temperature-dependent traces.

In Section 4, the effects of phonon-exciton coupling are considered. This coupling appears as a result of an (assumed linear) distance-dependence of the exchange integrals, and can, in fact, play a significant role in determining the relative temperature-dependences of the line width and the spin concentration. The fact that the phonon coupling to the exchange interaction between the molecules of a given dimer is equivalent to an exciton-exciton repulsion will be shown with the aid of a canonical linear tranformation. The moment calculation of the effects of the phonon coupling will reveal the effects of this repulsion on the line shapes, and will include the coupling between dimers as well.

2. General Theory

It is possible to express the moments of an absorption line of a quite general system in terms of traces of temperature-dependent operators. We shall first develop such temperature-dependent expressions in the form most convenient for the present calculation, and then present a brief re-derivation of the theory of absorption operators.

2.1 Temperature-dependent Absorption

We consider a system represented by a hamiltonian $\mathcal{H}$, absorbing power from a periodic perturbing field V. The perturbation of this oscillating potential is assumed to be sufficiently small to justify the use of first order perturbation theory for obtaining the transition probabilities. The eigenstates, $|j\rangle$, and eigenvalues, E_j, of the hamiltonian are defined by

$$\mathcal{H}|j\rangle = E_j|j\rangle \quad . \tag{2.1}$$

If the system is initially in state $|j\rangle$, the probability per unit time that V will induce a transition to state $|k\rangle$, with the emission of a photon of energy ω, is given by

$$\Gamma_{jk} = \frac{2\pi}{\hbar} |\langle j|V|k\rangle|^2 \, \delta(E_k - E_j + \omega). \tag{2.2}$$

We assume that the system is in thermal equilibrium at temperature T, and can therefore be described by the density matrix

$$\rho = \frac{e^{-\beta \mathcal{H}}}{\mathrm{Tr}\; e^{-\beta \mathcal{H}}} \,, \tag{2.3}$$

where $\mathrm{Tr}\, X \equiv \sum_{|j} \langle j | X | j \rangle$,

and $\beta \equiv \frac{1}{kT}$.

The probability that the system is originally in state $|j\rangle$ is

$$\frac{e^{-\beta E_j}}{\mathrm{Tr}\; e^{-\beta \mathcal{H}}} \,,$$

and the probability that a photon of frequency ω is absorbed in such a transition is

$$\frac{(e^{-\beta E_k} - e^{-\beta E_j})}{\mathrm{Tr}\; e^{-\beta \mathcal{H}}} \, \Gamma_{jk}.$$

The power absorbed at frequency ω is thus

$$f(\omega) = \frac{2\pi}{\hbar} \sum_{|j\rangle\, |k\rangle} \frac{(e^{-\beta E_k} - e^{-\beta E_j})}{\mathrm{Tr}\; e^{-\beta \mathcal{H}}} \, |\langle j | V | k \rangle|^2 (E_j - E_k)\, \delta(E_j - E_k - \omega). \tag{2.4}$$

We can, at least formally, decompose V into its harmonic components with respect to $\mathcal{H}$. That is, we write

$$V = \sum_{\omega'} V(\omega') \,, \tag{2.5}$$

where

$$[\,\mathcal{H},\ V(\omega')\,] = \omega' \, V(\omega'). \tag{2.5a}$$

This decomposition is unique.

V (ω') has the property that when acting upon an eigenstate of $\mathcal{H}$, it yields another eigenstate of $\mathcal{H}$, with energy ω' greater than that of the initial state. We can now absorb the δ-function appearing in the sum (2.4), because

$$\langle j | V | k \rangle \, \delta\,(E_j - E_k - \omega) = \langle j | V(\omega) | k \rangle. \tag{2.6}$$

We observe, further, that

$$\langle k | V^\dagger | j \rangle \, (e^{-\beta E_k} - e^{-\beta E_j}) = \langle k | [e^{-\beta \mathcal{H}},\ V^\dagger] | j \rangle \,, \tag{2.7}$$

so that equation (2.4) may be written

$$f(\omega) = \frac{2\pi}{\hbar} \sum_{|j\rangle, |k\rangle} \omega \, \frac{\langle k | [\, e^{-\beta\mathcal{H}},\ V^\dagger] | j \rangle}{\mathrm{Tr}\ e^{-\beta\mathcal{H}}} \langle j | V(\omega) | k \rangle \,, \tag{2.8a}$$

or

$$f(\omega) = \frac{2\pi}{\hbar} \, \omega \, \frac{\mathrm{Tr}[\, e^{-\beta\mathcal{H}},\ V^\dagger]\ V(\omega)}{\mathrm{Tr}\ e^{-\beta\mathcal{H}}} \tag{2.8b}$$

Since Tr ABC = Tr CAB, we can also express (2.8b) as

$$f(\omega) = \frac{2\pi}{\hbar}\ \omega\ \frac{\mathrm{Tr}\ e^{-\beta\mathcal{H}}[V^{\dagger}, V(\omega)]}{\mathrm{Tr}\ e^{-\beta\mathcal{H}}} \quad . \tag{2.9}$$

This form of the expression for the power absorbed at frequency ω has a distinct advantage over Eq. (2.4), in that it is invariant with respect to the choice of basis states. That is, the traces appearing in Eq. (2.9) can be taken using any convenient complete set of states; the eigenstates of $\mathcal{H}$ need not be known. The harmonic components, $V(\omega)$, however, are not known, in general, without knowledge of the eigenstates of $\mathcal{H}$. We shall now show that, for a wide class of problems, it suffices to know only certain sums involving these operators, and that we can generate series to approximate these sums.

We assume that the hamiltonian can be written in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \ , \tag{2.10}$$

where the eigenvalues and eigenstates of $\mathcal{H}_0$ are <u>known</u>, and where $\mathcal{H}' \langle\langle \mathcal{H}_0$. Suppose, further, that the harmonic components of $\mathcal{H}'$ and V with respect to $\mathcal{H}_0$ are also known. That is, we know explicitly the sets of operators $\mathcal{H}'(\nu_\alpha)$ and $V(\nu_\beta)$ such that

$$\mathcal{H}' = \sum_{\nu_\alpha} \mathcal{H}'(\nu_\alpha) \ , \tag{2.11a}$$

$$[\mathcal{H}_0, \mathcal{H}'(\nu_\alpha)] = \nu_\alpha \mathcal{H}'(\nu_\alpha) , \tag{2.11b}$$

and

$$V = \sum_{\nu_\beta} V(\nu_\beta) , \tag{2.11c}$$

$$[\mathcal{H}_0, V(\nu_\beta)] = \nu_\beta V(\nu_\beta) . \tag{2.11d}$$

N. B.: We use ν to refer to the components of the spectrum of $\mathcal{H}_0$, and ω for the components of the spectrum of the complete hamiltonian, $\mathcal{H}$.

The frequencies ν of the spectrum of $\mathcal{H}_0$ are assumed to be discrete and widely spaced. Thus, in the limit $\mathcal{H}' \rightarrow 0$, the absorption spectrum is a set of discrete, infinitely sharp lines. The effect of a non-zero, but small, $\mathcal{H}'$ is to widen (and shift slightly) these lines. The frequencies ω, then, will assume values grouped about the central frequencies ν.

We shall concentrate our interest on that portion of the absorption spectrum which is in the neighborhood of some central frequency $\bar{\omega}$. This line, or set of lines, is assumed to have a width that is small compared to the separation from neighboring absorption peaks. The n^{th} moment of this line about $\bar{\omega}$ can be written

$$I_n(\overline{\omega}) = \sum_{\omega \approx \overline{\omega}} f(\omega)\,(\omega - \overline{\omega})^n \,, \tag{2.12}$$

or

$$I_n(\overline{\omega}) = \frac{\mathrm{Tr}\; e^{-\beta \mathcal{H}}\,[\,V^\dagger\,,\; g_{n+1}(\overline{\omega}) + \overline{\omega}\, g_n(\overline{\omega})\,]}{\mathrm{Tr}\; e^{-\beta \mathcal{H}}} \tag{2.13}$$

In Eq. (2.13) we have introduced the <u>absorption operators</u> $g_n(\overline{\omega})$, defined by

$$g_n(\overline{\omega}) = \sum_{\omega \approx \overline{\omega}} (\omega - \overline{\omega})^n\, V(\omega) \,. \tag{2.14}$$

Note that there is necessarily some inexactness in this definition; we sum over frequencies "in the neighborhood" of some central frequency $\overline{\omega}$. The degree of uncertainty in this definition diminishes as the line width: line separation ratio becomes small. That is, to the extent that the power absorbed in the frequencies <u>between</u> absorption peaks is vanishingly small, we have a clear-cut definition of individual absorption lines.

2.2 Absorption Operators

The theory of absorption operators for use in the calculation of the moments of the absorption spectra of spin systems has been developed in some detail by Hung Cheng[22]. As a result of Cheng's work, we can generate a series for the absorption operators (which are defined as sums over the unknown frequencies ω) in terms of the known quantities $V(\nu_\beta)$ and $\mathcal{H}'(\nu_\alpha)$. We do not have to truncate the hamiltonian in order to eliminate contributions to the moments from distant lines, and thereby avoid the danger of discarding portions of the hamiltonian which may in fact make contributions to the line of interest. In the discussion that follows, we present a brief rederivation of Cheng's results, and then apply these results to the triplet problem.

We obtain two different formal expansions of the operator $e^{i\mathcal{H}t} V e^{-i\mathcal{H}t}$: one expansion in terms of the harmonic components of the complete hamiltonian $\mathcal{H}$, the other in terms of the spectral frequencies of $\mathcal{H}_o$. Thus, from Eq. (2.5), we have

$$e^{i\mathcal{H}t}\, V(\omega)\, e^{-i\mathcal{H}t} = e^{i\omega t}\, V(\omega), \tag{2.15a}$$

whence

$$e^{i\mathcal{H}t}\, V e^{-i\mathcal{H}t} = \sum_{\omega} e^{i\omega t}\, V(\omega). \tag{2.15b}$$

Using the expansions of $e^{\pm i(\mathcal{H}_o + \mathcal{H}')t}$ in the forms

$$e^{i(\mathcal{H}_o + \mathcal{H}')t} = \sum_{n=o}^{\infty} (i)^n \sum_{\nu_{\alpha_1}\ldots\nu_{\alpha_n}} \mathcal{H}'(\nu_{\alpha_n})\ldots\mathcal{H}'(\nu_{\alpha_1}) \cdot$$

$$\int_o^t dt_1 \ldots \int_o^{t_{n-1}} dt_n\, e^{i(\nu_{\alpha_1} t_1 \ldots \nu_{\alpha_n} t_n)}\, e^{i\mathcal{H}_o t}, \tag{2.16a}$$

and

$$e^{-i(\mathcal{H}_0+\mathcal{H}')t} = e^{-i\mathcal{H}_0 t}\sum_{n=0}^{\infty}(-i)^n \sum_{\nu_{\alpha_1}\dots\nu_{\alpha_n}} \mathcal{H}'(\nu_{\alpha_1})\dots\mathcal{H}'(\nu_{\alpha_n})\cdot$$

$$\int_0^t dt_1\dots\int_0^{t_{n-1}} dt_n\, e^{i(\nu_{\alpha_1} t_1+\dots\nu_{\alpha_n} t_n)}\,, \qquad (2.16b)$$

it can be shown that

$$e^{i\mathcal{H}t}Ve^{-i\mathcal{H}t} = \sum_{n=0}^{\infty}(i)^n \sum_{\nu_{\alpha_1}\nu_\beta\dots\nu_{\alpha_n}} e^{i\nu_\beta t}[\mathcal{H}'(\nu_{\alpha_n}),\dots[\mathcal{H}'(\nu_{\alpha_1}),V(\nu_\beta)]\dots]$$

$$\int_0^t dt_1\dots\int_0^{t_{n-1}} dt_n\, e^{i(\nu_{\alpha_1} t_1+\dots+\nu_{\alpha_n} t_n)}$$

$$(2.17)$$

From the (assumed widely spaced) set of frequencies appearing in the exponentials of the terms of the series (2.17), we choose the central frequency of interest, $\overline{\omega}$, and collect all terms containing this factor. These terms can be collected in the form

$$e^{i\overline{\omega}t}\sum_{k=0}^{\infty}\frac{(it)^k}{k!}\,a_k(\overline{\omega})\,. \qquad (2.18)$$

Equations (2.15) and (2.17) are different expressions for the same quantity, and must therefore be equal. In Eq. (2.17), we were able to separate the different frequency components directly; in

Eq. (2.15), however, the frequencies appearing in the exponentials cover a range around the central frequency $\overline{\omega}$. To the extent that this range is small, it is a sum over these terms having exponential frequencies near $\overline{\omega}$ that we wish to equate to Eq. (2.17). That is

$$\sum_{\omega\approx\overline{\omega}} e^{i\omega t}\, V(\omega) = e^{i\overline{\omega} t} \sum_{k=o}^{\infty} \frac{(it)^k}{k!}\, a_k(\overline{\omega}) \,. \tag{2.19}$$

The left side of Eq. (2.19) can be written

$$e^{i\overline{\omega}t} \sum_{\omega\approx\overline{\omega}} e^{i(\omega-\overline{\omega})t}\, V(\omega) = e^{i\overline{\omega}t} \sum_{k=o}^{\infty} \frac{(it)^k}{k!} \sum_{\omega\approx\overline{\omega}} V(\omega)\,(\omega-\overline{\omega})^k \tag{2.20}$$

From Eqs. (2.19) and (2.20), we obtain

$$a_k(\overline{\omega}) = \sum_{\omega\approx\overline{\omega}} V(\omega)\,(\omega-\overline{\omega})^k \,. \tag{2.21}$$

Comparison with Eq. (2.14) reveals that the $a_k(\overline{\omega})$'s obtained in this way are in fact the absorption operators $g_k(\overline{\omega})$ in terms of which we have expressed the moments about $\overline{\omega}$ of the absorption line centered at $\overline{\omega}$. By examining the terms of Eq. (2.17), from which the $a_k(\overline{\omega})$'s are generated, Hung Cheng arrives at the following prescription:

(1) Choose all sets of $\mathcal{H}'(\nu_\alpha)$'s the successive application of which, together with a chosen $V(\nu_\beta)$, will give an energy change equal

to the mean energy of the absorption line of interest. (If there are several ways of achieving this that are of the same order, all of them must be taken into account.)

(2) From this set, form all possible multiple commutators of the $\mathcal{H}'(\nu_\alpha)$'s with $V(\nu_\beta)$, each divided by the weighting factor $(\nu_{\alpha_n})\cdot(\nu_{\alpha_n}+\nu_{\alpha_{n-1}})\ldots(\nu_{\alpha_n}+\ldots+\nu_{\alpha_1})$; i.e., form the set:

$$O^E = \frac{[\mathcal{H}'(\nu_{\alpha_n}),[\mathcal{H}'(\nu_{\alpha_{n-1}})\ldots,[\mathcal{H}'(\nu_{\alpha_1}),V(\nu_\beta)]\ldots]}{\nu_{\alpha_n}(\nu_{\alpha_n}+\nu_{\alpha_{n-1}})\ldots(\nu_{\alpha_n}+\nu_{\alpha_{n-1}}+\ldots\nu_{\alpha_1})} \qquad (2.22)$$

where $\nu_{\alpha_n}+\nu_{\alpha_{n-1}}+\ldots+\nu_{\alpha_1}+\nu_\beta=\bar{\omega}$.

The absorption operator $g_k(\bar{\omega})$ can be written as the sum of two types of terms:

(3) The energy conserving terms, O^E_k, of $g_k(\bar{\omega})$ are obtained by taking all commutators (2.22) with exactly k zero factors in the denominator, and throwing away the zeros.

(4) All the other terms of $g_k(\bar{\omega})$ are obtained by forming multiple commutator brackets of $\mathcal{H}'(\nu_\alpha)$'s with O^E_k, i.e.

$$[\mathcal{H}'(\nu_{\alpha_n}),[\mathcal{H}'(\nu_{\alpha_{n-1}}),\ldots[\mathcal{H}'(\nu_{\alpha_1}),O^E_k]\ldots] \quad \text{, with}$$

coefficient

$$\left[\left(-\sum_{r=1}^{n} \nu_{\alpha_r}\right)\left(-\sum_{r=1}^{n-1} \nu_{\alpha_r}\right)\dots\left(-\nu_{\alpha_1}\right) \right]^{-1} .$$

If there are p zero factors in this coefficient, discard them and obtain the value of

$$\frac{1}{p!} \quad \frac{d^p}{dE^p} \left[\left(E-\sum_{r=1}^{n} \nu_{\alpha_r}\right)\left(E-\sum_{r=1}^{n-1} \nu_{\alpha_r}\right)\dots\left(E-\nu_{\alpha_1}\right)\right]^{-1} , \quad (2.23)$$

evaluated at $E=0$, as the appropriate coefficient. (The terms $(E-\sum \nu_{\alpha_r})$ appearing in Eq. (2.23) contain only those sums, $\sum \nu_{\alpha_r}$, which are non-zero.)

Note that for any $g_k(\bar{\omega})$ generated by this prescription there are an infinite number of commutator brackets contributing. That is, we generate an infinite series in powers of $\frac{\langle \mathcal{H}' \rangle}{\langle \mathcal{H}_o \rangle}$ (or $\langle \mathcal{H}' \rangle / \nu_\alpha$) for each g_k. Inasmuch as $\mathcal{H}_o \rangle \rangle \mathcal{H}'$, we expect this series to converge quite rapidly.

In calculating the moments of an absorption line, it is frequently convenient to make use of the fact that

$$\mathrm{Tr}\; e^{-\beta \mathcal{H}} [V^{\dagger} , g_{k_1+k_2} \;(\bar{\omega})] = \mathrm{Tr}\; e^{-\beta \mathcal{H}} [g^{\dagger}_{k_1}(\bar{\omega}) , g_{k_2}(\bar{\omega})] . \quad (2.24)$$

The calculation of the $(k_1 + k_2)^{th}$ moment of a line is most easily performed by choosing k_1 and k_2 as nearly equal as possible.

3. Spin Absorption in Wurster's Blue Perchlorate

In this section we determine the moments of the resonance spectrum of a linear-chain triplet exciton system, neglecting phonon interactions. The hamiltonian developed will use the low-temperature WBP crystal as a model, but should be representative of the behavior of a large class of triplet systems.

3.1 Model Hamiltonian

For purposes of determining the spin resonance spectrum of Wurster's blue perchlorate, we consider a single (assumed independent) linear chain of WB cations (see p. 3). The molecular sites are denoted by p = 1, 2, ..., 2N; the dimerized pairs are those nearest neighbors designated by (2p-1), (2p). Cyclic boundary conditions are imposed $(p + N \equiv p)$.

Each cation (p. 2) has a single unpaired electron in a p-orbital. The spin interaction between the molecules of a dimer can, in the presence of a strong external magnetic field, be represented by

$$J\hat{S}_{2p-1}\cdot\hat{S}_{2p} + D\hat{S}^{z}_{2p-1}\,\hat{S}^{z}_{2p} + \Delta\,(\hat{S}^{z}_{2p-1} + \hat{S}^{z}_{2p})\,. \qquad (3.1)$$

J is a two-center exchange integral, and is positive for triplet systems; the term with coefficient D is the diagonal portion of a general anisotropic spin interaction; and $\Delta/g\beta_e$ is the magnitude of the external magnetic field, which defines the z direction.

The exchange interaction is by far the largest term in Eq. (3.1) with $J = 246\ \mathrm{cm}^{-1}$ for WBP. The magnetic field is assumed to be large compared to the anisotropy interaction (for WBP, with magnetic field along the chain axis, $D = .02\ \mathrm{cm}^{-1}$; in the experiments of McConnell et al.[5,6], $\Delta = .316\ \mathrm{cm}^{-1}$). Note that it is only for a large magnetic field that we are justified in taking this simple form for the dimer hamiltonian (neglecting the small off-diagonal portions of the anisotropic interaction). We assume that the individual spins are precessing strongly about the direction of the external field.

The spin $\frac{1}{2}$ operators, $\hat{S}_p$, appearing in Eq. (3.1), are defined in the usual way on the "spin-up", "spin-down" eigenstates of $\hat{S}_p^z$:

$$\hat{S}_p^z |u\rangle_p = \tfrac{1}{2} |u\rangle_p \tag{3.2a}$$

$$\hat{S}_p^z |d\rangle_p = -\tfrac{1}{2} |d\rangle_p \tag{3.2b}$$

$$\hat{S}_p^+ |u\rangle_p \equiv (\hat{S}_p^x + i\hat{S}_p^y) |u\rangle_p = 0 \tag{3.2c}$$

$$\hat{S}_p^- |u\rangle_p \equiv (\hat{S}_p^x - i\hat{S}_p^y) |u\rangle_p = |d\rangle_p \tag{3.2d}$$

(In these equations, we have set $\hbar = 1$.)

The interaction between nearest neighbor dimers contains an exchange term

$$J' \hat{S}_{2p} \cdot \hat{S}_{2p+1} ,$$

and in general, anisotropic terms analogous to D. Inasmuch as

$J' \ll J$ (which will be so to the extent that dimerization is strong), the anisotropic coupling between dimers, which is small compared to J', will be negligibly small. In the present calculation, then, we retain only the isotropic exchange coupling between dimers.

As our model hamiltonian for linear chains of WB cations, we therefore take the following form:

$$\mathcal{H} = J\sum_{p=1}^{N} \hat{S}_{2p-1} \cdot \hat{S}_{2p} + J'\sum_{p=1}^{N} \hat{S}_{2p} \cdot \hat{S}_{2p+1} + D\sum_{p=1}^{N} \hat{S}^{z}_{2p-1} \cdot \hat{S}^{z}_{2p} + \Delta\sum_{p=1}^{2N} \hat{S}^{z}_{p} \tag{3.3}$$

It is convenient to re-express this hamiltonian in a triplet representation. Instead of $|u\rangle$, $|d\rangle$ eigenstates of S^z for a spin $\frac{1}{2}$ molecule, we use the four eigenstates of S^z for a dimer to describe the new basis. Thus we define the dimer states:

$$|f_1\rangle_p \equiv |u_{2p-1}, u_{2p}\rangle \tag{3.4a}$$

$$|f_2\rangle_p \equiv 2^{-\frac{1}{2}} [\, |u_{2p-1}, d_{2p}\rangle + |d_{2p-1}, u_{2p}\rangle] \tag{3.4b}$$

$$|f_3\rangle_p \equiv |d_{2p-1}, d_{2p}\rangle \tag{3.4c}$$

$$|\alpha\rangle_p \equiv 2^{-\frac{1}{2}} [\, |u_{2p-1}, d_{2p}\rangle - |d_{2p-1}, u_{2p}\rangle]. \tag{3.4d}$$

In this representation, the indices p run from 1 to N, numbering the N dimers in the chain. The three states $|f_i\rangle$ are the $S^z = 1$, 0, -1 projections of the excited triplet; $|\alpha\rangle$ is the singlet ground state. A complete set of operators conveniently defined in this basis is the set B_{pf_i}, $B^\dagger_{pf_i}$ with matrix elements determined by:

$$B^\dagger_{pf_i}\,|\alpha\rangle_p = |f_i\rangle_p \tag{3.5a}$$

$$B^\dagger_{pf_i}\,|f_j\rangle_p = 0 \tag{3.5b}$$

$$B_{pf_i}\,|f_j\rangle_p = \delta_{ij}\,|\alpha\rangle_p \tag{3.5c}$$

$$B_{pf_i}\,|\alpha\rangle_p = 0 \tag{3.5d}$$

Observe that the number operator for the state $|f_i\rangle$ is $B^\dagger_{pf_i}B_{pf_i}$; the number operator for the singlet $|\alpha\rangle$ is $B_{pf_i}B^\dagger_{pf_i}$ (i.e., for <u>any</u> value of i, $B_{pf_i}B^\dagger_{pf_i}\,|\alpha\rangle = |\alpha\rangle$.

The $B_{pf_i}B^\dagger_{pf_i}$'s **satisfy** quasi-Pauli relations:

$$[B^\dagger_{pf_i}, B^\dagger_{qf_j}] = [B_{pf_i}, B_{qf_j}] = 0 \tag{3.6a}$$

$$[B_{pf_i}, B^\dagger_{qf_j}] = 0 \quad \text{for } p \neq q \tag{3.6b}$$

$$N_p(f) + N_p(\alpha) = 1 \tag{3.6c}$$

In Eg. (3.6c), the triplet and singlet occupation numbers, $N_p(f)$ and $N_p(\alpha)$, are defined by

$$N_p(f) = \sum_i B^\dagger_{pf_i}B_{pf_i} \tag{3.7a}$$

$$N_p(\alpha) = B_{pf_i}B^\dagger_{pf_i} \tag{3.7b}$$

If we were dealing with an excited singlet instead of an excited triplet, Eq. (3.6c) would be equivalent to the usual Pauli anti-commutation relation, and the B_{pf_i}'s would be true Pauli operators. Note that this equation is simply a statement of the fact that each dimer must be in *some* state.

We also define the vector spin 1 operators S_p by

$$S_p = \hat{S}_{2p-1} + \hat{S}_{2p}. \tag{3.8}$$

These spin operators can be expressed in terms of the basis operators:

$$S_p^z = B^\dagger_{pf_1} B_{pf_1} - B^\dagger_{pf_3} B_{pf_3} \tag{3.9a}$$

$$S_p^+ \equiv S_p^x + iS_p^y = \sqrt{2}\,(B^\dagger_{pf_2} B_{pf_3} + B^\dagger_{pf_1} B_{pf_2}) \tag{3.9b}$$

$$S_p^- \equiv S_p^x - iS_p^y = \sqrt{2}\,(B^\dagger_{pf_3} B_{pf_2} + B^\dagger_{pf_2} B_{pf_1}) \tag{3.9c}$$

The operators S_p annihilate the singlet state , i.e.

$$S_p \, |\alpha\rangle_p = 0 \; ,$$

and commute with triplet occupation number:

$$[\, S_p, N_q(f)] = 0$$

In the triplet representation, the hamiltonian Eq. (3.3), to within an additive constant, is:

$$\mathcal{H} = \mathcal{H}_J + \mathcal{H}_\Delta + \mathcal{H}_D + \mathcal{H}_{J'} + \mathcal{H}_T + \mathcal{H}'(J) + \mathcal{H}'(-J)$$

$$+ \mathcal{H}'(2J) + \mathcal{H}'(-2J) \qquad (3.10)$$

where

$$\mathcal{H}_J = J\sum_p N_p(f)$$

$$\mathcal{H}_\Delta = \Delta \sum_p S_p^z$$

$$\mathcal{H}_D = \frac{D}{2} \sum_p S_p^z\, S_p^z$$

$$\mathcal{H}_{J'} = \frac{J'}{4} \sum_p \mathbf{S}_p \cdot \mathbf{S}_{p+1}$$

$$\mathcal{H}_T = \frac{-J'}{4} \sum_p \sum_i \left(B_{pf_i}^\dagger\, B_{p+1,f_i} + B_{pf_i}\, B_{p+1,f_i}^\dagger\right)$$

$$\mathcal{H}'(J) = \frac{J'}{4}\Bigg[\sum_p \quad S_p^z\, B_{p+1,f_2}^\dagger - B_{pf_2}^\dagger\, S_{p+1}^z + \frac{S_p^+}{\sqrt{2}}\, B_{p+1,f_3}^\dagger$$

$$-B_{pf_3}^\dagger\, \frac{S_{p+1}^+}{\sqrt{2}} + B_{pf_1}^\dagger\, \frac{S_{p+1}^-}{\sqrt{2}} - \frac{S_p^-}{\sqrt{2}}\, B_{p+1,f_1}^\dagger\Bigg]$$

$$\mathcal{H}'(-J) = [\mathcal{H}'(J)]^\dagger$$

$$\mathcal{H}'(2J) = -\frac{J'}{4} \sum_p \Bigg[B_{pf_1}^\dagger\, B_{p+1,f_3}^\dagger + B_{pf_3}^\dagger\, B_{p+1,f_1}^\dagger$$

$$- B_{pf_2}^\dagger\, B_{p+1,f_2}^\dagger \Bigg]$$

$$\mathcal{H}'(-2J) = [\mathcal{H}'(2J)]^\dagger$$

The triplet exciton self-energy is obtained from the first three terms above: the exchange interaction, $\mathcal{H}_J$; the interaction with the constant external magnetic field, $\mathcal{H}_\Delta$; and the anisotropic spin interaction, $\mathcal{H}_D$. The exchange interaction between excitons includes: an $S_p \cdot S_{p+1}$ scattering term, $\mathcal{H}_{J'}$; an exciton transfer term, $\mathcal{H}_T$, which moves an existing exciton to an unexcited neighboring site; double creation, $\mathcal{H}'(2J)$, and double annihilation, $\mathcal{H}'(-2J)$, terms, which create and destroy spin-zero pairs of neighboring excitons; and single creation, $\mathcal{H}'(J)$, and annihilation, $\mathcal{H}'(-J)$, terms, which virtually create or destroy an exciton in the field of a real neighboring triplet.

3.2 Harmonic Spectrum

The interaction of the chain of spins with the (small) oscillating magnetic field (taken to be in the x direction), is represented by:

$$V = V_0 \sum_p S_p^x = \tfrac{1}{2} V_0 \sum_p (S_p^+ + S_p^-) \tag{3.11}$$

V commutes with $\mathcal{H}_J$; i.e., it conserves exciton number. S_p^- corresponds to a spin flip which decreases the energy of the chain in a strong constant magnetic field; it represents emission of a photon of energy approximately equal to Δ. S_p^+ corresponds to absorption of this quantum of energy, and in obtaining absorption operators, we may represent V by this component only; i.e., we take

$$V = \tfrac{1}{2} V_0 \sum_p S_p^+ \tag{3.12}$$

In the limit of very low temperature, i.e., for very low exciton concentration, we expect the system to behave approximately like a non-interacting exciton gas. If we neglect the exciton-exciton interactions, the hamiltonian is

$$\mathcal{H} = \mathcal{H}_J + \mathcal{H}_\Delta + \mathcal{H}_D .$$

The absorption spectrum for the non-interacting system consists of two infinitely sharp lines, one at $\Delta + D/2$, the other at $\Delta - D/2$. From Eq. (2.9), the power absorbed at these frequencies is

$$f\left(\Delta \pm \frac{D}{2}\right) = \left(\Delta \pm \frac{D}{2}\right) \frac{\mathrm{Tr}\, e^{-\beta H} \left[V^+, V(\Delta \pm D/2)\right]}{\mathrm{Tr}\, e^{-\beta H}}$$

The spectral components of V are

$$V\left(\Delta + \frac{D}{2}\right) = + \frac{V_0}{2} \sum_p S_p^z S_p^+$$

$$V\left(\Delta - \frac{D}{2}\right) = - \frac{V_0}{2} \sum_p S_p^- S_p^z$$

and, using the techniques developed in Section 3.5 for taking temperature-dependent traces, we find

$$\frac{f\left(\Delta + \frac{D}{2}\right)}{f\left(\Delta - \frac{D}{2}\right)} = \frac{\Delta + \frac{D}{2}}{\Delta - \frac{D}{2}} \cdot \frac{1 - e^{-\beta\left(\Delta + \frac{D}{2}\right)}}{e^{\beta\left(\Delta - \frac{D}{2}\right)} - 1} \approx e^{-\beta\Delta} .$$

(The last step above follows if $\Delta \gg \frac{D}{2}$.)

This result is, of course, what would be expected on elementary physical grounds. The line at $\Delta + D/2$ arises from transitions in which S_p^z changes from 0 to 1; the line at $\Delta - D/2$ from transitions from $S_p^z = 0$ to $S_p^z = -1$. Since the probabilities of population of the initial states are in the ratio $e^{-\beta\Delta} : 1$, this is the ratio of line intensities.

When we include the effects of exciton-exciton interactions, we would be tempted to take

$$\mathcal{H}_0 = \mathcal{H}_J + \mathcal{H}_\Delta + \mathcal{H}_D , \tag{3.13}$$

and calculate the moments of the $\Delta + D/2$ and $\Delta - D/2$ lines individually. However, whereas the interaction terms of the hamiltonian commute with the magnetic field term

$$\left[\mathcal{H}_\Delta, \mathcal{H}_{J'}\right] = \left[\mathcal{H}_\Delta, \mathcal{H}_T\right] = \left[\mathcal{H}_\Delta, \mathcal{H}'(\pm J)\right] = \left[\mathcal{H}_\Delta, \mathcal{H}'(\pm 2J)\right] = 0 ,$$

they do not commute with anisotropy term. This means that the spectrum of $\mathcal{H}'$ with respect to $\mathcal{H}_0$ of equation (3.13) will contain frequency components ~ D. The series for the absorption operators would then be in powers of J'/D. Since J' is almost certainly greater than D, and is probably large compared to it, this series will at best converge only very slowly (and may be divergent).

For this reason, we are led to separate the hamiltonian as follows:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \tag{3.14a}$$

$$\mathcal{H}_0 = \mathcal{H}_J + \mathcal{H}_\Delta \tag{3.14b}$$

$$\mathcal{H}' = \mathcal{H}'(0) + \mathcal{H}'(J) + \mathcal{H}'(-J) + \mathcal{H}'(2J) + \mathcal{H}'(-2J) \qquad (3.14c)$$

where

$$\mathcal{H}'(0) = \mathcal{H}_D + \mathcal{H}_{J'} + \mathcal{H}_T$$

and

$$\left[\mathcal{H}_0, \mathcal{H}'(\nu)\right] = \left[\nu \mathcal{H}'(\nu)\right],$$

and we use

$$V(\Delta) = \frac{V_0}{2}\sum_p S_p^+$$

This separation leads to a calculation of the moments of the combined lines, i.e., of all the absorption in the vicinity of Δ. Note that we do not require that $\Delta \gg J'$, since Δ is not one of the harmonic components of $\mathcal{H}'$ with respect to $\mathcal{H}_0$, and therefore will not appear as an energy denominator in the absorption operator expansions. These expansions will be in powers of J'/J and D/J, and we do require that these ratios be small in order to assure rapid convergence.

3.3 Absorption Operators

We now apply the prescriptions of Section 2 for obtaining g-functions to the hamiltonian (3.14). We assume that J'/J is sufficiently small to justify neglecting terms of order $(J'/J)^2$ or higher in the absorption operator expansions. Observing that $[\mathcal{H}'(\nu), V(\Delta)] = 0$ for $\nu \neq 0$, we list the g-functions sufficient to calculate the first five moments of the $g = 2$ absorption lines below, correct to first order in (J'/J):

$$g_0 = V(\Delta) \qquad (3.15a)$$

$$g_1 = [\mathcal{H}'(0),V(\Delta)] - \sum_{\nu\neq 0} \frac{1}{\nu} [\mathcal{H}'(\nu),[\mathcal{H}'(0),V(\Delta)] \qquad (3.15b)$$

$$g_2 = \Big[\mathcal{H}'(0),[\mathcal{H}'(0),V(\Delta)]\Big] \qquad (3.15c)$$

$$+ \sum_{\nu\neq 0} \frac{1}{\nu} \Big[\mathcal{H}'(\nu),\big[\mathcal{H}'(-\nu),\,[\mathcal{H}'(0),V(\Delta)]\big]\Big]$$

$$- \sum_{\nu\neq 0} \frac{1}{\nu} \Big[\mathcal{H}'(\nu),\,\big[\mathcal{H}'(0),\,[\mathcal{H}'(0),V(\Delta)]\big]\Big] \qquad (3.15c)$$

$$g_3 = \Big[\mathcal{H}'(0),\,\big[\mathcal{H}'(0),\big[\mathcal{H}'(0),\ V(\Delta)\big]\big]\Big] \qquad (3.15d)$$

$$+ \sum_{\nu\neq 0} \frac{1}{\nu} \Big[\mathcal{H}'(\nu),\,\big[\mathcal{H}'(-\nu),\,[\mathcal{H}'(0),\,[\mathcal{H}'(0),V(\Delta)]]\big]\Big]$$

$$+ \sum_{\nu\neq 0} \frac{1}{\nu} \Big[\mathcal{H}'(0),\,\big[\mathcal{H}'(\nu),\,[\mathcal{H}'(-\nu),\,[\mathcal{H}'(0),V(\Delta)]]\big]\Big]$$

$$- \sum_{\nu\neq 0} \frac{1}{\nu} \Big[\mathcal{H}'(\nu),\,\big[\mathcal{H}'(0),\,[\mathcal{H}'(0)[\mathcal{H}'(0),V(\Delta)]]\big]\Big]$$

Those terms in Eqs. (3.15) with negative sign all represent non-energy-conserving portions of the absorption operators. They can contribute to the line moments only if commuted with other non-energy-conserving terms (with frequency of opposite sign), or when multiplied by appropriate off-diagonal terms from the expansion of $e^{-\beta H}$.

It is by using the fact that

$$\mathrm{Tr}e^{-\beta H}[V^+, g_{k_1+k_2}] = \mathrm{Tr}e^{-\beta H}[g_{k_1}^+, g_{k_2}]$$

that we are able to determine the first five moments from the set (g_0, g_1, g_2, g_3).

Those portions of the commutators of the form (3.16) which may have non-zero trace to the order of the calculation have been evaluated explicitly, and are tabulated in Appendix A.

The problem of calculating, to any order, the moments of the resonance absorption lines of WBP has now been reduced to that of taking temperature-dependent traces of multi-site spin operators. Before proceeding to a discussion of trace-taking techniques, however, we consider a re-interpretation of the quantities to be calculated -- one based on the fact that experimental data is taken at constant frequency as opposed to constant magnetic field.

3.4 Absorption vs. Magnetic Field

The expressions derived in Section 2 for the moments of absorption lines were applicable to the spectrum of the power absorbed vs. frequency of the oscillating field, at fixed constant magnetic field. In practice, however, experimental considerations dictate that data be taken at fixed frequency, equal to the central frequency $\bar{\omega}$ of the line of interest, while slowly varying the magnitude Δ of the "constant" field. Thus, whereas we have derived expressions for

$$I_n(\bar{\omega}) \equiv \int_{\omega=\bar{\omega}-\delta}^{\bar{\omega}+\delta} f(\omega,\Delta_0)(\omega-\bar{\omega})^n \, d\omega \ , \qquad (3.16)$$

in order to have direct comparison with experiment we wish to calculate the quantities

$$M_n(\Delta_0) \equiv \int_{\Delta=\Delta_0-\delta'}^{\Delta_0+\delta'} f(\bar{\omega},\Delta)(\Delta-\Delta_0)^n \, d\Delta \ . \qquad (3.17)$$

In these expressions, δ and δ' are small compared to $\bar{\omega}$ and Δ_0, and are chosen to include the line of interest but no other absorption peaks. Inasmuch as the power absorbed falls to zero between absorption maxima, we expect the integrals to be insensitive to the exact values of δ and δ'.

Expressions (3.16) and (3.17) can be related to one another fairly easily. Ordinarily, it is assumed that frequency and field strength are interchangeable, i.e., that they are linearly related.* We shall see that, although this is true to zeroth order, the first-order corrections are significant, and, in fact, simplify the expressions for the moments in terms of absorption operators.

From Eq. (2.4), the power absorbed at frequency ω and magnetic field strength Δ is

$$f(\omega,\Delta) = \omega \sum_{|j\rangle,|k\rangle} (e^{-\beta E_k} - e^{-\beta E_j}) \ |\langle j|V|k\rangle|^2 \delta(E_j - E_k - \omega) \qquad (2.4)$$

---

* See, e.g., McMillan and Opechowski (*21*).

Since the interaction, ΔS^z, of the spins with the constant external magnetic field commutes with the hamiltonian, the eigenstates $|j\rangle$, $|k\rangle$ of $\mathcal{H}$ are eigenstates of S^z, and remain unchanged upon variation of Δ. The only effect upon expression (2.4) of varying Δ by x, then, is a change in the energy of state $|j\rangle$ by xm_j, where $S^z\,|j\rangle = m_j\,|j\rangle$. Thus we have

$$f(\omega,\Delta+x) = \omega \sum_{|j\rangle|k\rangle} \left[e^{-\beta(E_k+xm_k)} - e^{-\beta(E_j+xm_j)} \right]$$

$$\times\ |\langle j|V|k\rangle|^2\,\delta(E_j - E_k - \omega + xm_j - xm_k). \qquad (3.18)$$

But $V = \frac{1}{2}S^+$ changes S^z by one unit, i.e.

$$\langle j|V|k\rangle = \delta_{m_j,m_{k+1}}\,\langle j|V|k\rangle,$$

whence $\qquad m_j - m_k = 1.$

The change x in the magnetic field is small compared to the total magnetic field strength Δ. (The excursion in field strength need cover only a range that is of the order of the line width.) At all temperatures of interest we may neglect βx compared to 1 (but we shall <u>retain</u> all terms in x/Δ). To this order, Eq. (3.18) becomes

$$f(\omega,\Delta+x) = \omega \sum_{|j\rangle,|k\rangle} (e^{-\beta E_k} - e^{-\beta E_j})\,|\langle j|V|k\rangle|^2\,\delta(E_j - E_k - \omega + x)$$

$$= \frac{\omega}{\omega - x}\,f(\omega - x,\Delta). \qquad (3.19)$$

This equation is exactly true at temperatures such that $\beta x \ll 1$; it has not been necessary to make any further assumptions regarding the relative magnitudes of x, Δ, and ω.

Equations (3.16) and (3.17) can be rewritten

$$I_n(\bar{\omega}) = (-1)^n \int_{-\delta}^{\delta} f(\bar{\omega} - x, \Delta_0) x^n \, dx \tag{3.20}$$

and

$$M_n(\Delta_0) = \int_{-\delta'}^{\delta'} f(\bar{\omega}, \Delta_0 + x) x^n \, dx$$

$$= \int_{-\delta'}^{\delta'} f(\omega - x, \Delta_0) x^n \frac{\bar{\omega}}{\omega - x} \, dx \tag{3.21}$$

This last integral can be expanded as

$$M_n(\Delta_0) = \sum_{p=0}^{\infty} \int_{-\delta'}^{\delta'} f(\bar{\omega} - x, \Delta_0) \frac{x^{n+p}}{\omega^p} \, dx \tag{3.22}$$

Inasmuch as these integrals are insensitive to their limits, Eq. (3.21) can be written

$$M_n(\Delta_0) = \sum_{p=0}^{\infty} \frac{(-1)^{n+p}}{\omega^p} I_{n+p}(\bar{\omega}). \tag{3.23}$$

However, from Section 2 we know that

$$I_n(\bar{\omega}) = \frac{\mathrm{Tr}\, e^{-\beta H} [V^+, \bar{\omega} g_n + g_{n+1}]}{\mathrm{Tr}\, e^{-\beta H}}$$

as a result of which the sum (3.22) collapses, and we have

$$M_n(\Delta_0) = (-1)^n \overline{\omega} \, \frac{\mathrm{Tr}\, e^{-\beta H}[V^+, g_n]}{\mathrm{Tr}\, e^{-\beta H}} \tag{3.24}$$

We observe that whereas the n + 1 order g-function had to be calculated in order to obtain the nth moment of the absorption vs. frequency, we need calculate only the nth order g-function to obtain the nth moment of the magnetic field spectrum. Thus, in addition to yielding a result that is more directly applicable to experimental observations , the field-spectrum calculation entails less computation than does the frequency-spectrum calculation.

3.5 Temperature-Dependent Traces

The expressions derived for the moments of resonance lines require calculation of terms of the form

$$\frac{\mathrm{Tr}\, e^{-\beta H} C}{\mathrm{Tr}\, e^{-\beta H}} \tag{3.25}$$

where C is an n-site operator:

$$C = \sum_p \mathcal{O}_p \mathcal{O}'_{p+1} \cdot \cdot \cdot \mathcal{O}''_{p+n-1} .$$

In order to evaluate such expressions, we expand $e^{-\beta H} = e^{-\beta(H_0 + H')}$ in the familiar fashion:

$$e^{-\beta H} = e^{-\beta H_0} \left[1 - \sum_{\nu_1} \int_0^{\beta} d\beta_1 \, e^{\beta_1 \nu_1} H'(\nu_1) \right.$$

$$+ \sum_{\nu_1 \nu_2} \int_0^{\beta} d\beta_1 \int_0^{\beta} d\beta_2 \, e^{(\beta_1 \nu_1 + \beta_2 \nu_2)} H'(\nu_1) H'(\nu_2)$$

$$\left. + \ldots \right] \tag{3.26}$$

Traces of the form

$$\mathrm{Tr} e^{-\beta H_0} \mathcal{O}_p \mathcal{O}'_{p+1} \cdot \cdot \cdot \mathcal{O}''_{p+n-1} \qquad (3.27$$

can be evaluated simply. Since all of the $\mathcal{O}$'s commute (all spin operators commute unless the site indices are identical), and since we can write

$$e^{-\beta H_0} = \prod_q e^{-\beta (H_0)q},$$

where

$$(H_0)q = JNq + \Delta S_q^z ,$$

we can write

$$\mathrm{Tr} e^{-\beta H_0} \mathcal{O}_p \mathcal{O}'_{p+1} \cdot \cdot \cdot \mathcal{O}''_{p+n-1}$$

$$= \mathrm{Tr}_p (e^{-\beta (H_0)p} \mathcal{O}_p) \, \mathrm{Tr}_{p+1} (e^{-\beta (H_0)p+1} \mathcal{O}'_{p+1}) \cdot \cdot \cdot$$

$$\mathrm{Tr}_{p+n-1} (e^{-\beta (H_0)p+n-1} \mathcal{O}''_{p+n-1}) \cdot \prod_q{}' \mathrm{Tr}_q (e^{-\beta (H_0)q} \tag{3.28}$$

The symbol $\prod_q{}'$ represents an excluded product; i.e., q takes on all values from 1 to N except for the values p, p+1, ...p+n-1.

We have also introduced the operation Tr_q, which is defined as a sum over the four site states; i.e.

$$\mathrm{Tr}_q(x_q) \equiv \langle \alpha_q | x_q | \alpha_q \rangle + \sum_{i=1}^{3} \langle (f_i)_q | x_q | (f_i)_q \rangle .$$

We can now write

$$\mathrm{Tr}\, e^{-\beta H_0} O_p O'_{p+1} \cdots O''_{p+n-1} = \Gamma^{N-n} \langle O_p \rangle \langle O'_{p+1} \rangle \cdots \langle O''_{p+n-1} \rangle \qquad (3.29)$$

where

$$\Gamma \equiv \mathrm{Tr}_q\, e^{-\beta (H_0)_q} = 1 + e^{-\beta J}(1 + 2 \cosh \beta\Delta) \qquad (3.29a)$$

and

$$\langle x_p \rangle \equiv \langle \alpha_p | x_p | \alpha_p \rangle + e^{-\beta(J+\Delta)} \langle (f_1)_p | x_p | (f_1)_p \rangle + e^{-\beta J} \langle (f_2)_p | X_p | (f_2)_p \rangle$$
$$+ e^{-\beta(J-\Delta)} \langle (f_3)_p | x_p | (f_3)_p \rangle . \qquad (3.29b)$$

The trace of a general term of the expansion (3.26) for $\mathrm{Tr}\, e^{-\beta H_C}$ is somewhat more complicated. Each factor of $\mathcal{H}'(\nu)$ is a sum over site indices. These multiple sums can, in general, be dissociated into sums of the form

$$A_p B_q \ . \ . \ . \ D_r$$

where p,q,...,r are all distinct. Each such term will have a coefficient that gives the total number of ways the site indices may be chosen to yield the same result. These combinatorial coefficients will, in general, contain higher powers of N than the first.

As an example, consider

$$\mathrm{Tr}e^{-\beta H_0} H_{J'} \sum_p O_p = \mathrm{Tr}e^{-\beta H_0} \sum_{p,q} (H_{J'})_{p,p+1} O_q \tag{3.30}$$

This may be decomposed into

$$N\mathrm{Tr}e^{-\beta H_0}(H_{J'})_{p,p+1} O_p + N\,\mathrm{Tr}e^{-\beta H_0} (H_{J'})_{p,p+1} O_{p+1}$$

$$+ N(N-2)\,\mathrm{Tr}e^{-\beta H_0} (H_{J'})_{p,p+1} O_{p+2} \tag{3.31}$$

Each of the three components of this equation involves traces that can be evaluated with the aid of Eq. (3.29). We know that

$$\frac{\mathrm{Tr}e^{-\beta H} \sum_p O_p}{\mathrm{Tr}e^{-\beta H}}$$

must be proportional to the first power of N (in the limit N → ∞). That this is so can be seen from the facts that:

(1) $\dfrac{\mathrm{Tr}e^{-\beta H} O_p}{\mathrm{Tr}e^{-\beta H}}$ is independent of p, from which it follows that

(2) $$\frac{\mathrm{Tr}e^{-\beta H} \sum_p O_p}{\mathrm{Tr}e^{-\beta H}} = N \frac{\mathrm{Tr}e^{-\beta H} O_p}{\mathrm{Tr}e^{-\beta H}} ;$$

(3) The expectation value of O_p is bounded above by its maximum eigenvalue, which is independent of N.

It then follows that

$$\lim_{N\to\infty} \frac{1}{N} \frac{\mathrm{Tr}\, e^{-\beta H} \sum_p O_p}{\mathrm{Tr}\, e^{-\beta H}}$$

is finite.

We must, then, show that the apparent higher order N-dependence exhibited by Eq. (3.31) is spurious. In order to do this, we write

$$\frac{\mathrm{Tr}\, e^{-\beta H} C_p}{\mathrm{Tr}\, e^{-\beta H}} = \left(\frac{\mathrm{Tr}\, e^{-\beta H} C_p}{\mathrm{Tr}\, e^{-\beta H_0}}\right)\left(\frac{\mathrm{Tr}\, e^{-\beta H_0}}{\mathrm{Tr}\, e^{-\beta H}}\right)$$

and expand each of the factors on the right-hand side in powers of $\mathcal{H}'/\mathcal{H}_0$. Since these series contain powers of N, we must, for the moment, require that $\mathcal{H}'$ is sufficiently small that $N\mathcal{H}'/\mathcal{H}_0$ is less than unity. This restriction will be relaxed when the final result is obtained. The expectation value of C_p must be independent of N for large enough N (the requirement is essentially that N be greater than twice the order to which the expansion is taken). This means that all terms in the expansion which are proportional to a positive (non-zero) power of N must cancel identically when the product is formed. This can be verified to any given order by actually performing the expansions.

Since the series for $\frac{\mathrm{Tr}\, e^{-\beta H_0}}{\mathrm{Tr}\, e^{-\beta H}}$ is equal to unity plus terms at least linear in N, the only terms remaining in the product are those terms of the expansion of $\frac{\mathrm{Tr}e^{-\beta H_C}}{\mathrm{Tr}e^{-\beta H_0}}$ that are independent of N. The restriction on the size of $N\mathcal{H}'/\mathcal{H}_0$ may now be relaxed, since the resultant series converges so long as $\mathcal{H}'/\mathcal{H}_0$ is less than unity.

The prescription for identifying the desired terms in an expansion for $\frac{\mathrm{Tr}e^{-\beta H_C}}{\mathrm{Tr}e^{-\beta H}}$ is thus very simple: expand $\frac{\mathrm{Tr}e^{-\beta H_C}}{\mathrm{Tr}e^{-\beta H_0}}$ as described above, and discard all those terms which do not have the proper N-dependence.

In the example considered above (Eg. (3.31)), we retain only

$$N\,\mathrm{Tr}e^{-\beta H_0}\,(H_{J'})_{p,p+1}\,O_p + N\,\mathrm{Tr}e^{-\beta H_0}\,(H_{J'})_{p,p+1}\,O_{p+1}$$

$$-\ 2N\,\mathrm{Tr}e^{-\beta H_0}(H_{J'})_{p,p+1}\,O_{p+2}\ .$$

As a simple application of the techniques for performing temperature-dependent traces, we calculate the zero-field magnetic susceptibility of a linear triplet system. In low field the anisotropic dipole-dipole coupling should include not only the diagonal interaction ($\mathcal{H}_D$), but also an off-diagonal term of the form

$$\mathcal{H}_E = \frac{E}{2}\sum_p (S_p^+ S_p^+ + S_p^- S_p^-)$$

where x,y, and z are principal axes of the fine structure interaction.

The zero-field susceptibility along the z-axis can be written as

$$\chi = \beta \, \frac{\mathrm{Tr}\, e^{-\beta H} (S^z)^2}{\mathrm{Tr}\, e^{-\beta H}} \tag{3.32}$$

where the hamiltonian now includes $\mathcal{H}_E$. Note that $\mathcal{H}_E$ can contribute to the susceptibility only when terms of at least second order in the expansion of $e^{-\beta H}$ are considered.

A typical second-order term in the expansion of Eq. (3.32) is

$$\beta \cdot \frac{\beta}{2} \frac{J'^2}{16} \, \mathrm{Tr} \left[e^{-\beta H_0} \left(\sum_p S^z_p S^z_{p+1} \right) \left(\sum_q S^z_q S^z_{q+1} \right) \left(\sum_r S^z_r \right) \left(\sum_t S^z_t \right) \right] \tag{3.33}$$

In the zero-field limit $\left\langle \left(S^z_p\right)^{2n+1} \right\rangle = 0$, and $\left\langle \left(S^z_p\right)^{2n} \right\rangle = 2e^{-\beta J}/\Gamma$. The multiple sums of Eq. (3.33) therefore give non-zero contributions only when the overlap of site indices is such that each site has an even number of S^z's on it. Thus we encounter terms of the form

$p = q \neq r, \;\; r = t$:

$$N(N-2)\, \mathrm{Tr}\, e^{-\beta H_0} (S^z_p)^2 (S^z_{p+1})^2 (S^z_{p+2})^2$$

$$\rightarrow \; -2N \left\langle (S^z_p)^2 \right\rangle^3 = -16N \, \frac{e^{-3\beta J}}{\Gamma^3}$$

$p = q-1,\ r = p,\ t = p+1$:

$$N\,\mathrm{Tr}\,e^{-\beta H_0}\,(S_p^z)^2\,(S_{p+1}^z)^2\,(S_{p+2}^z)^2 = N\left\langle (S_p^z)^2 \right\rangle^3 = 8N\,\frac{e^{-3\beta J}}{\Gamma^3}$$

$p = q = r = t$:

$$N\,\mathrm{Tr}\,e^{-\beta H_0}\,(S_p^z)^4\,(S_{p+1}^z)^2 = N\left\langle (S_p^z)^2 \right\rangle^2 = 4N\,\frac{e^{-2\beta J}}{\Gamma^2}$$

etc.

In second order, all terms of the hamiltonian contribute to the susceptibility (including exciton creation, annihilation, and transfer terms). The result may be written:

$$\chi = N\beta\,\frac{e^{-\beta J}}{\Gamma^3}\left\{\left[2 - \beta D + \frac{\beta^2}{2}\left(\frac{J'^2}{4} + \frac{D^2}{2} + 2E^2\right) + \frac{\beta J'^2}{8J}\right]\right.$$

$$+\ e^{-\beta J}\left[12 - \beta(2J' + 4D) + \frac{\beta^2}{2}(2DJ' + 8E^2) - 3\frac{\beta J'^2}{J}\right]$$

$$+\ e^{-2\beta J}\left[18 - \beta(6J' + 3D) + \frac{\beta^2}{2}\left(\frac{9}{4}J'^2 - \frac{1}{2}D^2 + 6E^2\right.\right.$$

$$\left.\left.\left. +\ 2DJ'\right) + \frac{23}{8}\,\frac{\beta J'^2}{J}\right]\right\} \tag{3.34}$$

A plot of susceptibility vs. temperature, for a typical set of parameters is given in Fig. 2.

Observe that the second-order terms in J' that appear in Eq. (3.34) are of two types: $(\beta J')^2$ and $(\beta J')(J'/J)$. In general, nth order contributions to traces will involve sums over terms of the form

$$A_{np}(\beta J')^{n-p}(J'/J)^{p}$$

The $p = 0$ terms arise from the factor $[\mathcal{H}'(0)]^{n}$ in the expansion of $e^{-\beta H}$; terms with $p \neq 0$ appear as a result of bringing down components $\mathcal{H}'(\nu)$, of non-zero frequency.

3.6 Results

Applying the technique of Section 3.5 to the calculation of the traces of commutators of Appendix A, we obtain the first five moments about Δ of the pair of resonance lines near $g = 2$. The complete results (to first order in interaction parameters) are tabulated in Appendix B. We shall be concerned with interpreting these results for temperatures at which exciton concentration is fairly small ($e^{-\beta J} \lesssim .01$). The dominant portions of the moments at such low temperatures (for which $\beta\Delta$ is also small compared to unity) are:

$$M_0 = NL\Delta \sinh \beta\Delta \left(1 - \frac{\beta\Delta}{2} - \beta J' L \cosh \beta\Delta\right) \tag{3.35a}$$

$$M_1(\Delta) = - NL\Delta \left\{\frac{D}{2}(\cosh \beta\Delta - 1) - \frac{\beta D^2}{4} \cosh \beta\Delta\right\} \tag{3.35b}$$

$$M_2(\Delta) = \frac{D^2}{4} M_0 \tag{3.35c}$$

$$M_3(\Delta) = \frac{D^2}{4} M_1(\Delta) + NL^2\Delta \frac{\beta D^2 J'^2}{8} (\cosh \beta\Delta + 2) \tag{3.35d}$$

$$M_4(\Delta) = \frac{D^4}{16} M_0 + NL^2 \Delta \frac{D^2 J'^2}{8} \sinh \beta \Delta \left\{ 3 - \frac{3}{2} \beta D - \frac{\beta J'}{4} \left[3 + 2L(5 \cosh \beta \Delta + 4) \right] \right\} \tag{3.35e}$$

$$M_5(\Delta) = \frac{D^2}{4} M_3(\Delta) + NL^2 \Delta \frac{\beta D^2 J'^2}{16} \left\{ 3D^2 + \frac{DJ'}{4} (7 \cosh \beta\Delta + \sinh \beta\Delta - 15) + \frac{J'^2}{8} \left[9(\cosh \beta\Delta + 2) + \frac{6}{\Gamma} (\cosh \beta\Delta + 1) + L(\cosh \beta\Delta + 1)(62 \cosh \beta\Delta - 5) \right] \right\} \tag{3.35f}$$

In these equations:

$$L \equiv \frac{e^{-\beta J}}{\Gamma} ,$$

$$\Gamma = 1 + e^{-\beta J}(1 + 2 \cosh \beta\Delta).$$

In general, portions of the moment expressions containing factors of L^n ($e^{-n\beta J}/\Gamma^n$) come from the traces of n-site operators and represent contributions from the interactions of n excitons. The complete moment expressions exhibit such terms with n as large as four.

Notice that (particularly for the odd moments, although also , to some extent, for M_4) the first-order terms may be comparable to those of the zeroth order. This is due to the fact that $\beta\Delta \ll 1$; i.e., although we have treated the magnetic field dependence of the moments exactly, terms of zeroth order in $\beta J'$, J'/J, etc. may contain small coefficients which are functions of field. (For example, terms like (cosh $\beta\Delta$ - 1) may be smaller than $\beta J'$ cosh $\beta\Delta$.) By the time second-order contributions are considered, however, such "accidental" anomalies in relative magnitudes can no longer be important; in all moments, there are at least some leading terms (of order no higher than the first) which do not contain coefficients that are small as a result of $\beta\Delta$'s being small.

Thus, in order to estimate the size of the largest terms neglected in the present calculation, we need only observe that they are smaller than the calculated quantities by at least a factor of $\beta J'$ (or J'/J). As we shall observe in Section 3.7, rough quantitative agreement with experiment is obtained if $J' \sim .1\text{-}5\ \mathrm{cm}^{-1}$, so that $\beta J' < 0.1$ for the temperature range of interest. Thus the (neglected) second-order contributions to line moments cause errors of the order of 10% or less in the odd moments, and probably of order 1% or less in the (more important) even moments.

3.7 Interpretation and Discussion of Results

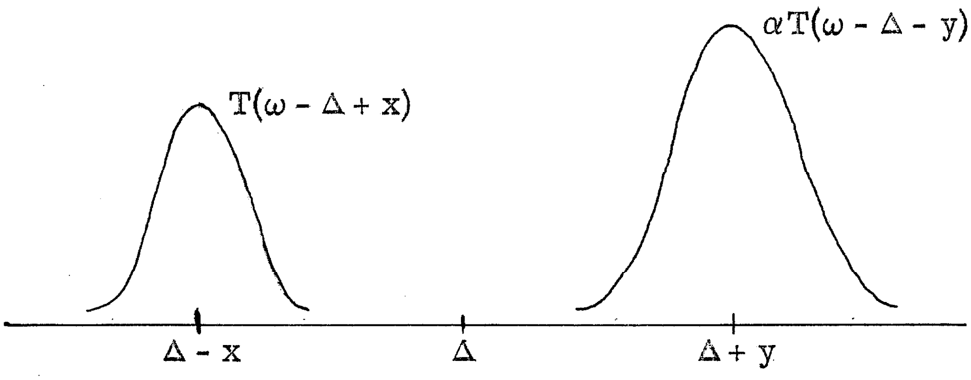
From a theoretical viewpoint, the most satisfactory application of the results obtained above would entail a direct comparison of measured moments of observed resonance lines with the calculated moments. Unfortunately, because of noise which obscures the structure of the tails of the absorption, the experiment data cannot be readily treated in this way. Instead, we adopt a simple model which enables us to determine (approximately) the line widths and shifts of the separate resonance peaks from the calculated moments.

To accomplish this, we assume:

(1) that the temperature is low enough so that the separation of the fine structure lines is large compared to the width of a single line;

(2) that absorption falls off so rapidly as we move away from the peak that high order moments of each individual line about its own center are negligibly small;

(3) that both lines are of the same shape (although possibly of different size).



The lines are represented schematically above. We assume that they have the same functional form, differing only in a scaling factor, α. The origin of the function T(x) is chosen such that

$$\int_{-\infty}^{\infty} x\, T(x)\, dx = 0 .$$

The centers of the two resonance lines are taken to be at $\Delta + y$ and $\Delta - x$. The moments of these combined lines about Δ can be written as:

$$M_0(\Delta) = T_0(1 + \alpha) \qquad (3.36a)$$

$$M_1(\Delta) = T_0(-x + \alpha y) \qquad (3.36b)$$

$$M_2(\Delta) = T_0(x^2 + \alpha y^2) + T_2(1 + \alpha) \qquad (3.36c)$$

$$M_3(\Delta) = T_0(-x^3 + \alpha y^3) + T_2(-3x + 3\alpha y) \qquad (3.36d)$$

$$M_4(\Delta) = T_0(x^4 + \alpha y^4) + T_2(6x^2 + 6\alpha y^2), \qquad (3.36e)$$

where

$$T_n \equiv \int_{-\infty}^{\infty} T(u)\, u^n\, du,$$

$$T_1 = 0.$$

For low temperature, $|x|, |y| \approx D/2$.

In equations (3.36a) - (3.36e) we have dropped terms with factors of T_3 and T_4, because of the assumption that

$$\frac{T_3}{D/2}, \frac{T_4}{(D/2)^2} << T_2 .$$

For narrow lines, the shifts of the centers from the zero-temperature positions will be quite small. If we linearize Eqs.(3.36a) -(3.36e) in these shifts and in the difference in heights of the peaks, we may solve for

$$\alpha = 1 + \frac{1}{2} \left(3 \frac{M_1(\Delta)}{\frac{D}{2} M_0} - \frac{M_3(\Delta)}{\frac{D^3}{8} M_0} \right), \tag{3.37}$$

$$x = \frac{D}{2} \left[1 - \frac{\nu_4}{4} + \frac{1}{2} \left(\frac{M_1(\Delta)}{\frac{D}{2} M_0} - \frac{M_3(\Delta)}{\frac{D^3}{8} M_0} \right) \right], \tag{3.38}$$

$$\frac{T_2}{T_0} = \frac{D^2}{4} \frac{\nu_4}{4}, \tag{3.39}$$

where

$$\nu_4 \equiv \frac{M_4(\Delta)}{\frac{D^4}{16} M_0} - 1 .$$

In obtaining these results, we have made use of the fact that, for the moments calculated,

$$M_2(\Delta) = \frac{D^2}{4} M_0 .$$

The degree of asymmetry, described by the deviation of α, the ratio of intensities, from unity, is quite small, since the calculated odd moments are small. $\alpha - 1$ is plotted as a function of temperature, for various values of J', in Fig. (3). The other parameters, from experiments on WBP [5,6], are taken to be

$$J = 246 \text{ cm}^{-1}$$

$$\Delta = .316 \text{ cm}^{-1}$$

$$D = .02 \text{ cm}^{-1} \quad .$$

Inasmuch as the odd moments are small compared to ν_4, the shifts of the two lines will be very nearly equal. If we also assume that the line width is related to the normalized second moment by

$$W \propto \left[\frac{T_2}{T_0} \right]^{1/2} \tag{3.40}$$

we get the usual relation between line width and shift:

$$W \propto \left[\left(\frac{D}{2} - x \right) \right]^{1/2} = [\text{ Line Shift }]^{1/2} .$$

The "width," as given by Eq.(3.40), is plotted as a function of temperature and J' in Fig. (4). The exciton concentration, ρ, which is proportional to the line intensity, M_0 , is also shown in Fig. (4).

Note that, for small enough J′ , we find the exciton concentration varying like

$$\rho \sim e^{-\beta J} ,$$

and the width like

$$W \sim e^{-\beta J/2} .$$

Previous treatments,[1,2,15] based on various models of highly mobile excitons, have predicted that

$$\rho \sim e^{-\beta J}$$

$$W \sim e^{-\beta J} ,$$

It should be observed that if J′ is sufficiently large higher order multi-exciton processes can become important. In general, the line width takes the form

$$W = \left[\sum_{n=1}^{\infty} a_n \, e^{-n\beta J} \right]^{1/2} .$$

For large J′ the a_n's do not drop off rapidly, so that the overall dependence can be like $e^{-\beta J}$. This tends to reconcile the present calculation with the results of the previous models, since large J′ produces the high exciton mobility which they assume.

In Fig. (5) are presented experimental spectra for WBP[6] . Observe that the widths of the lines become comparable to the separation at a temperature of approximately 60°K. In order for the theoretical results to give quantitative agreement with this aspect of the experimental data, we should require that J′ $\sim .1\text{-}5\ \text{cm}^{-1}$. Although there exists no experimental determination of the size of the actual distortion in WB chains, theoretical calculations[23] based on isolated dimers suggest that this value is rather smaller than what would be expected. The inclusion of phonon interactions, as in Section 4, however, produces a renormalization of both J and J′ which might be large enough to account for (J′)'s being so small.

In Fig. (6) are plotted the experimental values of line width and exciton concentration as a function of temperature. The line width exhibits an anomolous broadening, corresponding to an activation energy for exciton-exciton interactions. Such a phenomenon does not appear as a result of the present calculation in the absence of phonons. We shall see in Section 4, however, that phonon-exciton processes do indeed predict such an effect.

A significant fact that emerges from this treatment concerns the role of exciton creation, annihilation, and transfer processes.

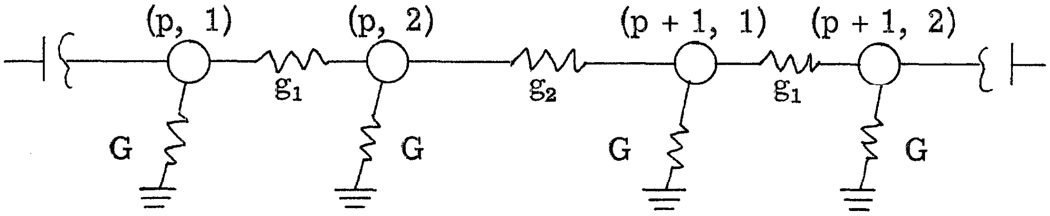
To the order calculated, these processes have no effect on the zeroth through fourth moments of the combined lines, and only the transfer terms contribute to the fifth moment. It is indeed so that their effect will be felt in higher order, but, in light of the estimate of the magnitude of higher order contributions Section 3. 6, this should be relatively unimportant at temperatures for which the fine structure lines are distinct.

Finally, we note that the dependence of the moments on magnetic field is determined essentially exactly in the present treatment. The fact that experiments tend to be performed at magnetic field so that $\beta \Delta << 1$ makes knowledge of this detailed structure somewhat unnecessary. We suggest that if experiments were performed at much higher fields (perhaps a factor of ten), the measured field dependence of line shapes could provide perhaps the best experimental confirmation of the present theory.

4. Exciton-Phonon Interactions

4.1 Interaction Hamiltonian

We now include the effects of phonon-exciton interactions in the calculation of the moments of the absorption spectrum of the linear triplet system. The dimerized chain is represented with two molecules per unit cell, coupled as shown schematically below.



The α^{th} molecule in the p^{th} unit cell is denoted by (p, α), where $p = 1, 2 \ldots, N$, and $\alpha = 1, 2$. Each molecule so designated has spin $\frac{1}{2}$. Cyclic boundary conditions are imposed; i.e., $(p + N, \alpha) \equiv (p, \alpha)$.

The interactions included in this model are:

(1) The nearest-neighbor spin interactions previously discussed, now considered with position-dependent exchange integrals;

(2) Van der Waals interactions between nearest-neighbor molecules in the same chain. For lattice vibrations of (assumed) small amplitude, we use the harmonic approximation, representing these interactions by effective springs, with spring constants

determined by the curvature of the potential at the equilibrium position. These spring constants are denoted by g_1 for the coupling between the molecules of a dimer [i.e., for the interaction between molecules (p, 1) and (p, 2)], and by g_2 for nearest neighbors in different unit cells [i.e., between (p, 2) and (p + 1, 1)];

(3) Effective quadratic interactions between molecules of the chain and the rest of the crystal. These interactions, represented by spring constant G, are an attempt to account, at least approximately, for the actual three-dimensional character of the lattice. The result is to suppress free translations (in the zero frequency mode) of the chain considered.

The hamiltonian for this system can be written

$$\mathcal{H} = \mathcal{H}_{ss} + \mathcal{H}_{sp} + \mathcal{H}_{p}, \tag{4.1}$$

where:

$$\mathcal{H}_{ss} = \sum_{p=1}^{N} \left[\Delta \left(\hat{S}^{z}_{p,1} + \hat{S}^{z}_{p,2} \right) + D \left(\hat{S}^{z}_{p,1} \hat{S}^{z}_{p,2} \right) \right] \tag{4.1a}$$

$$\begin{aligned} \mathcal{H}_{sp} = \sum_{p=1}^{N} \Big[& J_{p,2;p+1,1}\, \hat{S}_{p,2} \cdot \hat{S}_{p,1} \\ & + J'_{p+1,1;p,2}\, \hat{S}_{p,2} \cdot \hat{S}_{p+1,1} \Big] \end{aligned} \tag{4.1b}$$

$$\begin{aligned} \mathcal{H}_{p} = \frac{1}{2m} \sum_{p=1}^{N} \sum_{\alpha=1}^{2} \Pi^{2}_{p,\alpha} + \frac{1}{2} \sum_{p=1}^{N} \Big[& G \left(x^{2}_{p,1} + x^{2}_{p,2} \right) \\ & + g_1 \left(x_{p,2} - x_{p,1} \right)^{2} + g_2 \left(x_{p+1,1} - x_{p,2} \right)^{2} \Big]. \end{aligned} \tag{4.1c}$$

In these equations:

$x_{p,\alpha}$ is the displacement of the (p, α) molecule from the equilibrium position (in the absence of spin interactions);

$\Pi_{p,\alpha}$ is the momentum operator for the (p, α) molecule;

m is the mass of a single molecule;

$\hat{S}_{p,\alpha}$ is the spin operator for the (p, α) molecule $(s = \frac{1}{2})$;

the terms with coefficients J and J′ are the nearest neighbor exchange interactions;

the term with coefficient D is the (small) anisotropic spin interaction;

the term with coefficient Δ is the interaction with a constant d. c. magnetic field.

The position and momentum operators, x and Π, satisfy the usual commutation rules:

$$[\Pi_{p,\alpha}, x_{q,\beta}] = -i\hbar\ \delta_{pq}\,\delta_{\alpha\beta}\,. \tag{4.2}$$

For small displacements from equilibrium, linear variation of the exchange integrals with distance is assumed. Thus, we take

$$J_{p,2;\,p,1} = J_0 - j\,(x_{p,2} - x_{p,1}), \tag{4.3a}$$

$$J'_{p+1,1;\,p,2} = J_0' - j'\,(x_{p+1,1} - x_{p,2}). \tag{4.3b}$$

The hamiltonian can now be written as

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}'_p + \mathcal{H}_I + C, \tag{4.4}$$

where:

$\mathcal{H}_s$ is identical with the spin hamiltonian of preceding sections, with constant coefficients;

$$J = J_0 + \frac{3}{2}\ \frac{j^2}{G + 2\,(g_1 + g_2)}\,, \tag{4.4a}$$

$$J' = J'_0 - \frac{3}{2} \frac{j j'}{G + 2(g_1 + g_2)} ; \tag{4.4b}$$

$$\mathcal{H}'_p = \frac{1}{2m} \sum_{p, \alpha} \Pi^2_{p, \alpha} + \frac{1}{2} \sum_p [G (y^2_{p,1} + y^2_{p,2}) + g_1 (y_{p,2} - y_{p,1})^2 + g_2 (y_{p+1,1} - y_{p,2})^2] ; \tag{4.4c}$$

$$\mathcal{H}_I = - j \sum_p (y_{p,2} - y_{p,1}) N_p - j' \sum_p (y_{p+1,1} - y_{p,2}) \hat{S}_{p,2} \cdot \hat{S}_{p+1,1} ; \tag{4.4d}$$

and

$$C = - \frac{9}{8} \frac{j^2}{G + 2(g_1 + g_2)} . \tag{4.4e}$$

In these equations, we have obtained $y_{p,\alpha}$ from $x_{p,\alpha}$ by the translations:

$$y_{p,\alpha} = x_{p,\alpha} + (-1)^{\alpha} \frac{j}{G + 2(g_1 + g_2)} . \tag{4.5}$$

The translations were used in order to remove a linear term in the displacements. This term arises from the zero-point energy of the singlet state of a dimerized pair of molecules. [In Eq. (4.4d) $N_p = 0$ if the dimer in cell p is in its singlet spin state, and $N_p = 1$ if this pair is in one of the three triplet spin states.] We will, then, be obtaining phonons representing vibrations about a new equilibrium position. Rigorously, we should then reinterpret the spring constants and the derivatives of the exchange integrals as those measured at this new equilibrium point.

4.2 Diagonalization of the Phonon Hamiltonian

A transformation diagonalizing $\mathcal{H}'_p$ is:

$$y_{p,\alpha} = \frac{1}{\sqrt{N}} \sum_{k,\mu} (u_{k\mu\alpha} e^{ikp} b_{k\mu} + u^*_{k\mu\alpha} e^{-ikp} b^\dagger_{k\mu}), \tag{4.6}$$

$$\Pi_{p,\alpha} = -\frac{im}{\sqrt{N}} \sum_{k,\mu} (u_{k\mu\alpha} e^{ikp} b_{k\mu} - u^*_{k\mu\alpha} e^{-ikp} b^\dagger_{k\mu}) \, \omega_{k\mu}. \tag{4.6a}$$

Here:

$k = -\pi + \frac{\pi}{N} + \frac{2\pi r}{N}$, $r = 0, 1, 2, \ldots N - 1$;

$\mu = 1, 2$;

$\alpha = 1, 2$.

The operators $b^\dagger_{k\mu}$, $b_{k\mu}$ are boson creation and annihilation operators; i.e., they satisfy the commutation relations

$$[b_{k\mu}, b^\dagger_{k'\nu}] = \delta_{kk'} \, \delta_{\mu\nu} \tag{4.7}$$

$$[b_{k\mu}, b_{k'\nu}] = [b^\dagger_{k\mu}, b^\dagger_{k'\nu}] = 0. \tag{4.7a}$$

The c-numbers $u_{k\mu\alpha}$ and $\omega_{k\mu}$ are obtained from the secular equation

$$\det \left| \sum_{\beta} L_{k\alpha\beta} u_{k\mu\beta} - m\,\omega^2_{k\mu} u_{k\mu\alpha} \right| = 0, \tag{4.8}$$

where:

$$L_{k11} = L_{k22} = G + g_1 + g_2$$

$$L_{k12} = L^*_{k21} = -(g_1 + g_2 e^{ik}).$$

The $u_{k\mu\alpha}$'s are normalized by either of the following (equivalent) equations:

$$\sum_{\alpha} u_{k\mu\alpha} u^*_{k\nu\alpha} = \frac{1}{2m\omega_{k\mu}} \delta_{\mu\nu}, \tag{4.9a}$$

or

$$\sum_{\mu} u_{k\,\mu\alpha}\, u^*_{k\,\mu\beta}\, \omega_{k\,\mu} = \frac{1}{2m}\, \delta_{\alpha\beta} \,. \tag{4.9b}$$

Solutions to equations (4.8) and 4.9) are

$$m\omega^2_{k\mu} = L_{k11} - (-1)^{\mu} \left| L_{k12} \right| \tag{4.10}$$

$$u_{k\,\mu 1} = (4\, m\omega_{k\mu})^{-\frac{1}{2}} \tag{4.10a}$$

$$u_{k\mu 2} = (-1)^{\mu}\, \frac{\left| L_{k12} \right|}{L_{k12}}\, u_{k\,\mu 1} \,. \tag{4.10b}$$

The hamiltonian (4.4) can now be written, to within an additive constant, as

$$\begin{aligned} \mathcal{H} = \mathcal{H}_s &+ \sum_{k\mu} \omega_{k\mu}\, b^{\dagger}_{k\mu}\, b_{k\mu} + \sum_{k\mu p} (c_{k\mu} e^{ikp}\, b_{k\mu} + \text{h.c.})\, N_p \\ &+ \sum_{k\mu p} (d_{k\mu} e^{ikp}\, b_{k\mu} + \text{h.c.})\, \hat{S}_{p,2} \cdot \hat{S}_{p+1,1} \,, \end{aligned} \tag{4.11}$$

where

$$c_{k\mu} = - \frac{j}{\sqrt{N}} (u_{k\mu 2} - u_{k\mu 1}) \,, \tag{4.11a}$$

and

$$d_{k\mu} = - \frac{j'}{\sqrt{N}} (u_{k\,\mu 1} e^{ik} - u_{k\mu 2}) \,. \tag{4.11b}$$

4.3 Effects of Variations in J on Line Shapes

For a strongly dimerized chain (i.e., J ≫J′), it is to be expected that variations in J due to lattice vibrations will produce much larger changes in line shapes than will phonon-coupled variations in J′. Thus, even for vibrations that are "small" in the sense that the harmonic approximation to the phonons is applicable and variation of

J and J′ is linear, it may be that the changes in J are in fact larger than J′ itself. In this section we (for the moment) neglect variations in J′ (i.e., we set $j' = 0$), and consider the hamiltonian (4.11) with $d_{k\mu} = 0$. Two different treatments of this problem are presented. First, we show that the phonon interaction can be expressed in terms of an effective interaction between triplet excitons, and from this effective interaction deduce the nature of the change in the absorption lines. Then we shall carry out the moment calculation on the hamiltonian with $j' = 0$ to terms of second order in $c_{k\mu}$, thereby allowing this parameter (which is proportional to the change in J) to be moderately large and still obtain qualitatively significant results.

4.3a Effective Interaction

An effective interaction between triplet excitons due to phonon-coupled variation of the exchange integral, J, has been calculated by McConnell and Soos[12]. In their treatment, this interaction was obtained using lowest order perturbation theory. We shall obtain a result that is, in fact, equivalent to theirs, without approximation. This is obtained by performing a linear canonical transformation of the phonon creation and annihilation operators to new boson operators.

With $j' = 0$, the hamiltonian is

$$\mathcal{H} = \mathcal{H}_s + \sum_{k\mu} \omega_{k\mu} b^\dagger_{k\mu} b_{k\mu} + \sum_{k\mu p} (c_{k\mu} e^{ikp} b_{k\mu} + \text{h.c.}) N_p \quad (4.12)$$

We define new boson operators $P^{\dagger}_{k\mu}$ and $P_{k\mu}$ by

$$P_{k\mu} = b_{k\mu} + \sum_{p} \frac{c^{*}_{k\mu}}{\omega_{k\mu}} e^{-ikp} N_p , \tag{4.13a}$$

$$P^{\dagger}_{k\mu} = b^{\dagger}_{k\mu} + \sum_{p} \frac{c_{k\mu}}{\omega_{k\mu}} e^{ikp} N_p . \tag{4.13b}$$

Observe that

$$[N_p, N^{\dagger}_q] = [N_p, b_{k\mu}] = [N_p, b^{\dagger}_{k\mu}] = 0 ,$$

so that the new operators do indeed obey Bose commutation relations.

The hamiltonian can now be written

$$\begin{aligned} \mathcal{H} = \mathcal{H}_s &+ \sum_{k\mu} \omega_{k\mu} P^{\dagger}_{k\mu} P_{k\mu} - \sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} \sum_{p,q} e^{ik(p-q)} N_p N_q \\ = \mathcal{H}_s &+ \sum_{k\mu} \omega_{k\mu} P^{\dagger}_{k\mu} P_{k\mu} - \sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} \sum_{p} N_p \\ &- 2 \sum_{k\mu} \sum_{p} \sum_{n>0} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} \cos nk \; N_p N_{p+n} . \end{aligned} \tag{4.14}$$

Using the sums derived in Appendix (C), this can be expressed as

$$\begin{aligned} \mathcal{H} = \mathcal{H}_s &+ \sum_{k\mu} \omega_{k\mu} P^{\dagger}_{k\mu} P_{k\mu} - \epsilon_0 \sum_{p} N_p \\ &+ \epsilon_1 \sum_{p} \sum_{n>0} e^{-\lambda n} N_p N_{p+n} , \end{aligned} \tag{4.15}$$

where

$$\epsilon_0 = \frac{j^2 [G + g_2 (1 - e^{-\lambda})]}{\alpha_1 \sqrt{1 - \alpha_2^2}} ,$$

$$\epsilon_1 = \frac{j^2 G (G + 2g_2)}{g_1 \alpha_1 \sqrt{1 - \alpha_2^2}} \quad ,$$

$$\lambda = \ln \left[\frac{1 + \sqrt{1 - \alpha_2^2}}{\alpha_2} \right] \quad ,$$

$$\alpha_1 = G^2 + 2\, G\, (g_1 + g_2) + 2g_1 g_2 \ ,$$

$$\alpha_2 = 2g_1 g_2 / \alpha_1 \quad .$$

It is to be noted that the new boson operators P and $P^\dagger$ contain both phonon and spin coordinates. To the extent that exciton creation, annihilation, and transfer terms of $\mathcal{H}_S$ are unimportant, however, P and $P^\dagger$ can be considered to be independent of spin (that is, P and $P^\dagger$ commute with all of the spin hamiltonian $\mathcal{H}_S$, except for these three terms). It will be recalled that in Section (3.6) we concluded that creation, annihilation and transfer of triplet excitons does not affect the shape of the absorption lines to the order to which the calculation was performed, and that higher order effects were expected to be small. In the following, then, we shall discuss the hamiltonian (4.15) assuming that site excitation number, N_p, is conserved.

The effective exciton-exciton interaction exhibited in Eq. (4.15) is seen to contain two terms:

(1) The ϵ_0 term, an exciton self-energy correction, resulting in a renormalization of J. The new effective exciton excitation energy is J - ϵ_0 ;

(2) The ϵ_1 term, representing a repulsion between excitons, decaying exponentially with distance.*

Related to these two effects is the change in the equilibrium separation of the molecules of a dimer. From Eqs. (4.6),(4.11a) and (4.11b) we have

$$\begin{aligned} y_{p2} - y_{p1} &= -\frac{1}{j} \sum_{k\mu} (c_{k\mu} e^{ikp} b_{k\mu} + \text{h.c.}) \\ &= -\frac{1}{j} \sum_{k\mu} (c_{k\mu} e^{ikp} P_{k\mu} + \text{h.c.}) \\ &\quad + \frac{2\epsilon_0}{j} N_p - \frac{2\epsilon_1}{j} \sum_{n>0} e^{-\lambda n} N_{p+n}. \end{aligned}$$

In the ground state of the $P_{k\mu}$'s, for example, we see that if dimer p is excited, this excitation increases the dimer length by $2\epsilon_0/j$ (corresponding to the decrease in J indicated above; half of this is offset by zero-point energy of the new "phonons"). Neighboring excitations tend to decrease this bond length.

Of the two terms of the effective interaction, it is the exciton repulsion that is particularly significant with respect to line shapes. The self-energy term, indeed, will affect the temperature dependence of exciton concentration, but since we do not know the magnitude of the unrenormalized exchange integral on *a priori* grounds, this effect is not observable. By comparing the temperature dependence

---

* This repulsion is equivalent to Eq. (13) of McConnell and Soos (*12*), although expressed in a different form.

of the line width with that of the exciton concentration, however, we can measure the effect of the repulsion. This repulsion would be expected to diminish the line-broadening exciton nearest-neighbor interactions, and therefore to result in anomalously rapid decrease in line width with decrease in temperature. We shall observe presently that the moment calculation confirms this expectation, providing agreement with experiments on many triplet systems.

4.3b Moment Calculation ($j' = 0$)

With $j' = 0$, the second order corrections to the resonance-line moments can be calculated fairly easily, using the techniques previously developed. The hamiltonian is separated into

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \tag{4.16}$$

where

$$\mathcal{H}_0 = \mathcal{H}_J + \mathcal{H}_\Delta + \mathcal{H}_p$$

$$\mathcal{H}' = \mathcal{H}_{J'} + \sum_{k\mu p} (c_{k\mu} e^{ikp} b_{k\mu} + \text{h.c.})\, N_p + \mathcal{H}_D$$

$$\mathcal{H}_p = \sum_{k\mu} \omega_{k\mu} b^\dagger_{k\mu} b_{k\mu} .$$

The harmonic components of $\mathcal{H}'$ with respect to $\mathcal{H}_0$ are $\mathcal{H}'(0)$, $\mathcal{H}'(\pm 2J)$, as in the calculation without phonons, and

$$\mathcal{H}'(+\omega_{k\mu}) = \sum_p c^*_{k\mu} e^{-ikp} b^\dagger_{k\mu} N_p \tag{4.17a}$$

$$\mathcal{H}'(-\omega_{k\mu}) = \sum_p c_{k\mu} e^{ikp} b_{k\mu} N_p . \tag{4.17b}$$

The series for the absorption operators will now have components that vary like powers of $N^{\frac{1}{2}} c_{k\mu}/\omega_{k\mu}$. In order to assure rapid convergence of this expansion, we must therefore require that $\omega_{k\mu}$ be sufficiently large. Note that because of the inclusion of coupling of the chain to the (assumed stationary) three-dimensional lattice, the minimum phonon frequency is $\sqrt{\frac{G}{M}}$, not zero. The rms change in bond length of a dimer, for uncoupled lattice vibrations, is

$$\left\langle (y_{p2} - y_{p1})^2 \right\rangle^{\frac{1}{2}} = \left[\mathrm{Tr} e^{-\beta H p} \frac{1}{j^2} \left| \sum_{k\mu} c_{k\mu} e^{ikp} \, b_{k\mu} \right.\right.$$

$$\left.\left. + \text{h. c.} \right|^2 \Big/ \mathrm{Tr} e^{-\beta H p} \right]^{\frac{1}{2}}$$

$$= \frac{1}{j} \left[\frac{\mathrm{Tr} e^{-\beta H p} \sum_{k\mu} |c_{k\mu}|^2 (b^\dagger_{k\mu} b_{k\mu} + b_{k\mu} b^\dagger_{k\mu})}{\mathrm{Tr} e^{-\beta H p}} \right]^{\frac{1}{2}}$$

Using the fact that

$$\frac{\mathrm{Tr} e^{-\beta H p} \, b^\dagger_{k\mu} \, b_{k\mu}}{\mathrm{Tr} e^{-\beta H p}} = \frac{1}{e^{\beta \omega_{k\mu}} - 1} \tag{4.17c}$$

we find

$$\left\langle (y_{p2} - y_{p1})^2 \right\rangle^{\frac{1}{2}} = \frac{1}{j} \left[\sum_{k\mu} |c_{k\mu}|^2 \, \frac{e^{\beta \omega_{k\mu}} + 1}{e^{\beta \omega_{k\mu}} - 1} \right]^{\frac{1}{2}} .$$

We shall see that the values of $\omega_{k\mu}$ are such that $\beta \omega_{k\mu} \sim 1$ for the temperatures of interest. Thus

$$\frac{N^{\frac{1}{2}} c_{k\mu}}{\omega_{k\mu}} \sim \frac{j \left\langle (y_{p2} - y_{p1})^2 \right\rangle^{\frac{1}{2}}}{\omega_{k\mu}} .$$

The physical requirement corresponding to convergence of the g—function expansions, then, is that the lattice vibrational frequencies be large compared to the exciton excitation energy changes corresponding to variations in bond length. This condition is satisfied if the slope of the exchange integral vs. bond length curve (j) is sufficiently small, or if the temperature is sufficiently low. A more detailed discussion of the conditions which we are led to impose on the magnitude of $\omega_{k\mu}$ appears in Section 4.4, in which we allow j′ to be non-zero.

In this calculation, we retain second-order terms in j, but still assume that second-order terms in J′ and D are negligibly small. An examination of the general expressions for the g-functions to second order reveals that to this order the presence of j produces no changes in them that can contribute to the moments. The zeroth-order g-functions are unchanged because $\mathcal{H}'$ (0) is unaffected by the phonon coupling; the first-order g—functions are also unchanged, because

$$\left[N_p, \left[\mathcal{H}'(0), \left[\mathcal{H}'(0), V(\Delta)\right]\right]\right] = \left[N_p, \left[\mathcal{H}'(0). V(\Delta)\right]\right] = 0,$$

from which it follows that

$$\left[\mathcal{H}'(\omega_{k\mu}), \left[\mathcal{H}'(0), \left[\mathcal{H}'(0), V(\Delta)\right]\right]\right] = \left[\mathcal{H}'(\omega_{k\mu}), \left[\mathcal{H}'(0), V(\Delta)\right]\right] = 0.$$

The changes in the second order g—functions are all either zero or off-diagonal in phonon operators (i.e., of frequency $\omega_{k\mu}$). These off-diagonal terms can contribute to the line moment only in third order, since the trace of such terms will be zero unless multiplied by (at least) first order terms of the expansion of $e^{-\beta H}$.

As a result, changes in line moments due to a non-zero j will come entirely from changes in the traces of the old g- functions. This change in the trace of an operator arises from the diagonal second-order terms of the expansion of $e^{-\beta H}$, and is quadratic in j. If C is taken to be a pure spin operator, the change in its temperature-dependent trace is

$$\delta\left[\frac{\mathrm{Tr}\,e^{-\beta H}C}{\mathrm{Tr}\,e^{-\beta H}}\right]$$

$$= \frac{1}{\mathrm{Tr}\,e^{-\beta H_0}}\left[\sum_{\omega_{k\mu}>0} \gamma(\omega_{k\mu}, -\omega_{k\mu})\,\mathrm{Tr}\,e^{-\beta H_0}\mathcal{H}'(\omega_{k\mu}) \times \mathcal{H}'(-\omega_{k\mu})\left(C - \frac{\mathrm{Tr}\,e^{-\beta H_0}C}{\mathrm{Tr}\,e^{-\beta H_0}}\right) - \sum_{\omega_{k\mu}>0} \gamma(-\omega_{k\mu}, \omega_{k\mu})\,\mathrm{Tr}\,e^{-\beta H_0}\mathcal{H}'(-\omega_{k\mu}) \times \mathcal{H}'(\omega_{k\mu})\left(C - \frac{\mathrm{Tr}\,e^{-\beta H_0}C}{\mathrm{Tr}\,e^{-\beta H_0}}\right)\right] \tag{4.18}$$

where

$$\gamma(\omega, -\omega) = \frac{e^{\beta\omega} - 1 - \beta\omega}{\omega^2}$$

H_0 can be separated into spin and phonon components. Since the basic spin and phonon operators commute, general traces over all states of the system can be factored in the following manner. If $A_{k\mu}$ is an arbitrary phonon operator, and E_p an arbitrary spin operator, we can write

$$\frac{\mathrm{Tr}e^{-\beta H_0}A_{k\mu}E_p}{\mathrm{Tr}e^{-\beta H_0}} = \left(\frac{\mathrm{Tr}_s e^{-\beta(H_J + H_\Delta)}E_p}{\mathrm{Tr}_s e^{-\beta(H_J + H_\Delta)}}\right)\left(\frac{\mathrm{Tr}_p e^{-\beta H_p}A_{k\mu}}{\mathrm{Tr}_p e^{-\beta H_p}}\right)$$

where Tr_s represents the sum over <u>spin</u> states (only), and Tr_p a sum over <u>phonon</u> states (only). Using Eq. (4.17c) to evaluate the phonon traces, Eq. (4.18) becomes:

$$\delta\left[\frac{\mathrm{Tr}e^{-\beta H}C}{\mathrm{Tr}e^{-\beta H}}\right] = \sum_{k\mu pq}\beta\frac{|c_{k\mu}|^2}{\omega_{k\mu}}e^{ik(p-q)} \times \frac{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}N_pN_q\left\{C - \left(\frac{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}C}{\mathrm{Tr}e^{-\beta H_0^{(s)}}}\right)\right\}}{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}} \qquad (4.19)$$

where: $H_0^{(s)} = H_J + H_\Delta$

If the spin operator C is a sum of n-site operators, i.e., of the form

$$C = \sum_r A_r B_{r+1} \cdots D_{r+n-1} , \tag{4.20}$$

we can evaluate Eq. (4.19) in a more specific form. This form will, in fact, allow us to use the previous results for the moments in a particularly simple way.

If C is given by Eq. (4.20), it is straightforward to show that

$$\frac{\mathrm{Tr}_s e^{-\beta H_0^{(s)}} N p N q C}{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}} = \frac{1}{\Gamma^2} \left\{ 2n(\Gamma-1) + n(2-\Gamma)\delta_{pq} + \sum_{r=1}^{n-1} (n-r)\left(\delta_{p,q+r} + \delta_{p,q-r}\right) \right\} \times \frac{\mathrm{Tr}_s e^{-\beta H_0^{(s)}} C}{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}} , \tag{4.21}$$

from which it follows from Eq. (4.19) that

$$\delta \left[\frac{\mathrm{Tr} e^{-\beta H} C}{\mathrm{Tr} e^{-\beta H}} \right] = \frac{\beta}{\Gamma^2} \sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} \left\{ 2n(\Gamma-1) N \delta(k) + n(2-\Gamma) + \sum_{r=1}^{n-1} (n-r) 2 \cos kr \right\} \frac{\mathrm{Tr}_s e^{-\beta H_0^{(s)}} C}{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}} . \tag{4.22}$$

Using the results of Appendix (C) to evaluate the phonon sums, we find

$$\delta\left[\frac{\mathrm{Tr}e^{-\beta H_0}C}{\mathrm{Tr}e^{-\beta H}}\right] = \frac{\beta}{\Gamma^2}\left\{n\left[(2-\Gamma)\epsilon_0 + (\Gamma-1)\epsilon_2\right] - \sum_{r=1}^{n-1}(n-r)\,e^{-\lambda r}\epsilon_1\right\}\frac{\mathrm{Tr}e^{-\beta H_0^{(s)}}C}{\mathrm{Tr}e^{-\beta H_0^{(s)}}} \qquad (4.23)$$

where ϵ_0 and ϵ_1 are defined by Eq. (4.15) and

$$\epsilon_2 = 2j^2/G + 2(g_1 + g_2).$$

If the components of C all have zero matrix elements on the singlet state (i.e., non-zero matrix elements only within the excited triplet), we can write

$$\frac{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}C}{\mathrm{Tr}_s e^{-\beta H_0^{(s)}}} = \frac{N e^{-n\beta J}}{\Gamma^n} \ll C \gg , \qquad (4.24)$$

where $\ll C \gg$ is independent of J. Inasmuch as the parameter j is small, the change in the trace of the n-site operator C can be incorporated into a renormalization of the value of J appearing in the exponential of Eq. (4.24), plus a (repulsive) activation energy for exciton pair formation. We define

$$\bar{J} \equiv J - \frac{(2-\Gamma)}{\Gamma^2}\epsilon_0 - \frac{(\Gamma-1)}{\Gamma^2}\epsilon_2 , \qquad (4.25a)$$

and

$$E_R(n) \equiv \sum_{r=1}^{n-1} (n-r)e^{-\lambda r} \epsilon_1/\Gamma^2 , \qquad (4.25b)$$

$$E_R(1) = 0.$$

We can now write

$$\frac{\mathrm{Tr}e^{-\beta H_C}}{\mathrm{Tr}e^{-\beta H}} = \frac{N \ll C \gg}{\Gamma^2} e^{-\beta(n\bar{J} + E_R\langle n\rangle)} + 1^{\mathrm{st}} \text{ order terms } (\beta J', \beta D). \qquad (4.26)$$

In Eq. (4.26), the first order terms in $\beta J'$ and βD are the same as those in the calculation without phonons. $E_R(n)$ is simply the total repulsive energy of excitons appearing on n consecutive sites (the factor (n-r) is the number of pairs of excitons separated by r; $e^{-\lambda r} \epsilon_1/\Gamma^2$ is the repulsive energy of such a pair). Observe that in the low temperature limit, for which $\Gamma = 1 + e^{-\beta J}(1 + 2 \cosh \beta\Delta) \rightarrow 1$, the renormalization of J and the exciton-pair repulsion reduce exactly to the values predicted by the effective interaction technique of the preceding section.

Applying this result to the zeroth and second moments of Section (3.6), which arise from traces of single-site operators, we find

$$M_0 = \frac{4}{D^2} M_2(\Delta) = \frac{Ne^{-\beta\bar{J}}}{\Gamma} \sinh\beta\Delta$$

$$- \frac{Ne^{-\beta J}}{\Gamma} \beta \sinh\beta\Delta \left\{ \frac{D}{2} \left(1 - \frac{2e^{-\beta J}}{\Gamma} \cosh\beta\Delta\right) \right.$$

$$\left. + \frac{J' e^{-\beta J}}{\Gamma} \left(\cosh\beta\Delta - \frac{2e^{-\beta J}}{\Gamma} \sinh^2\beta\Delta \right) \right\} \qquad (4.27)$$

The fourth moment, $M_4(\Delta)$, contains one-, two-, and three-site contributions to its zeroth order trace. The new value of M_4 is

$$M_4(\Delta) = \frac{D^4}{16} M_0 + \tfrac{3}{8} D^2 J'^2 \frac{N}{\Gamma^2} \sinh\beta\Delta \, e^{-\beta(2\bar{J}+E_R\langle 2\rangle)}$$

$$+ \tfrac{1}{4} D^2 J'^2 \frac{N}{\Gamma^3} \sinh\beta\Delta \, (\cosh\beta\Delta - 1) \, e^{-\beta(3\bar{J}+E_R\langle 3\rangle)}$$

+ 1^{st} order terms ($\beta J'$, βD), identical to those of Appendix B. (4.28)

At temperatures sufficiently low so that the second moments of the individual lines contributing to these moments can be approximated by

$$\frac{D^2}{16} \nu_4 = \frac{D^2}{16} \; \frac{M_4(\Delta)}{\frac{D^4}{16} M_0} - 1$$

we find that the <u>exciton density</u> ρ varies like

$$\rho \sim e^{-\beta\bar{J}} \qquad (4.29a)$$

whereas the width W of a single line has temperature dependence of the form

$$W \sim \sqrt{\nu_4} \sim \left[\frac{e^{-\beta(2\bar{J} + E_R\langle 2\rangle)}}{e^{-\beta\bar{J}}}\right]^{\frac{1}{2}} \tag{4.29b}$$

$$W \sim e^{-\beta(\bar{J} + E_R\langle 2\rangle)/2} .$$

Recall that in the absence of phonon coupling,we found

$$\rho \sim e^{-\beta J} ,$$

$$W \sim e^{-\beta J/2}.$$

Thus, the repulsive energy between triplet excitons due to phonon-coupled variation of the exchange integral J results in an activation energy, $E_R\langle 2\rangle$, for line broadening processes. Low temperature measurements on WBP[6] determine excitation density varying like

$$\rho \sim e^{-\beta(246\ \mathrm{cm}^{-1})}$$

and line width like

$$W \sim e^{-\beta(392\ \mathrm{cm}^{-1})}.$$

The phonon coupling, then, yields a correction to the temperature dependence of line shapes that is at least qualitatively correct. In order to obtain quantitative agreement with experiment, however, the repulsive energy would have to be so large that many higher orders in the expansions used should be employed. McConnell and Soos[12] using data on the bond lengths of WB dimers in solution[24], estimate that $E_R\langle 2\rangle$ may indeed be this large (as an upper limit, they obtain 500 cm^{-1}!). In any event, it is clear that a coupling mechanism of the sort examined in this section can, in principle, explain the anomalous line broadening which has been observed in triplet systems

4.4 Moment Calculation ($j' \neq 0$)

We now consider the more general phonon-coupled hamiltonian, for which we do not assume that j' is negligibly small. In addition to those components previously discussed, the spectrum of $\mathcal{H}'$ now contains additional components of frequencies $\pm\,\omega_{k\mu}$, and new terms of frequencies $\pm J \pm \omega_{k\mu}$, $\pm\, 2J \pm \omega_{k\mu}$, all of which are included in the interaction

$$\sum_{k\mu p} (d_{k\mu} e^{ikp} b_{k\mu^+} + \text{h.c.})\ \hat{S}_p\,,\ \hat{S}_{p+1} \tag{4.30}$$

We shall calculate the first-order changes in the even moments of the absorption lines due to this interaction, keeping terms that contain factors of

$$\frac{d_{k\mu}\, c^*{}_{k\mu}}{\omega_{k\mu}} \sim \frac{(\delta\mathcal{H}_{J'})(\delta\mathcal{H}_J)}{\omega_{k\mu}}\ ,$$

but, since we assume that j' is quite small, dropping terms like

$$\frac{|d_{k\mu}|^2}{\omega_{k\mu}} \sim \frac{|\delta\mathcal{H}_{J'}|^2}{\omega_{k\mu}} \quad .$$

In this case, the changes in the g-functions are significant to the order of interest. (Recall that with $j' = 0$ changes in the g-functions did not affect the moments to second order.) The series for the absorption operators will contain powers of the characteristic phonon-exciton interaction energy divided by phonon frequency, $d_{k\mu}c_{k\mu}/\omega_{k\mu}$. Thus, for purposes of convergence, the interaction must be sufficiently small.

In addition, these expansions will contain energy denominators like

$$|n\omega_{k\mu} \pm mJ|^{-1}$$

which can represent resonant phonon-exciton processes. The phonon frequencies that are expected to be characteristic of WBP, although fairly large, should be small compared to the exciton excitation energy, J. ($J = 246$ cm^{-1}; we anticipate $\omega_{k\mu} \sim 50 - 100$ cm^{-1}.) Thus, any resonant processes described by

$$n\omega_{k\mu} - mJ = 0$$

can occur only for a rather large number of phonons in virtual interaction. The large contributions from such multi-phonon interactions are, in a sense, spurious. They must correspond to large lattice vibrational energies, for which the harmonic approximation to the phonon hamiltonian is a poor one. The damping due to these anharmonic terms, plus the fact that an n-phonon process contains a factor of $e^{-n\beta\omega_{k\mu}}$, will limit the magnitude of such terms. In the present calculation, we restrict the analysis to consideration of (at most) a few phonon processes, and disregard possible high-order resonances.

Examination of the general absorption operator expansions reveals that the changes in the previously calculated zeroth- and second-moments are zero to first order:

$$\delta M_0 = \delta M_2(\Delta) = 0 \tag{4.31}$$

but that change in the fourth moment is non-zero. This change can be written as

$$\delta M_4(\Delta) = \frac{\mathrm{Tr}\, e^{-\beta H}\left[P_2^{\dagger}, \sum_{\nu=\pm\omega_{k\mu}} \frac{1}{\nu}\left[\mathcal{H}'(\nu), \left[\mathcal{H}'(-\nu), [\mathcal{H}'(0), V(\Delta)]\right]\right]\right]}{\mathrm{Tr}\, e^{-\beta H}} \tag{4.32}$$

where

$$P_2^{\dagger} = \left[\mathcal{H}'(0), \left[\mathcal{H}'(0), V(\Delta)\right]\right]^{\dagger}.$$

Discarding $|d_{k\mu}|^2/\omega_{k\mu}$ terms, and performing phonon traces, this can be expressed as

$$\delta M_4(\Delta) = -\sum_{k\mu pq} \frac{d_{k\mu}\, c^*_{k\mu}}{\omega_{k\mu}}\, e^{ik(q-p)} + \text{h.c.})$$

$$\times \frac{\mathrm{Tr}_s e^{-\beta H_s} [\, P_2{}^\dagger, \left(\hat{P}_2\right)_{q,q+1} \, Np\,]}{\mathrm{Tr}_s\, e^{-\beta H_s}} , \tag{4.33}$$

where:

$$\left(\hat{P}_2\right)_{q,q+1} \equiv \frac{1}{J'} \left[P_2 - \frac{D^2}{4}\, V(\Delta) \right]_{q,q+1} .$$

The commutator $\left[P_2{}^\dagger,\, P_2 \right]$ has already been determined in the phonon-free calculation and involves sums over two- and three-site spin operators. If we define

$$\hat{P}_4 \equiv \frac{1}{J'} \left(D^2 J'^2 \text{ part of } [\, P_2{}^\dagger,\, P_2] \right) ,$$

then it can be shown that

$$\delta M_4(\Delta) = -\sum_{k\mu} \left(\frac{d_{k\mu}\, c^*_{k\mu}}{\omega_{k\mu}} \left[N\delta(k)\, \frac{(\Gamma - 1)}{\Gamma} + \frac{1 + e^{-ik}}{\Gamma} \right] + \text{h.c.} \right)$$

$$\times \frac{\mathrm{Tr} e^{-\beta H_0{}^{(s)}}\, \hat{P}_4}{\mathrm{Tr} e^{-\beta H_0{}^{(s)}}} - \frac{1}{2} \sum_{k\mu} \left(\frac{d_{k\mu}\, c^*_{k\mu}}{\omega_{k\mu}}\, \frac{[\, e^{-2ik} + e^{ik}]}{\Gamma} + \text{h.c.} \right)$$

$$\times \frac{\mathrm{Tr} e^{-\beta H_0{}^{(s)}}\, \hat{P}_4(3-s)}{\mathrm{Tr} e^{-\beta H_0{}^{(s)}}} \tag{4.34}$$

In equation (4.34), $\hat{P}_4(3\text{-s})$ represents the three-site part of the operator $\hat{P}_4$.

Evaluating Eq. (4.34) with the aid of the phonon sums of Appendix (C), we find

$$\delta M_4(\Delta) = \frac{Ne^{-2\beta J}}{\Gamma^3} D^2 J' \sinh\beta\Delta \left\{ \tfrac{3}{8}\epsilon_2 + \tfrac{1}{4}(\epsilon_2 - \epsilon_3)\frac{e^{-\beta J}}{\Gamma}(\cosh\beta\Delta - 1) \right\} \quad (4.35)$$

where:

$$\epsilon_2 = 2jj' \left\{ \frac{(\Gamma - 1)}{G + 2(g_1 - g_2)} + \frac{G(I_0 + I_1) + g_2(I_0 - I_2)}{\alpha_1} \right\}$$

$$\epsilon_3 = \frac{jj'}{\alpha_1}\,\frac{G}{g_1}\,(G + g_1 + 2g_2)(I_1 + I_2).$$

If we again assume that the widths of the individual lines can be represented as proportional to $\sqrt{\nu_4}$, and consider only the dominant, zeroth order parts of ν_4, we find

$$\overline{W}^2 = (W + \delta W)^2 \sim \nu_4 + \delta\nu_4 = \nu_4 + \frac{\delta M_4(\Delta)}{\Delta^2 M_0} \sim \nu_4\left(1 + \frac{\epsilon_2}{J'}\right).$$

The effect of a non-zero j' to lowest order is simply a renormalization of the width (an increase), approximately temperature independent. It is only at extremely low temperature , where the factor $(\Gamma - 1)$ appearing in ϵ_2 is significant, that such a renormalization could conceivably be detected by observation of temperature-dependent line shapes, and at such low temperatures the expansions used converge very slowly. Perhaps the most significant result of this portion of the calculation is the negative one: the lowest order effects of a non-zero phonon-coupled variation in the exchange interaction between dimers does not produce any anomolous temperature variation of exciton concentration or resonance line width.

Appendix (A)

The following commutators of g-functions, the traces of which must be taken in order to obtain line moments, are not complete: terms which, by virtue of being sufficiently off-diagonal, have zero trace to the order of the present calculation have been dropped. (In the results tabulated below we have set V_0 , the magnitude of the oscillating perturbing field, equal to unity.)

$$[V^{\dagger}, g_0(\Delta)] = -\frac{1}{2}\sum_p S_p^z ,$$

$$[V^{\dagger}, g_1(\Delta)] = \frac{D}{4}\sum_p (Q_p + S_p^z) ,$$

$$[V^{\dagger}, g_2(\Delta)] = -\frac{D^2}{8}\sum_p S_p^z + \frac{3DJ'}{16}\sum_p (S_p^z S_p^+ S_{p+1}^- - S_p^+ S_{p+1}^- S_{p+1}^z + \text{flip}),$$

$$[V^{\dagger}, g_3(\Delta)] = \frac{D^3}{16}\sum_p (Q_p + S_p^z) + \frac{DJ'}{32}\sum_p \{ \frac{3J'}{2}[-S_p^+ S_{p+1}^- S_{p+1}^z - S_p^z S_p^+ S_{p+1}^- + 2 S_p^- S_p^z S_{p+1}^z S_{p+1}^+ + 2(Q_p + S_p^z)(S_{p+1}^z + S_{p+1}^z S_{p+1}^z) + S_p^- S_{p+1}^z S_{p+1}^+ S_{p+2}^z - S_p^z S_p^+ S_{p+1}^- S_{p+2}^z$$

(continued)

$$+ S_p^+ S_{p+1}^- S_{p+1}^z S_{p+2}^z - S_p^- S_p^z S_{p+1}^+ S_{p+2}^z \;]$$

$$+ D [Q_p (Q_{p+1} + 2 S_{p+1}^z) + 5 S_p^z S_p^+ S_{p+1}^- + 5 S_p^+ S_{p+1}^- S_{p+1}^z$$

$$- 10 S_p^z S_p^+ S_{p+1}^- S_{p+1}^z - 2 S_p^+ S_{p+1}^-] + \text{flip} \} ,$$

$$[g_2^\dagger (\Delta), \; g_2 (\Delta)] = - \frac{D^4}{32} \sum_p S_p^z + \frac{D^2 J'^2}{128} \sum_p \{ - 3 S_p^z (S_{p+1}^+ S_{p+1}^- + Q_{p+1})$$

$$-6 S_p^- S_{p+1}^z S_{p+1}^+ - 6 S_p^+ S_{p+1}^z S_{p+1}^- + 2 S_p^z Q_{p+1} Q_{p+2} - Q_p S_{p+1}^z Q_{p+2}$$

$$+ 2 S_p^z Q_{p+1} S_{p+2}^z$$

$$- (S_p^+ S_{p+1}^- S_{p+1}^z + S_p^- S_{p+1}^z S_{p+1}^+) (Q_{p+2} + 2 S_{p+2}^z) - 2 (S_p^+ S_{p+1}^- + S_p^- S_{p+1}^+) S_{p+2}^z$$

$$+ (S_p^z S_p^+ S_{p+1}^- + S_p^- S_p^z S_{p+1}^+) Q_{p+2} + 2 (S_p^- S_p^z S_{p+1}^z S_{p+1}^+ + S_p^z S_p^+ S_{p+1}^- S_{p+1}^z) S_{p+2}^z$$

$$+ \text{flip} \} .$$

$$[\, g_2^\dagger(\Delta),\ g_3(\Delta)\,] = \frac{D^2}{4}\,[\, V_,^\dagger\ g_3(\Delta)\,] + \frac{D^2 J'}{128} \sum_p \{ D^2 [\, Q_p(Q_{p+1} + 2\, S^z_{p+1})$$

$$- (2S^+_p + S^z_p S^+_p)\, S^-_{p+1} + (\, 2S^z_p S^+_p - S^+_p)\, S^-_{p+1} S^z_{p+1}\,]$$

$$+ \frac{3J'^2}{4} [\ -2\, S^-_p (\ S^z_{p+1} S^+_{p+1} + 3\, S^+_{p+1}) + 2\, S^-_p S^z_p\, (2S^z_{p+1} S^+_{p+1} - S^+_{p+1})$$

$$- 4\, S^+_p S^-_p S^z_p S^-_{p+1}\, S^+_{p+1} S^z_{p+1} - 2\, S^-_p\, S^z_p\, S^+_p\, (3\, S^z_{p+1} S^z_{p+1} - S^-_{p+1} S^z_{p+1} S^+_{p+1})$$

$$- (S^-_p\, S^+_{p+1} + S^+_p S^-_{p+1})\, S^-_{p+2} S^+_{p+2}$$

$$- (S^-_p S^z_p\, S^+_{p+1} + S^z_p\, S^+_p\, S^-_{p+1})\, (2S^z_{p+2} + S^-_{p+2} S^z_{p+2}\, S^+_{p+2})$$

$$-(\, S^-_p - 2\, S^-_p\, S^z_p)\, (S^z_{p+1}\, S^+_{p+1})\, S^-_{p+2}\, S^z_{p+2}\, S^+_{p+2}$$

$$+(S^+_p - 2\, S^z_p\, S^+_p)\, (S^-_{p+1}\, S^z_{p+1})\, S^-_{p+2}\, S^z_{p+2}\, S^+_{p+2}$$

$$+ S^-_p\, S^+_p\ (\, Q_{p+1} S^z_{p+2} + Q_{p+1}\, Q_{p+2} + S^z_{p+1}\, S^z_{p+2})$$

$$+\ S^z_p\, (Q_{p+1} + 2\, S^z_{p+1})\, Q_{p+2}\,]$$

$$+ \frac{J'^2}{8} [\ 2(Q_p S^z_{p+1} - S^z_p\, Q_{p+1})\, (S^-_{p+2}\, S^z_{p+2}\, S^+_{p+3} + S^z_{p+2} S^+_{p+2} S^-_{p+3}$$

$$- S^-_{p+2} S^z_{p+3}\, S^+_{p+3} - \ S^+_{p+2} S^-_{p+3} S^z_{p+3})$$

(continued)

$$+ 2 S^z_p Q_{p+1} (Q_{p+2} S^z_{p+3} - 2 S^z_p Q^z_{p+3}) + 2 Q_p S^z_{p+1} S^z_{p+2} Q_{p+3}$$

$$+ 2 S^z_p (2S^+_{p+1} S^-_{p+2} + 4 S^z_{p+1} S^+_{p+1} S^-_{p+2} S^z_{p+2} - 3 S^z_{p+1} S^+_{p+1} S^-_{p+2}$$

$$-3 S^-_{p+1} S^z_{p+1} S^+_{p+2}) \quad S^z_{p+3}$$

$$+ Q_p S^+_{p+1} S^-_{p+2} Q_{p+3}$$

$$+ Q_p (2 S^-_{p+1} S^+_{p+2} + 2 S^+_{p+1} S^-_{p+2} - 5 S^-_{p+1} S^z_{p+1} S^+_{p+2} - 5 S^z_{p+1} S^+_{p+1} S^-_{p+2}$$

$$+ 3 S^+_{p+1} S^-_{p+2} S^z_{p+2} + 3 S^-_{p+1} S^z_{p+2} S^+_{p+2}) S^z_{p+3}$$

$$+ 2 Q_p (Q_{p+1} S^z_{p+2} S^z_{p+2} - S^z_{p+1} S^z_{p+1} Q_{p+2} + S^z_{p+1} S^+_{p+2} S^-_{p+2} S^z_{p+2})$$

$$- 2 S^z_p Q_{p+1} (2 S^z_{p+2} + S^-_{p+2} S^+_{p+2} S^z_{p+2})$$

$$- 4 S^z_p S^+_{p+1} S^-_{p+1} S^z_{p+1} Q_{p+2} - 4 S^z_p S^z_{p+1} (6 S^z_{p+2} S^z_{p+2}$$

$$- S^+_{p+2} S^-_{p+2} S^z_{p+2}$$

$$+ 4 S^-_{p+2} S^z_{p+2} S^+_{p+2}) - 12 S^z_p S^-_{p+1} S^z_{p+1} S^+_{p+1} S^z_{p+2}$$

(continued)

$$- (S^-_p S^+_{p+1} + S^+_p S^-_{p+1}) (5 S^+_{p+2} S^-_{p+2} S^z_{p+2} + 12 S^-_{p+2} S^+_{p+2})$$

$$+ (S^-_p S^z_{p+1} S^+_{p+1} + S^+_p S^z_{p+1} S^-_{p+1}) (8 S^z_{p+2} - S^-_{p+2} S^z_{p+2} S^+_{p+2})$$

$$- (S^z_p S^+_p S^-_{p+1} + S^-_p S^z_p S^+_{p+1}) (22 S^z_{p+2} + S^-_{p+2} S^z_{p+2} S^+_{p+2})$$

$$+ 2 (S^z_p S^+_p S^-_{p+1} S^z_{p+1} + S^-_p S^z_p S^z_{p+1} S^+_{p+1}) S^-_{p+2} S^z_{p+2} S^+_{p+2}] + \text{flip} \}$$

+ three- and four- site terms from the exciton transfer part of $\mathcal{H}$.

In the equations above, the operator Q_p is defined by

$$Q_p = - S^+_p S^-_p S^z_p + S^-_p S^z_p S^+_p .$$

The operation (+flip) is defined, on an n-site operator, by:

$$A_p B_{p+1} \cdots C_{p+n-1} + \text{flip} \equiv \left\{ \begin{matrix} A_p B_{p+1} \cdots C_{p+n-1} + \\ C_p \cdots B_{p+n-2} A_{p+n-1} . \end{matrix} \right\}$$

The exciton-transfer contribution to [g_2^+ , g_3] was not written out above; its effect on the fifth moment is most simply determined by direct calculation of the traces of the factors which comprise the commutator. The fifth moment, as tabulated in Appendix (B), <u>does</u> contain the full contribution of exciton transfer.

Appendix (B)

Listed below are the zeroth through fifth moments of the resonance near g=2 for the triplet system in the absence of phonon interactions, correct to first order in J′ and D.

$$M_0 = NL\Delta \sinh \beta\Delta \{ 1 - \frac{\beta D}{2} (1 - 2L \cosh \beta\Delta)$$

$$- \beta J' L (\cosh \beta\Delta - 2L \sinh^2 \beta\Delta) \} ,$$

$$M_1(\Delta) = -NL\Delta \{ \frac{D}{2} (\cosh \beta\Delta - 1) - \frac{\beta D^2}{4} \cosh \beta\Delta [1 - 2L(\cosh \beta\Delta - 1)]$$

$$- \beta \frac{DJ'}{2} L \sinh^2 \beta\Delta [1 - 2L(\cosh \beta\Delta - 1) \} ,$$

$$M_2(\Delta) = \frac{D^2}{4} M_0 ,$$

$$M_3(\Delta) = \frac{D^2}{4} M_1(\Delta) - NL^2\Delta \frac{D^2 J'}{4} \{ 2(\cosh \beta\Delta - 1) - \beta D (1 - 4L \cosh \beta\Delta)$$

$$\cdot (\cosh \beta\Delta - 1)$$

$$- \frac{\beta J'}{2} [\cosh \beta\Delta + 2 + 2L \sinh^2 \beta\Delta - 12L^2 \sinh^2 \beta\Delta$$

$$\cdot (\cosh \beta\Delta - 1)] \} ,$$

$$M_4(\Delta) = \frac{D^4}{16} M_0 + NL^2\Delta \frac{D^2 J'^2}{8} \sinh \beta\Delta \{ 3 + 2L (\cosh \beta\Delta - 1)$$

(continued)

$$- \frac{\beta D}{2} \left[3 - 4L(2\cosh\beta\Delta - 1) - 12L^2 \cosh\beta\Delta(\cosh\beta\Delta - 1)\right]$$

$$- \frac{\beta J'}{4} \left[3 + 2L(5\cosh\beta\Delta + 4) - 4L^2(\cosh\beta\Delta - 1)(7\cosh\beta\Delta + 9)\right.$$

$$\left. - 32L^3 \sinh^2\beta\Delta(\cosh\beta\Delta - 1)\right]\Big\} ,$$

$$M_5(\Delta) = \frac{D^2}{4} M_3(\Delta) - NL^2\,\Delta\,\frac{D^2 J'}{8}\Big\{ D^2(\cosh\beta\Delta - 1)$$

$$- \frac{DJ'}{2}(\cosh\beta\Delta - 1)\left[1 + 2L(\cosh\beta\Delta - 1)\right]$$

$$+ \frac{9}{4} J'^2 (\cosh\beta\Delta - 1)\left[1 + 2L(\cosh\beta\Delta + 1)\right]$$

$$- \frac{\beta D^3}{2}(\cosh\beta\Delta - 1)\left[1 - 4L\cosh\beta\Delta\right]$$

$$- \frac{\beta D^3}{2}(\cosh\beta\Delta - 1)\left[1 - 4L\cosh\beta\Delta\right]$$

$$- \frac{\beta D^2 J'}{2}\left[3 + L(\cosh\beta\Delta - 1)(\cosh\beta\Delta + 2)\right.$$

$$\left. - 6L^2(\cosh\beta\Delta - 1)^2\right]$$

(continued)

$$-\frac{\beta D J'^{2}}{8}\,[\,7\cosh\beta\Delta + \sinh\beta\Delta - 15 - 2L(\cosh\beta\Delta - 1\,)$$

$$(3\cosh\beta\Delta - 13\,)$$

$$-\;4L^{2}\sinh^{2}\beta\Delta\,(26\cosh\beta\Delta - 1\,)$$

$$+\;32L^{3}\sinh^{2}\beta\Delta\,(\cosh\beta\Delta - 1\,)^{2}\,]$$

$$-\frac{\beta J'^{3}}{16}\,[9(\cosh\beta\Delta + 2\,) + \frac{6}{\Gamma}(\cosh\beta\Delta + 1\,)$$

$$+\;L\,(\cosh\beta\Delta + 1\,)\,(62\cosh\beta\Delta - 5) - 2\,\frac{L}{\Gamma}\,\sinh^{2}\beta\Delta$$

$$-\;2L^{2}\,(\cosh\beta\Delta - 1\,)\,(28\cosh^{2}\beta\Delta - 11\cosh\beta\Delta - 41)$$

$$-\;288\,L^{3}\sinh^{4}\beta\Delta\,]\,\}\,.$$

In these equations:

$$L \equiv \frac{e^{-\beta J}}{\Gamma}\,,$$

$$\Gamma \equiv 1 + e^{-\beta J}\,(\,1 + 2\cosh\beta\Delta\,).$$

Appendix C

In Section 4 , sums of the following forms arise in the determination of the effects of the exciton-phonon interactions:

$$\sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} N\delta(k), \qquad \sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} \cos nk,$$

$$\sum_{k\mu} \left(\frac{d_{k\mu} c^*_{k\mu}}{\omega_{k\mu}} + \text{h.c.} \right) N\delta(k) \ , \quad \sum_{k\mu} \left(\frac{d_{k\mu} c^*_{k\mu}\, e^{-ink}}{\omega_{k\mu}} + \text{h.c.} \right)$$

where:

$$c_{k\mu} = -\frac{j}{\sqrt{N}} (u_{k\mu 2} - u_{k\mu 1}) \ ,$$

$$d_{k\mu} = -\frac{j'}{\sqrt{N}} (u_{k\mu 1}\, e^{ik} - u_{k\mu 2}),$$

$$u_{k\mu 1} = (4m\omega_{k\mu})^{-\frac{1}{2}} \ ,$$

$$u_{k\mu 2} = (-1)^{\mu+1} \frac{|L_{k12}|}{L_{k12}} u_{k\mu 1} \ ,$$

$$m\omega^2_{k\mu} = L_{k11} + (-1)^{\mu+1} |L_{k12}| \ ,$$

$$L_{k11} = G + g_1 + g_2 \ ,$$

$$L_{k12} = -(g_1 + g_2\, e^{ik}).$$

The sums over μ are most easily executed with the aid of the orthonormality conditions (4.9). The results are:

$$\sum_{\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} = \frac{j^2}{N\alpha_1} \cdot \frac{(G + g_2 - g_2 \cos k)}{1 - \alpha_2 \cos k} \;,$$

$$\sum_{\mu} \left(\frac{d_{k\mu} c^{*}_{k\mu} e^{-ink}}{\omega_{k\mu}} + \text{h.c.} \right) = \frac{jj'}{\alpha_1} \; \frac{1}{(1 - \alpha_2 \cos k)}$$

$$\times \Big\{ g_2 \left[\cos(n+1)k + \cos(n-2)k \right]$$

$$- \; (G + g_2) \left[\cos nk + \cos(n-1)k \right] \Big\} \;,$$

where:

$$\alpha_1 = L^2_{k11} - g_1^{2} - g_2^{2} \;,$$

$$\alpha_2 = 2g_1g_2/\alpha_1 \;.$$

In the limit of large N, we can replace sums over k by integrals, i.e.:

$$\sum_{k} f(k) \rightarrow \frac{N}{2\pi} \int_{-\pi}^{\pi} f(\theta)\, d\theta$$

Integrals to be evaluated are of the form

$$I_n \equiv \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\cos n\theta \, d\theta}{1 - \alpha_2 \cos\theta} \;,$$

Simple contour integration yields:

$$I_n = \frac{1}{\sqrt{1 - \alpha_2^2}} \left(\frac{1 - \sqrt{1 - \alpha_2^2}}{\alpha_2} \right)^{|n|} .$$

(Note that $0 \leq \alpha_2 \leq 1$).

The required phonon sums, expressed in terms of I_n, are listed below:

$$\sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} N\delta(k) = \frac{j^2}{m\omega_{01}^{\ 2}} = \frac{j^2}{G + 2(g_1 + g_2)} \ ;$$

$$\sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} = \frac{j^2}{\alpha_1} \left[(G + g_2) I_0 - g_2 I_1 \right] > 0 \ ;$$

For $n \geq 1$:

$$\sum_{k\mu} \frac{|c_{k\mu}|^2}{\omega_{k\mu}} \cos nk = - \frac{j^2}{\alpha_1} \frac{G(G + 2g_2)}{2g_1} I_n < 0$$

$$= - \frac{\epsilon_1}{2} e^{-\lambda |n|} \ ,$$

where:

$$\epsilon_1 = \frac{j^2 G(G + 2g_2)}{g_1 \alpha_1 \sqrt{1 - \alpha_2^2}} \ ,$$

$$\lambda = \ln \left[\frac{1 + \sqrt{1 - \alpha_2^2}}{\alpha_2} \right] ;$$

$$\sum_{k\mu}\left(\frac{d_{k\mu}c^{*}_{k\mu}}{\omega_{k\mu}}\, N\delta(k) + \text{h.c.}\right) = -\,\frac{2jj'}{G + 2(g_1 + g_2)} \quad ;$$

$$\sum_{k\mu}\left(\frac{d_{k\mu}\,c^{*}_{k\mu}\,e^{-ink}}{\omega_{k\mu}} + \text{h.c.}\right) = \sum_{k\mu}\left(\frac{d_{k\mu}\,c^{*}_{k\mu}\,e^{i(n-1)k}}{\omega_{k\mu}} + \text{h.c.}\right)$$

$$= -\,\frac{jj'}{\alpha_1}\left[G(I_0 + I_1) + g_2(I_0 - I_2)\right] < 0 \qquad \text{For } n = 0,1$$

$$\left.\begin{aligned} &= +\,\frac{jj'}{\alpha_1}\,\frac{G}{g_1}\,(G + g_1 + 2g_2)\,(I_{|n|} + I_{|n-1|}) > 0 \\ &= \frac{j'}{j}\left(1 + \frac{g_1}{G + 2g_2}\right)\epsilon_1\left(e^{-\lambda|n|} + e^{-\lambda|n-1|}\right) \end{aligned}\right] \begin{array}{l}\text{For}\\ n \geq 2\\ \text{or}\\ n \leq -1\end{array}$$

Legends to Figures

Fig. 1 Projection of the orthorhombic structure of Wurster's blue perchlorate onto the $\underline{a}_0\underline{c}_0$ plane. The perchlorate groups are not in the plane of the chains of WB cations (seen edge-on). (Figures 1, 5, and 6 are reproduced from reference 6 with the kind permission of the author.)

Fig. 2 Susceptibility vs. temperature for WBP. Above the transition temperature the crystal structure changes, and the present model is inapplicable.

Fig. 3 α - 1 vs. temperature. The curves are terminated at temperatures for which the width of the doublet lines becomes comparable to their separation. Note that the degree of symmetry of the lines is of the order of 5% or less.

Fig. 4 Line width, W, and exciton density, ρ, vs. 1/T. The exciton density is insensitive to the value of J$'$ for the ranges of parameters considered. The model used to determine line width is inapplicable for $\frac{2}{D} W \geqslant 1$.

Fig. 5 Paramagnetic resonance spectra of a WBP crystal at 74°, 64°, 45° and 30° K. (These curves represent the derivative of the absorption spectrum.)

Fig. 6 Experimental plot of (a) relative spin concentration and (b) exchange frequency vs. 1/T for a single crystal of WBP.

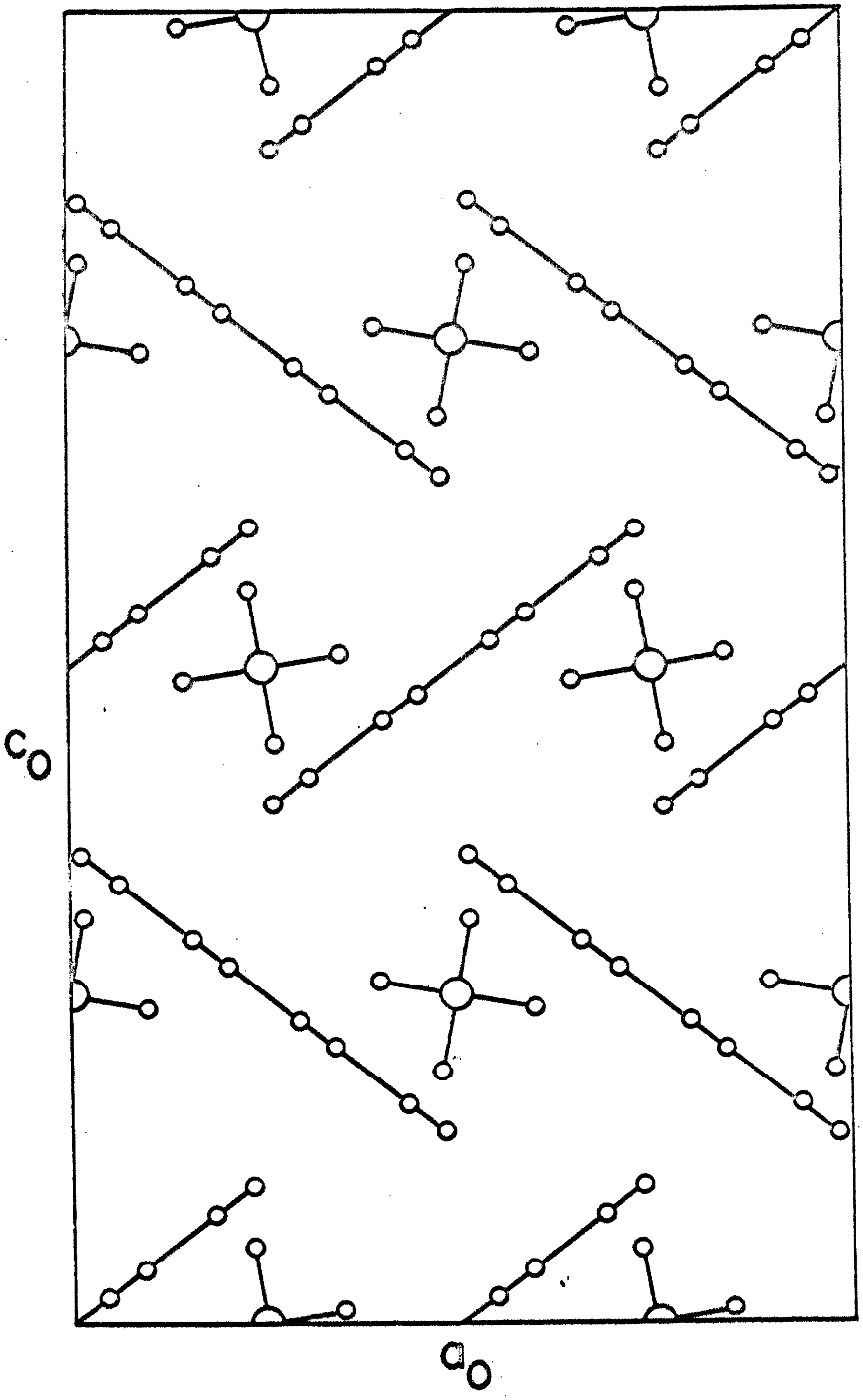


Figure 1

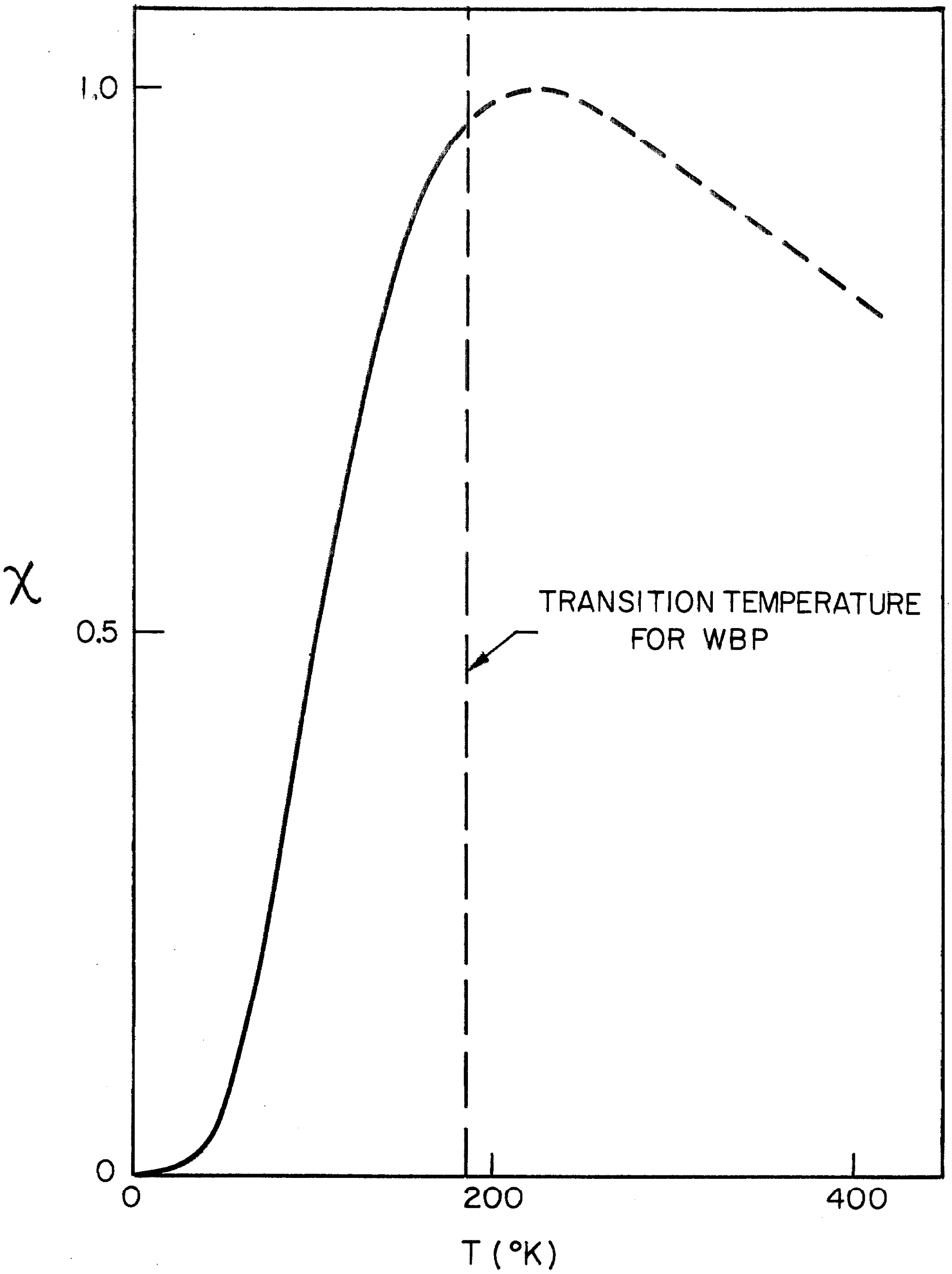


Figure 2

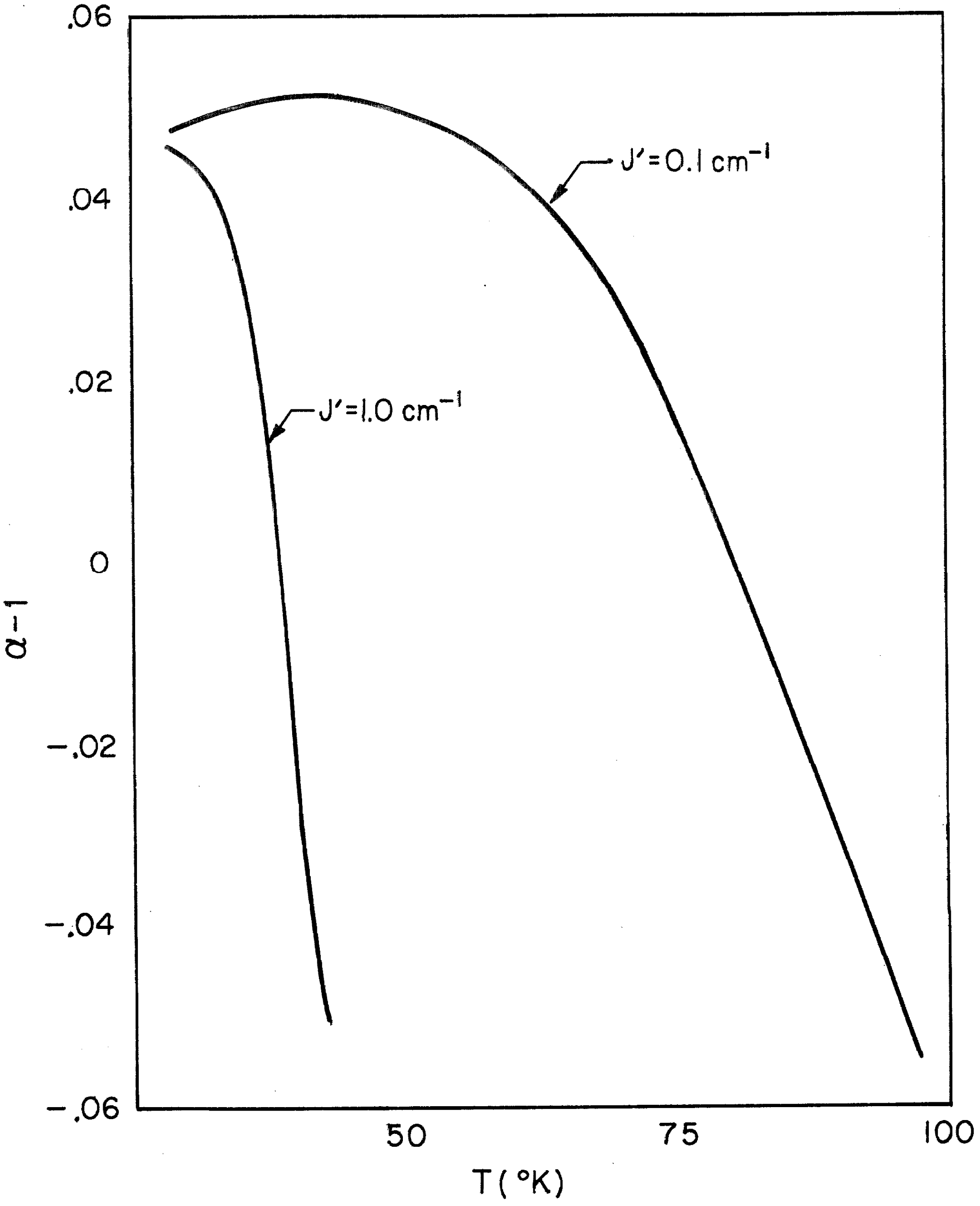


Figure 3

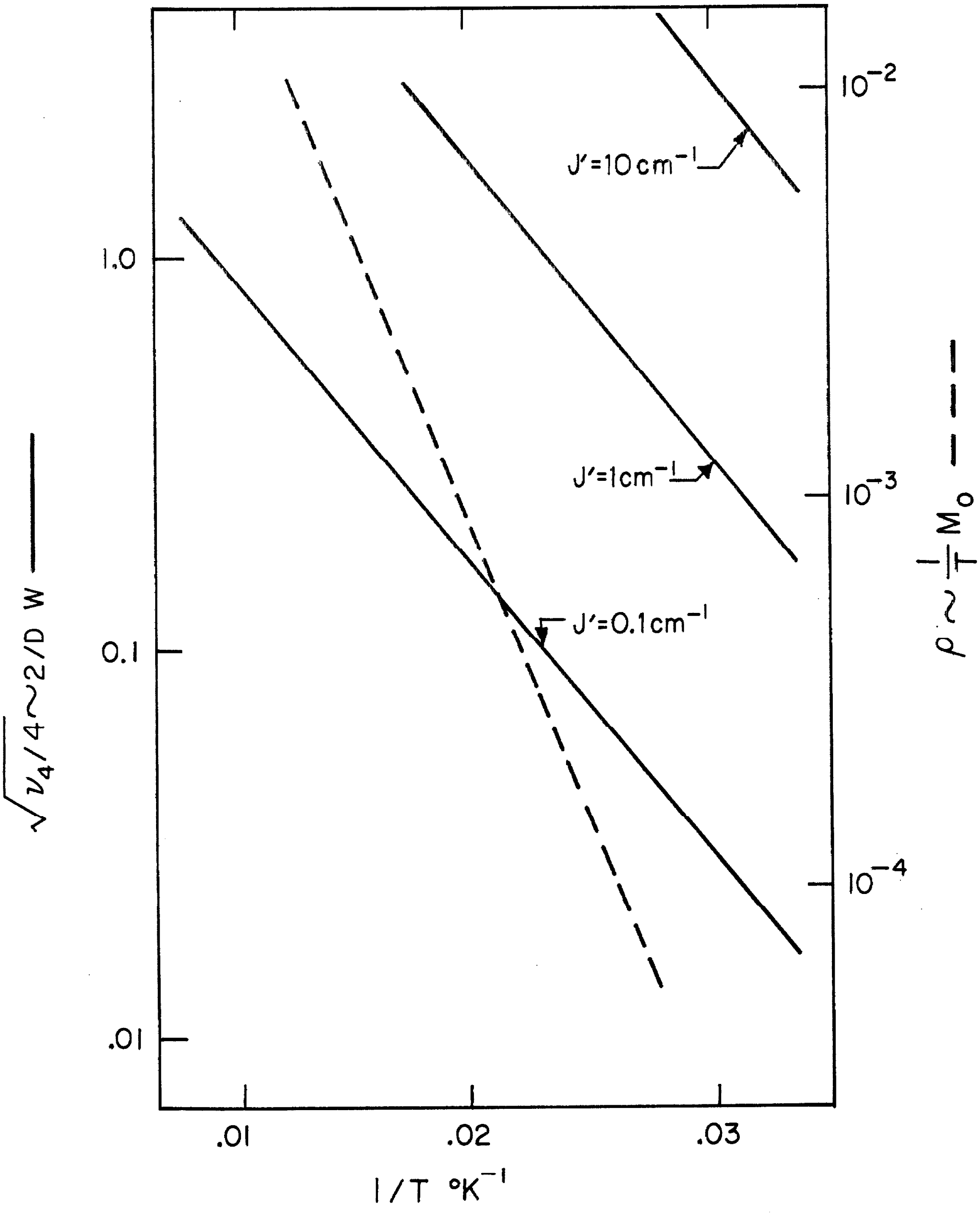

$\sqrt{\nu_4/4} \sim 2/D\ W$
1.0
0.1
.01
10^{-2}
10^{-3}
10^{-4}
$\rho \sim \frac{1}{T} M_o$
J′=10 cm⁻¹
J′=1 cm⁻¹
J′=0.1 cm⁻¹
.01
.02
.03
1/T °K⁻¹

Figure 4

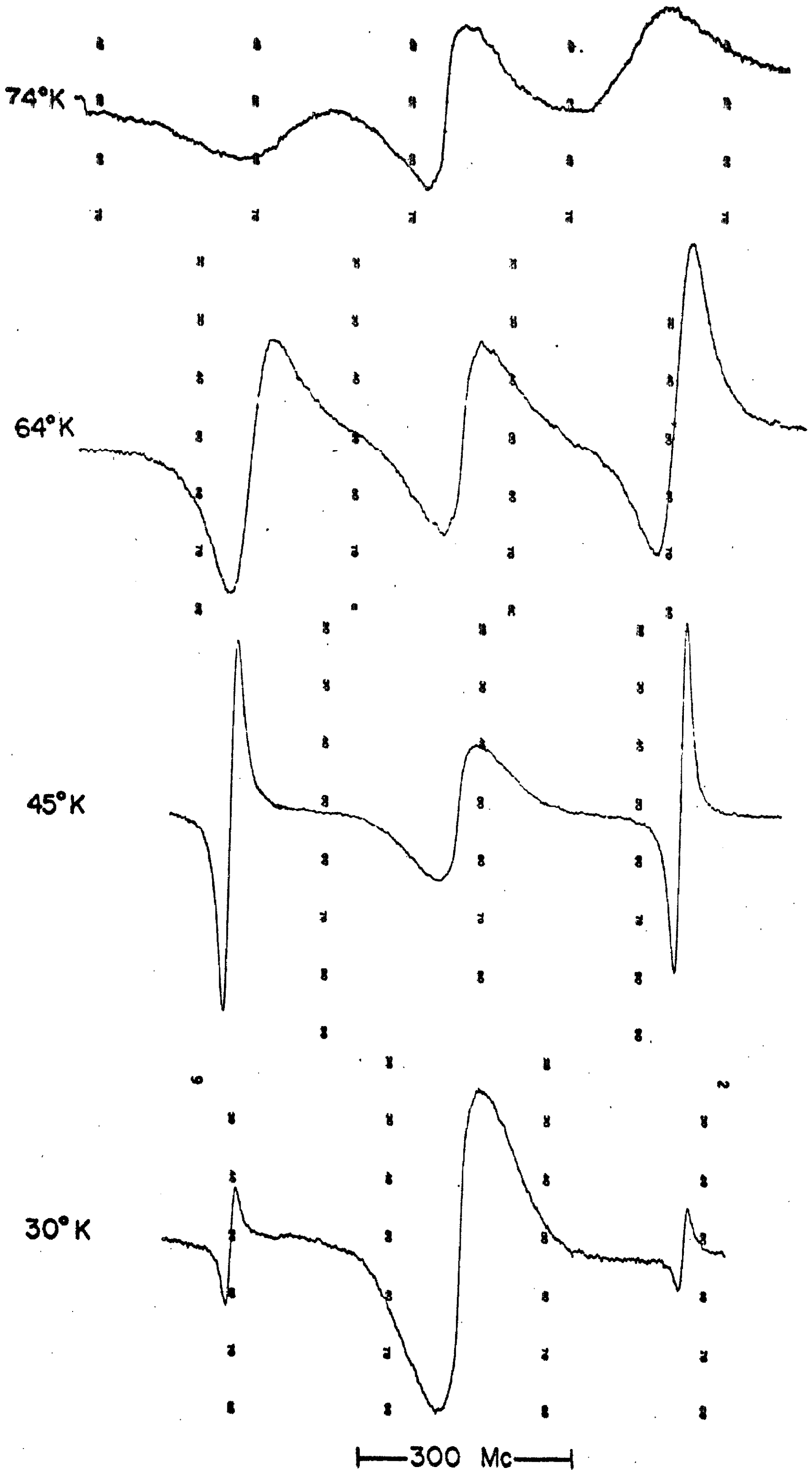


Figure 5

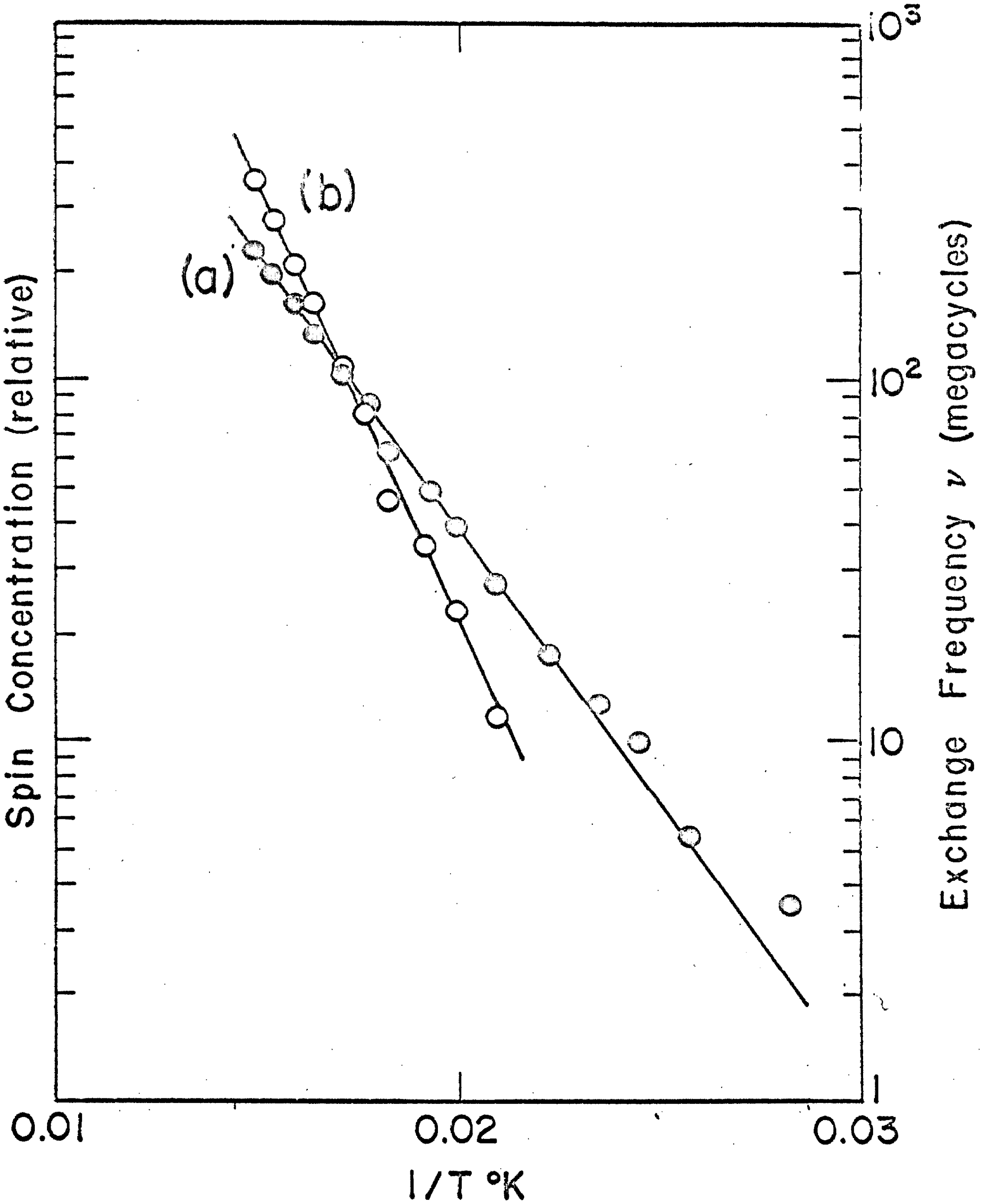

(b)
(a)
Spin Concentration (relative)
Exchange Frequency ν (megacycles)
10³
10²
10
1
0.01
0.02
0.03
1/T °K

Figure 6

REFERENCES

1. D.B. Chesnut and W.D. Phillips, J. Chem. Phys., **35**, 1002 (1961).
2. M. T. Jones and D. B. Chesnut, J. Chem. Phys., **38**, 1311 (1963).
3. D. B. Chesnut and P. Arthur, Jr., J. Chem. Phys., **36**, 2969 (1962).
4. D. D. Thomas, A. W. Merkl, A. F. Hildebrandt, and H. M. McConnell, J. Chem. Phys., **40**, 2588 (1964).
5. H. M. McConnell, D. Pooley, and A. Bradbury, Proc. Natl. Acad. Sci. (U.S.), **48**, 1480 (1962).
6. D. D. Thomas, H. Keller, and H. M. McConnell, J. Chem. Phys., **39**, 2321 (1963).
7. J. D. Turner and A. C. Albrecht, unpublished (See Ref. 6).
8. R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1956), p. 108.
9. H. C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. (London) **A 251**, 172 (1959).
10. Y. Ooshika, J. Phys. Soc. Japan, **12**, 1238 (1957); **14**, 747 (1959).
11. C. G. Montgomery, Thesis, California Institute of Technology (1964).
12. H. M. McConnell and Z. Soos, J. Chem. Phys., **40**, 586 (1964).

13. H. M. McConnell, and C. G. Montgomery, J. Chem. Phys., 39, 252 (1963).

14. H. Sternlicht, and H. M. McConnell, J. Chem. Phys., 37, 794 (1961).

15. R. M. Lynden-Bell and H. M. McConnell, J. Chem. Phys., 37, 794 (1962).

16. H. M. McConnell, and R. Lynden-Bell, J. Chem. Phys., 36, 2393 (1962).

17. L. J. F. Broer, Physica, 10, 801 (1943).

18. J. H. Van Vleck, Phys. Rev., 74, 1168 (1948).

19. A. Wright, Phys. Rev., 76, 1826 (1949).

20. K. Kambe, and T. Usui, Prog. Theo. Phys., 8, 302 (1952).

21. M. McMillan, and W. Opechowski, Can. J. Phys., 38, 1168 (1960); 39, 1369 (1961).

22. H. Cheng, Thesis, California Institute of Technology (1962).

23. M. Itzkowitz, private communication.

24. K. H. Hauser and J. N. Murrell, J. Chem. Phys., 27, 500 (1957).