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A. H. Zewail and C. B. Harris

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III.

COHERENCE IN ELECTRONICALLY EXCITED DIMERS.

II. THEORY AND ITS RELATIONSHIP TO EXCITON DYNAMICS

A. H. Zewail and C. B. Harris *

Inorganic Materials Research Division, Lawrence Berkeley Laboratory;
and Department of Chemistry; University of California
Berkeley, California 94720

*Alfred P. Sloan Fellow

ABSTRACT

A theory of microwave absorption in coherent or incoherent states of multi-dimensional crystals is developed. Application of the theory to the cluster states (dimer, trimer, tetramer, ... etc.) of linear chain systems and its relationship to microwave band-to-band transitions in coherent Frenkel excitons provides a new way of studying coherence in the excited levels of molecular solids. A quantitative treatment of the influence of exciton-phonon coupling on spin dynamics in a two-level system (dimer) and the extension to a multi-level system (exciton) is given. The results prove that zero field electron spin resonance can directly measure the cross-section of the scattering processes in the excited state and that the technique is applicable to other classes of solids. Moreover, the anisotropy and the magnitude of intermolecular interactions can be established from these experiments.

I. INTRODUCTION

The spectroscopy of molecular solids has been of considerable interest in recent years. This interest arises from the importance of the systems themselves as well as from the fact that the structure and packing of these molecules in the lattice determine the anisotropy of many properties in these solids. Band theory, developed by Frenkel[1,2] and Davydov,[3,4] was clearly the fundamental step toward our understanding of the molecular solid state in so far as it offered a direct relationship between the band structure in the delocalized limit and the molecular properties. When the excitation is associated with singlet electronic levels, singlet bands are formed with a width[5] determined by the nature of the interaction between the molecules. Likewise, a triplet exciton band will be formed from a crystal with molecules excited in their triplet electronic levels, and in a tight-binding theory the transfer integral is simply given by

$$\beta = \langle \phi_m | H | \phi_n \rangle \tag{1}$$

where H is the total Hamiltonian of the system and ϕ_n is the wavefunction[6] which is localized on the nth molecule.

The above considerations deal with "undressed excitons" in which the pure electronic excitation transfer results in a band free from any distortion and is confined only to electronic matrix elements. However, the exciton could be dressed by a vibronic and/or lattice excitation[7-13] which may couple to the pure electronic excitation,

resulting in a direct or indirect perturbation on the stationary states of the band. In dynamical language, this coupling of exciton states to a phonon bath initially results in the damping of the wave packet (characterized by some specific momentum vector k)[14-17] and these new linear combinations of wave vector states will then scatter further to other k states, say k', via the exciton-phonon Hamiltonian on a time scale determined by the magnitude of the coupling matrix element. This gives rise to a very important question that pertains to the relationship between the scattering cross-section and the coherent vs. incoherent properties of band states. A quantitative extraction of the scattering times as a measure of the mechanism of exciton-phonon coupling is not an easy task, particularly for experimentalists. This is because we are dealing with an ensemble of N-level systems (N is the number of molecules), hence the fluctuations of the off-diagonal elements of the time-dependent density matrix, which measure the degree of coherence, are a complex function for the coupling between the relaxation Hamiltonian and the N-levels of the band. If one can study such scattering processes on a two-level system which has a direct relationship to the properties of the N-level system , band states, the physics behind these processes could be better understood and a quantitative treatment could lead into a clearer picture of the relaxation Hamiltonian, coherence, and the influence of band dimensionality on exciton dynamics.

A dimer in a triplet state is electronically a system of two levels which are separated by 2β where β is the intermolecular interaction between the molecules. This dimer splitting is directly related to the triplet exciton splitting.[18] For example, in the nearest-neighbor approximation,[19,20] the splitting (2β) of translationally equivalent dimers is half the bandwidth (4β; energy separation between $k = 0$ and $k = \pm\pi/a$) for an exciton formed along the same translational axis. Moreover, the solution to the stationary Schrödinger equation yields $\psi(+)$ and $\psi(-)$ for the dimer which are conceptually related to the $\psi(k)$ of the band. These states are coherent for the lifetime of the excited state unless there is an interaction between them and the surroundings via a relaxation Hamiltonian. The Hamiltonian[21,22] describing the coupling (with amplitude A) between phonons of frequency ω and the exciton is

$$H_{\text{ex-ph}} = \sum_k E(k) a_k^+ a_k + \omega \sum_q b_q^+ b_q + A \sum_k \sum_q a_{k+q}^+ a_k (b_q + b_{-q}^+) \tag{2}$$

where b_q^+ and b_q are the intramolecular phonon (with q momentum) creation and annihilation operators, and a_k^+ and a_k are those of the exciton with energy $E(k)$. For a dimer, the scattering causes local and transition fluctuations[13] which determine the power spectrum, $J(\Omega)$,[23,24]

$$J(\Omega) = \int_{-\infty}^{\infty} \langle H(t)\, H(t+\tau) \rangle \exp(-i\Omega\tau)\, d\tau \tag{3}$$

where Ω is the frequency corresponding to the energy difference between the two levels. The autocorrelation function has a characteristic time, τ_c, which is the memory time or <u>coherence time</u>, since for this time

$$H(t) \simeq H(t + \tau_c) \tag{4}$$

Thus, the τ_c's of $\psi(+)$ and $\psi(-)$ are determined by fluctuations of the off-diagonal matrix elements of the time-dependent density matrix when the stationary states are solutions to the zeroth order Hamiltonian matrix responsible for the dimer splitting.

Experimentally, there are two important parameters needed to describe the scattering, τ_c and the values at different points in the correlation function, so that the full correlation function for scattering may be determined. Specifically, τ_c relative to the resonance transfer whose frequency is $2\beta/h$ establishes whether or not there is a coherence in the dimer. This is because coherence can only be established by determining the rate at which the time-dependent Hamiltonian[25,26] modulates the energies of the states relative to 2β.

If τ_c $(\pm) < h/2\beta$, the states are clearly incoherent and possibly indistinguishable. On the other hand, if τ_c $(\pm) > h/2\beta$, as when approaching the lifetime of the excited species in the state, the dimer is coherent because the phases of the wavefunctions are well-defined during that period of time. However, it should be remembered

that the measurement of τ_c is completely determined by the time scale of the experiment. For example, in optical experiments if the spectroscopic splittings between the two dimer states or, more generally, the Davydov components, and the optical linewidth of the plus and minus states are on the order of β, the system can appear to a large extent incoherent although the off-diagonal elements of the density matrix are not fluctuating at the rates 2β (or 8β for the Davydov splittings). In addition, the available optical techniques cannot measure the linewidth of the minus state of a translationally equivalent dimer since the transition moment from the ground state to that state is zero by symmetry.[27] If 2β is less than the optical linewidth, then conventional optical techniques cannot measure any of these parameters and many of the spectroscopic properties[28-34] of dimers cannot be obtained conventionally.

Avakian et al[35,36] have shown the importance of the linewidth of the Davydov component as well as the separation between the two components in anthracene in determining the dynamics of exciton migration. Furthermore, they measured diffusion constants and related them to the nature of excitation transfer. However, as realized by these authors,[35-37] the diffusion constants not only depend on the velocity[38,39] of the exciton but also on the scattering time and hence more experiments beside the diffusion constant are needed.

Magnetic Resonance spectroscopy (EPR), can be performed on a time scale which is very suitable for the measurements of coherence time and the detection of many of the anisotropic properties of magnetic interactions in the excited state. Schwoerer and Wolf[40,41] have shown that the EPR of the naphthalene pair are different from that of the monomer whose EPR spectra were well-known from Hutchison and Mangum experiments.[42,43] Moreover, they identified the pair as translationally inequivalent, and a "diffusion constant" for the excitation was computed from their measurements. However, the correlation time for scattering, in our opinion and also from the work of Hanson,[44] cannot be determined from these high field linewidth measurements. This is because the resonance linewidth depends on (i) magnetic field broadening induced by the field anisotropy, (ii) hyperfine splittings which have been proven to exist in the dimer spectra of naphthalene by Hutchison and King,[45] (iii) relaxation effects, and finally, (iv) the physics of stochastic Markoffian[46] processes must be taken[47] into account in extracting the coherence properties from such measurements.

As we will demonstrate, zero field EPR spectroscopy of dimers at low temperatures can be used to answer many of the above questions pertaining to the coherent and incoherent properties, particularly if the dimers are formed in crystals where the band dispersion is one-dimensional.[48]

Recently, the zero field phosphorescence microwave double resonance (PMDR)[49] spectroscopy of pairs of 1,4-dibromonaphthalene where the band dispersion for the exciton is one-dimensional[50,51] was reported.[52] The identification of the pairs as translationally equivalent was consistent with the resonance frequencies, and both the optical and EPR results manifest the strong interaction between the two molecules of the pair.[52,53] However, the dynamics of coherence could not be established from the experiments because of the interference between the $D + |E|$ and $D - |E|$ transitions which broadens the resonance lines and limits the resolution.

The first paper[54] of this series gave a brief account of our results on coherence in excited dimers of 1,2,4,5-tetrachlorobenzene crystal. In this paper we present the detailed theoretical grounds for understanding coherence in dimers and its relationship to coherence in excitons. The influence of the resonance interaction and the resonance between the molecules composing the pair on the stationary properties of the dimer is also given. The effect of phonon scattering on the microwave absorption in the dimer states is explicitly given and related to the physics

governing the scattering processes in the different limits of exchange; slow, intermediate and fast.

II. THE STATIONARY STATES OF DIMERS AND EXCITONS

In the rigid lattice approximation, the total Hamiltonian of the crystal is

$$H = H_m + \sum_{m<n} V_{mn} \tag{5}$$

H_m is the Hamiltonian for a molecule at the mth site and V_{mn} is the exciton interaction energy. This Hamiltonian may be written in another commonly used notation, occupation number formalism, if we define the vacuum state of the crystal by the following equation.[55]

$$a_m|0000\ldots 1_n \ldots 000\rangle = |0000\ldots 0\ldots 000\rangle\, \delta_{mn} \tag{6}$$

where a_m is the well-known annihilation operator and $|0000\ldots 1_n \ldots 000\rangle$ indicates that one quantum of excitation is on the nth site while all other sites are in the ground state. Thus

$$H_{ex} = \sum_m \varepsilon_m a_m^+ a_m + \sum_{m<n} V_{mn} a_n^+ a_m \tag{7}$$

If the unit cell of the lattice contains more than one molecule the full crystal eigenstate for a spinless exciton is[21]

$$|\psi_\nu(\vec{k})\rangle = \sum_{u\alpha} C_{u\alpha}^{(\nu)}(\vec{k})\,|\phi_\alpha(\vec{k})\rangle \tag{8}$$

where $u\alpha$ is the cell cordinate (u labels the unit cell, α the molecule in the unit cell), and $|\phi_\alpha(\vec{k})\rangle$ is the one-site exciton function . These Bloch functions[56] can be formed from the anti-symmetricized product of wavefunctions for the individual molecules. ν is the band index for the different exciton branches, which is equal to the number of molecules per unit cell.

For a paramagnetic (triplet) exciton, equation (8) may be substituted by

$$|\psi_\nu(\vec{k}), T_i\rangle = \sum_{u\alpha} C_{u\alpha}^{(\nu)}(\vec{k})|\phi_\alpha(\vec{k}), T_i\rangle \qquad (9)$$

where T_i are the zero field spin functions.

It is now clear that in order to determine the proper eigen-states of the system, $C_{u\alpha}$ must be obtained. Group-theoretical[57] arguments may be used to evaluate these coefficients at certain points in the Brillouin zone. This is strictly true for the $\vec{k} = 0$ point at which the full symmetry of the Brillouin zone can be used to classify the eigen-functions. Thus $CC^* = 1/2$ at this point of the zone. The same kind of simplifications can be made if $\vec{k}$ is directed along a symmetry axis of the crystal. For a general $\vec{k}$ this is not necessarily true. However the "restricted Frenkel limit" [58] was invoked to simplify the computation. Briefly, this approximation eliminates the translational resonance interactions skew to the crystallographic axes. Such an approximation seems to describe the triplet state excitonic properties of naphthalene and anthracene type lattices, perhaps because of the unique nature of the spatial

array of the molecules in the lattice. It is within this limit that the eigenfunctions, $|\psi_\nu(\vec{k}), T_i>$, for each ν and for all $\vec{k}$ (not just $\vec{k} = 0$ and along symmetry direction) have equal aplitudes from the one-site exciton functions. The energies for lattices with two molecules in the unit cell are

$$E_\nu(\vec{k}) = E_0 + L_{\alpha\alpha}(\vec{k}) + (-1)^\nu L_{\alpha\beta}(\vec{k}) \tag{10}$$

$L_{\alpha\alpha}$ and $L_{\alpha\beta}$ are the so-called <u>translationally equivalent</u> and <u>translationally inequivalent</u> interaction terms, and E_0 is the center of gravity of the exciton band (which can be written as the sum of the free gas excitation energy plus the crystal shift). More specifically, the dispersion relation of equation (10) for a monoclinic $P2_1/a$ lattice may be written in the following form.[3]

$$E_\nu(\vec{k}) = E_0 + \sum_{\mu=1}^{3} 2\beta_\mu \cos(\vec{k}\cdot\vec{r}_\mu) + (-1)^\nu 4\beta \cos\left[\frac{\vec{k}\cdot\vec{r}_1}{2}\right] \cos\left[\frac{\vec{k}\cdot\vec{r}_2}{2}\right] \tag{11}$$

where r_μ ($\mu = 1,2,3$) represent a,b,c lattice vectors, respectively. For a <u>one-dimensional exciton</u>, equation (11) reduces to

$$E(\vec{k}) = E_0 + 2\beta_a \cos(\vec{k}\cdot\vec{a}) \tag{12}$$

if the interaction is along the a-axis.

The above equations can be used to describe the stationary electronic properties of a molecular dimer in a crystal lattice, since the Hamiltonian for a pair of molecules (A and B) bound by the intermolecular potential V_{AB} is

$$H^{(D)} \equiv H(\text{Dimer}) = H_A + H_B + V_{AB} \tag{13}$$

which is derived from equation (5) for a two molecule chain. In addition, the one-site function for the pair is simply

$$A\psi_A^0\ (1,2)\ \psi_B^{(i)}\ (3,4) \tag{14}$$

in which the molecule B is excited into the triplet state while molecule A is in the ground state. i stands for a particular triplet spin sublevel, and $\psi(r_l, r_m)$ is the two-electron antisymmetrized function of the electron coordinates r_l and r_m. A permutes the electrons between the molecules and ψ_A is the product of a spatial function Φ (which is symmetric to electron interchange for a singlet state and antisymmetric for a triplet state), and a spin function.

Since V_{AB} of equation (13) is a spatial operator on the coordinates of all four electrons, one can show that

$$\langle A\psi_A^{(a)}\psi_B^{(b)}|V_{AB}|A\psi_A^{(c)}\psi_B^{(d)}\rangle = \langle\psi_A^{(a)}(12)\psi_B^{(b)}(34)|V_{AB}|\psi_A^{(c)}(12)\psi_B^{(d)}(34)\rangle -$$

$$\langle\psi_A^{(a)}(12)\psi_B^{(b)}(34)|V_{AB}|\psi_A^{(c)}(34)\psi_B^{(d)}(12)\rangle = J - \beta \tag{15}$$

Writing the explicit form for the wavefunctions clearly indicates that J = 0 for triplets if there is no spin-orbital interaction and that β (exchange excitation transfer matrix element) is primarily responsible for triplet dimer splittings.[59]

In zero field, the spin is correlated [60] along the molecular axes which are coincident with the symmetry axes if the molecular point group is C_{2v} or higher. Thus the total triplet function in zero field can be written as $\Phi \otimes T_i$ where i = x,y,z. The corresponding Bloch functions for a dimer are therefore given by

$$\psi_i(\pm) = \frac{1}{\sqrt{2}} \left[|\Phi_A^* T_i \Phi_B^0 S^0\rangle \pm |\Phi_A^0 S^0 \Phi_B^* T_i\rangle \right] \tag{16}$$

which could be abbreviated as follows.

$$\psi_i(\pm) = \frac{1}{\sqrt{2}} \left[|A\, T_i\rangle \pm |B\, T_i\rangle \right] \tag{17}$$

III. RESONANCE SPECTRA OF DIMERS AND TRIPLET FRENKEL EXCITONS

If the zero field splittings (ZFS) are comparable with the energy separation between the bands (i.e., in regions of the Brillouin zone where there are band degeneracies [61] or near degeneracies), the spin energies [19] of the exciton states can be obtained from the following secular equation.

$$|\langle\psi_\nu(\vec{k}), T_i|\Sigma H_D + \Sigma H_{SO}\, |\psi_{\nu'}(\vec{k}), T_j\rangle - E\delta_{ij}\, \delta_{\nu\nu'}| = 0 \tag{18}$$

where the sum is over all the electrons in the crystal.

For a dimer the solution is rather simple. The above six basis functions (see equation (17)) can be used to obtain the dimer energies for any value of $\langle V_{AB}\rangle$. A general matrix element for the Hamiltonian of equation (13) in the above basis is

$$\langle\psi_i(\pm)|H_A + H_B + V_{AB} + H_s^A + H_s^B|\psi_j(\pm)\rangle =$$
$$\delta_{\substack{+-\\-+}}\left[-\delta_{ij}D_{ij} \pm \langle V_{AB}\rangle\langle T_i^{(A)}|T_j^{(B)}\rangle\right] \tag{19}$$

D_{ij} are the fine-structure tensor elements, e.g. $D_{xx} = -X$, etc. The magnetic quantization in the dimer will therefore be determined by these spin projections, $\langle T_i^{(A)}|T_j^{(B)}\rangle$, which are simply the geometrical factors[62] for the molecules in the unit cell. In addition, this quantity does not necessarily equal the δ_{ij} Dirac function for translationally equivalent pairs,[52] since this will be determined by the local symmetry[53] of the dimer.

The resonance between the two molecules composing the pair will be manifested in the magnetic spectrum of the dimer. This is because the dimer spin Hamiltonian can be generally written as

$$H_s(\text{Dimer}) = \sum_{\alpha} C_\alpha^* C_\alpha H_s(\alpha) \qquad \alpha = A,B \tag{20}$$

where $H_s(\alpha)$ is the spin Hamiltonian for the αth molecule. Thus the degree of resonance between the two molecules, the matrix elements of V_{AB}, and the relative orientation of the molecules

determine the dimer EPR resonance frequencies. In the limit of large $\langle V_{AB} \rangle$ and for resonating molecules, $|C_\alpha|^2 = 1/2$ for both translationally equivalent and translationally inequivalent dimers.

One might think that the ZFS for translationally equivalent dimers will not change from that of the isolated molecule, even if $\beta \gg D_{ii}$ of the molecule. This is only true if the molecules are centrosymmetric.[52] On the other hand, the ZFS for translationally inequivalent dimers[19] is very sensitive to $\langle V_{AB} \rangle \equiv \beta$, even if the molecules have a center of symmetry. This is simply because the molecules in the unit cell have different orientation. For example, if the configuration of the pair magnetic axes is as those given in Figure 1 for the translationally inequivalent pairs of 1,2,4,5-tetrachlorobenzene (approximate representation), the energies of the six spin states of TCB dimer can be easily derived from equation (19). The results, neglecting intermolecular magnetic interactions, are rather simple for this particular configuration of the molecules. Specifically,

$$Y^*, X^* = \frac{X + Y}{2} \pm 1/2[(X - Y)^2 + 4\beta^2]^{1/2} \qquad (21)$$

and

$$Z^* = Z \pm \beta \qquad (22)$$

The above equations show the dependence of dimer spin splittings on β. If β is very small compared to D and E (zero field parameters) of the molecule, then

$$X^*, Y^*, Z^* \simeq X, Y, Z \tag{23}$$

respectively, However, in the limit where $\beta \gg D,E$, only one transition in both the plus and minus components will be located at $Z - \left[\frac{X + Y}{2}\right]$. It should be noted that to have an anisotropy in the Larmor frequencies of the two dimer (or, more generally, the exciton) states, a mixing between the plus and minus states via the magnetic Hamiltonian or spin-orbital interactions between the singlet and triplet (or triplet-triplet, for that matter) states must be considered. The former clearly depends on the symmetry of the plus and minus states. For states which are derived from centrosymmetric sites, these magnetic interactions will shift the spin levels to the same extent. The spin-orbital interaction, however, induces an anisotropy, even in centrosymmetric systems, as will be demonstrated in later sections.

IV. COHERENCE IN THE EXCITED STATES OF MOLECULAR AGGREGATES

(A) The Relationship between the Coherent Properties of Dimers and Those of the Band States.

The unique feature of the dimer is that it preserves many of the excitonic properties of interest, yet the problem is reduced

to a two-level system. For the discussion of excitation transfer in dimers, the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial\psi(t)}{\partial t} = H\psi(t) \tag{24}$$

can be used. The stationary states of the dimer are then given by

$$\psi_t(\pm) = \psi(\pm) \exp[-(i/\hbar)E_{\pm}t] \tag{25}$$

and a general non-stationary state by

$$\phi(t) = a_+\psi(+) \exp[-(i/\hbar)E_+t] + a_-\psi(-) \exp[-(i/\hbar)E_-t] = C_+\psi(+) + C_-\psi(-) \tag{26}$$

If $E_+ \neq E_-$, an oscillation of the excitation is expected in this dynamical picture and the resonance transfer rate, $|\langle\phi(t)|\psi_A^{(i)}\psi_B\rangle|^2$ divided by t, is given by

$$R_{A \leftrightarrow B} = 4|\beta|h^{-1} \tag{27}$$

$\psi_A^{(i)}\psi_B$ is the one-site function for the dimer. <u>This rate of transfer is directly related to that of a one-dimensional triplet exciton</u>, $(8|\beta|/h)$. The comparison between the coherence time with the rate of transfer establishes whether or not the dimer (or exciton) states are coherent.

In order to differentiate between coherent and diffusion limited triplet Frenkel exciton migration in molecular crystals, one must specify both the coherence time associated with the wavevector $\vec{k}$ and the correlation time associated with the particular

experimental approach used. It has been shown[63] that photons in the microwave region give the suitable experimental time scale for which the $\vec{k}$ state of an exciton will not decay completely; hence the coherent properties of such states may be extracted. Triplet states offer such great possiblities since the ZFS energies lie in the microwave region. At very low temperature, the influence of the phonon bath on the excitation dynamics is expected to be small and one might expect the frequency of scattering to be much less than the intermolecular exchange time. If the events of scattering take place on a time scale much longer than the total (radiative and radiationless) lifetime of the emitting state, a Frenkel exciton can be thought of as an excitation propagating[64,65] <u>coherently</u> (wave packet) at a velocity characteristic of both its energy and the linear combination of crystal $\vec{k}$ states which describe the wave packet. This velocity is known as the group velocity and is given by

$$V_g(k) = (2\pi/h)[dE(k)/dk] \tag{28}$$

E(k) is defined in equation (12) for a one-dimensional system. In the absence of scattering the group velocity of the wavevector states at the center of the band in one-dimensional systems is approximately 10^6 times the velocities of those associated with random walk migration.[65] In a <u>stochastic</u> model[46] the distance, $l(k)$, which an exciton propagates in a coherent fashion

without changing either its direction or velocity is

$$l(k) = V_g(k) \cdot \tau(k) \tag{29}$$

where $\tau(k)$ is the lifetime of the coherent state. Thus $l(k)$ is equivalent to a mean-free path and $\tau(k)$ corresponds to a correlation time for the wavevector state k or linear combination of k states and an energy E(k) associated with the zeroth order state.

These coherent properties for excitons are all related, conceptually, to the coherent properties of dimers; $\tau(k)$ is simply $\tau(+)$ and $\tau(-)$ for the two dimer states and $l(k)$ is just the lattice constant which is the distance between the interacting molecules of the pair. However, the physics that describe these scattering times in a dimer are much simpler to understand than those of the exciton. The lifetimes of the plus and minus states of a dimer in a host lattice (characterized by k_h band states) are given by

$$[\tau(\pm)]^{-1} = (\tau_{\substack{+-\\-+}})^{-1} + \sum_{k'_h} (\tau_{\pm k'_h})^{-1} = \Gamma(\pm) \tag{30}$$

In the zeroth order approximation (such as in the case of a dimer gas), the uncertainity width is the same for both the plus and minus states:

$$\Gamma(\pm) \equiv \Gamma = (\tau)^{-1} \tag{31}$$

Figure 2 shows the experimental observables associated with coherence in the plus and minus dimer states. For an exciton the picture is more complicated since a sum over all k states of the band must be carried out, even in the zeroth order approximation:[12]

$$\Gamma(k) \equiv [\tau(k)]^{-1} = \sum_{k'} (\tau_{kk'})^{-1} \tag{32}$$

$\tau_{kk'}$ is the probability of an exciton initially in an energy associated with the kth state scattered to a final energy with the state k'. The relationship between $V_g(k)$ and the band dispersion for excitons is given in Figure 3, which should be compared with the dimer coherent parameters given in Figure 2.

In addition to the above mentioned considerations needed for the description of coherence in dimers and excitons, the statistics[66] of population distribution must be included. This is because the population distribution amongst the plus and the minus states (or the different k states of the band) may determine the appropriate model[10,11,12] for phonon-exciton scattering as well as the resonance interactions between the molecules.

If a Boltzmann distribution of population is attained over all the k states, the number of excitons, N(k), propagating with a velocity, $V_g(k)$, at a given temperature is

$$N(k) = \rho(E) \exp[-E(k)/kT] \cdot z^{-1} \tag{33}$$

where $\rho(E)$ is the density of states and z is the partition function.

Such population distribution may arise at intermediate temperatures, where the inelastic phonon-exciton scattering conditions the magnitude of $\tau(k)$. In such cases, an exciton initially at an energy $E(k)$ scatters to other energies $E(k')$ via phonon interactions in a time short compared to the lifetime, but in a time long compared to $h/8\beta$. As a result the coherence time is shortened, the mean-free path or coherence length is reduced, and the individual k states acquire a width $\Gamma(k)$, given by the equation (32).

In the case of dimers, however, the partition function takes a very simple form:

$$z = 1 + e^{-2\beta/kT} = 1 + \epsilon \tag{34}$$

and therefore a simple temperature dependent experiment give directly β and establishes whether or not Boltzmann statistics determine the routes of excitation transfer in the pair. This will lead into a very important question: Do the radiative and non-radiative channels in the crystal lead to differences in the coherence time of $\psi(+)$ and $\psi(-)$ states?

(B) Detection of Coherence in Dimer States: Magnetic Properties of Dimers in the Rotating Frame

So far, we have given all the recipes for measuring the degree of coherence in excitons and dimers. However, the fundamental question is: What kind of experiment is needed for the extraction of coherent observables? In order to answer this question, let us treat the dynamics of the whole spin ensemble for a strongly coupled dimer using the density matrix formalism.[67,68]

In the presence of a time dependent rf Hamiltonian connecting, for example, the T_{x*} and T_{y*} magnetic sublevels of the dimer, the total spin Hamiltonian is

$$\mathcal{H}_S^{(D)} = \frac{1}{2}(\mathcal{H}_S^A + \mathcal{H}_S^B) - \gamma\mathcal{H}_1 S_{z*} \cos\omega t = \mathcal{H}_S^{(D)}(0) + \mathcal{H}_S^{(D)}(t) \qquad (35)$$

where $\gamma\mathcal{H}_1$ is the magnitude of the rf field, γ is the magnetogyric ratio of the electron, ω is the rf frequency, and S_{z*} is the magnetic dipole transition operator. The proper description of the spin system in the laboratory frame is given by the time-dependent density matrix, ρ, where

$$\dot{\rho} = i/\hbar\,[\rho, \mathcal{H}_S] \qquad (36)$$

In the interaction representation[69] the appropriate description of the spin system is again a time-dependent density matrix, ρ^*, where

$$\rho^* = U^{-1}\rho U, \qquad (37)$$

and the unitary transformation U connecting the laboratory and interaction representation is given by

$$U = \exp(iG(t)/\hbar) \qquad (38)$$

and the Hamiltonian, $\mathcal{H}_S^*$, associated with ρ^* satisfies the following equations:

$$\mathcal{H}_S^* = U^{-1}\mathcal{H}_S^{(D)}(t)U - (dG/dt) \qquad (39)$$

$$\dot{\rho}^* = i/\hbar\,[\rho^*, H_S^*] \tag{40}$$

The interaction representation can be viewed as a unitary transformation of the laboratory frame which effectively removes the zero field Hamiltonian of the dimer provided the transformation matrix U is explicitly defined as:

$$U(\text{Dimer}) = \exp[(i/2)(H_S^A + H_S^B)(t/\hbar)] \tag{41}$$

Therefore, the Hamiltonian matrix in the $x^* y^*$ basis is

$$\langle H_S^* \rangle = -(\gamma H_1 \hbar/2) i \exp[-i(X^* - Y^*)t/\hbar + i\omega t] \tag{42}$$

and is nonsecular unless $\omega = (E_{x*} - E_{y*})/\hbar$ where E_{x*} and E_{y*} are the eigenvalues of the zerofield dimer Hamiltonian, $1/2(H_S^A + H_S^B)$. At resonance the interaction Hamiltonian becomes secular in first order, and has the form of a "Zeeman Hamiltonian" in a rotating frame [70,71] at the resonance frequency. Thus

$$H_S^* = -(\gamma H_1 \hbar/2)\ S_{z*} \tag{43}$$

where the effective field γH_1 causes a "pseudo" magnetization to precess around z*. Stated in simplest terms, the motion of the pseudomagnetization in the rotating frame is equivalent to the dynamics of the zero field alignment of the populations associated with the dimer spin sublevels in the laboratory frame.

The detection of coherence in dimers will depend on the rate at which the well-defined phases in the wavefunction of equation (26) become random due to ensemble fluctuations. If we define σ as

the density matrix in the basis $\psi(+)$ and $\psi(-)$, the probability matrix which describes the time-evolution of dimer states is

$$\sigma(t) = \begin{bmatrix} \overline{C_+C_+^*} & \overline{C_+C_-^*} \\ \overline{C_-C_+^*} & \overline{C_-C_-^*} \end{bmatrix} \tag{44}$$

where

$$C_+C_-^* = a_+a_- \exp[-i(E_+ - E_-)t/\hbar] \tag{45}$$

The star on the matrix elements denoting the complex conjugate character should not be confused with the star on ρ which was used to characterize another representation of the density matrix. The bar on the products of the coefficients in the above matrix represents the ensemble average. Another form for the above matrix can be deduced from Feynman, Vernon and Hellwarth (FVH)[72] geometrical representation of the Schrödinger

equation:

$$\sigma(t) = \frac{1}{2}\begin{bmatrix} 1 + r_3 & (r_1 - ir_2) \\ (r_1 + ir_2) & 1 - r_3 \end{bmatrix} \tag{46}$$

where $r_1 \equiv (\sigma_{12} + \sigma_{21})$ and $r_2 \equiv (\sigma_{21} - \sigma_{12})(-i)$ give the coherence information of the ensemble. It is now clear that the coherence information in the dimer is contained in the off-diagonal elements of the density matrix, and that the polarization of the spin is manifested in the pseudomagnetization vector, r_3, which in turn depends on β and on the relative geometrical orientation of the molecules in the pair.

Measurements of the EPR resonance frequencies in the pair are therefore not expected to give information about the off-diagonal elements of the density matrix and only can be expressed in terms of r_3 which is given by

$$r_3 = |\sigma_{11}|^2 - |\sigma_{22}|^2 = \overline{|C_+|^2} - \overline{|C_-|^2} \tag{47}$$

For a dimer in a monoclinic lattice, e.g. naphthalene-like crystals, (C_{2h}^5 point group symmetry)[73] the spin Hamiltonian of the pair, $\mathcal{H}_S(D)$, can be written in terms of $\mathcal{H}_S(M)$ in the following form:

$$\mathcal{H}_S(D) = X^* S_{x^*}^2 + Y^* S_{y^*}^2 + Z^* S_{z^*}^2 + A_1(S_{x^*}S_{y^*} + S_{y^*}S_{x^*}) + A_2 r_3'(S_{x^*}S_{z^*} + S_{z^*}S_{x^*}) + A_3 r_3'(S_{y^*}S_{z^*} + S_{z^*}S_{y^*}) \qquad (48)$$

where X^*, Y^* and Z^* are the fine structure constants of the pair, and A_1, A_2 and A_3 are given by D and E of the monomer and the geometrical factors for the molecule in the lattice (direction cosines). r_3' now defines the difference in probabilities of finding the excitation on the molecules of the dimer. Of course, the above Hamiltonian can be transformed into a new set of principal axes which remove the off-diagonal terms and redefine the fine structure constants.

V. OPTICAL DETECTION OF MAGNETIC RESONANCE IN COHERENT STATES

In this section we shall treat the relationship between the dispersion in Larmor frequencies for dimers and excitons and the resonance interactions between molecules, using the properly antisymmetrized eigenfunctions. It will be shown that there is a direct correspondence between both dispersions. Although the solution to the dimer problem is simpler than that of the exciton, we shall treat the latter first since the solution to the former problem will emerge from the general case, exciton, if the number of k states is just two.

(A) Microwave Band-to-Band Transitions in Coherent Exciton States: Manifestations of k-dependent Interactions

The stationary properties of electronic triplet bands can be understood by the simple dispersion relationship of equation (12) if the coupling between the linear chains is neglected. Thus the one-site exciton functions can be explicitly written as

$$\psi^{\circ} = A \prod_{u\alpha} (\psi^{\circ}_{u\alpha} S^{\circ}) \tag{49}$$

for the ground singlet state, and as

$$\psi^{f_i}_{m\beta} = A(\psi^{f}_{m\beta} T_i) \prod_{u\alpha \neq m\beta} (\psi^{\circ}_{u\alpha} S^{\circ}) \tag{50}$$

for the ith spin state of the fth excited state. $\psi^{f}_{m\beta}$ and $\psi^{\circ}_{u\alpha}$ are the antisymmetrized molecular wavefunction and A is the permutation operator[74] effecting an interchange of electrons between molecules. The crystal eigenfunction is

$$\phi^{f_i}(k) = \frac{1}{\sqrt{N}} \sum_{m\beta}^{N} \exp[k \cdot r_{m\beta}] \, \psi^{f_i}_{m\beta} \tag{51}$$

where k (one-dimensional wavevectors) classifies both the symmetry and the energy of band states. In the zeroth order approximation, $\psi^{f} T_i$ has no electric dipole strength to the ground state simply because of the spin orthogonality between S and T_i. The orbital part of the wavefunction, ψ^{f}, transforms like the polar vectors of the molecular point group while the spin part transforms like the axial vectors. However, the molecules do not enjoy the full

molecular symmetry because of the crystal field, and thus the effective molecular symmetry, site symmetry, must be used to classify the different spin-orbit states. Since $|\langle H_{SO}\rangle|$ is much less than singlet-triplet splittings,[75] the molecular function (to a first order) is given by

$$|\psi^{f}T_{i}\rangle^{(1)} = a|\psi^{f}T_{i}\rangle^{(0)} + \sum_{r} \frac{\langle\psi^{f}T_{i}|H_{SO}|\psi^{r}\sigma\rangle}{(E_{f}^{0} - E_{r}^{0})} |\psi^{r}\sigma\rangle \qquad (52)$$

where $|\psi^{r}\sigma\rangle$ (space $\otimes$ spin) is either a singlet or a triplet state, and a is a normalization constant.

The magnetic anisotropy introduced to the three spin bands by the molecular spin-orbital coupling will certainly depend on the nature of the interaction between molecules in the lattice which could lead into different splittings in the different electronic states. Two cases would arise.

(i) <u>β is relatively large and no spin-orbit anisotropy: k-independent microwave dispersion.</u>

Because of the nature of the exchange Hamiltonian the triplet exciton bands are formed from each of the individual sublevels separately, in the absence of spin-orbital coupling. Thus in the absence of spin-orbital anisotropy a one-dimensional band is composed of three parallel spin bands with separations equal to the molecular ZFS. Hence, the microwave band-to-band transition is a single homogeneous line whose frequency is independent of the energy of the k state in the band,

even if the band width is very large. This is shown in Figure 4.

(ii) <u>β is relatively large and there is a finite spin-orbital anisotropy: k-dependent microwave dispersion</u>.

Combining equations (50) and (52), we get

$$\psi_{m\beta}^{f_i(1)} = A\prod_{u\alpha\neq m\beta} \psi_{u\alpha}^{0} S^{0} [a\psi_{m\beta}^{f} T_i + \sum_{r} \langle H_{S0}\rangle_{fr} \Delta E_{fr}^{-1} |\psi^{r}\sigma\rangle] \tag{53a}$$

$$= a\psi_{m\beta}^{f_i(0)} + \sum_{r} \langle H_{S0}\rangle_{fr} \Delta E_{fr}^{-1} |\psi^{r}\sigma\rangle (A\prod_{u\alpha\neq m\beta} \psi_{u\alpha}^{0} S^{0}) \tag{53b}$$

The corresponding Bloch functions are thus given by

$$\phi^{f_i(1)}(k) = a\phi^{f_i(0)}(k) + \sum_{r} \langle H_{S0}\rangle_{fr} \Delta E_{fr}^{-1} \phi^{f_{r\sigma}}(k) \tag{54}$$

a is now given by

$$(1 - \sum_{r} |\langle H_{S0}\rangle_{fr}|^{2} \Delta E_{fr}^{-2})^{1/2} \tag{55}$$

The energy spectrum of the crystal can be determined from the above equations by using the crystal Hamiltonian. Thus for singlet-triplet mixing, i.e. f = triplet (t), and r = singlet (s), we have

$$E^{t}(k) = a^{*}a[E_{g}^{t} + D^{t} + 2\beta_{t} \cos k\cdot a] + \sum_{s} |\langle H_{S0}\rangle_{ts}|^{2} \Delta E_{ts}^{-2} [E_{g}^{s} + D^{s} + L^{s}(k)] \tag{56}$$

For a one-dimensional singlet dispersion, the total energy of the ith spin state is thus given by

$$E_i^t(k) = (E_g^t + D^t) + 2\beta_t \cos k\cdot a - |\langle H_{SO}\rangle_{ts}|^2 \Delta E_{ts}^{-1} - |\langle H_{SO}\rangle_{ts}|^2 (D^t - D^s)\Delta E_{ts}^{-2} - |\langle H_{SO}\rangle_{st}|^2 \Delta E_{ts}^{-2}(2\beta_t - 2\beta_s) \cos k\cdot a + D_{ii} \quad (57)$$

$(E_g^t + D^t)$ is the crystal molecular energy in the triplet state; E_g^t is the gaseous excitation energy and D^t is the crystal shift. D_{ii} is the molecular fine structure constant in the absence of H_{SO}.

Equation (57) states that the spin-orbital interaction modulates the band energy and leads into a k-dependent anisotropy in the three spin bands, across the Brillouin zone. Of course the selectivity of H_{SO} in coupling singlet (or triplet) molecular states with the lowest triplet will ensure such anisotropy in the band-to-band energy dispersion. To calculate the microwave frequencies for all values of k, the energies in equation (57) must be corrected for the energy of the molecule in the crystal lattice. For two magnetic sublevels, $E_z(k)$ and $E_x(k)$, the transition energy is given by

$$\Delta E_{xz}(k) = |E_x(k) - E_z(k)|$$
$$= [x - z] - |\langle H_{SO}^{(z)}\rangle|^2 \Delta E^{-1}\left(1 + \frac{\Delta D}{\Delta E} + \frac{(2\beta_t - 2\beta_s)}{\Delta E} \cos ka\right) \quad (58)$$

Some of the subscripts were omitted for the purpose of simplification, and the z-component of the spin-orbit interaction was selected to give a simple solution. However, the extension to more than one level coupling is straightforward. A molecule at the crystal site has the following zero field transition energy:

$$\Delta E_{xz} = (x - z) - |\langle H_{SO}^{(z)}\rangle|^2 \Delta E^{-1} [1 + (\Delta D/\Delta E)] \tag{59}$$

Thus the microwave transition frequency <u>in the k-domain</u> is given by

$$(\Delta E_{xz}(k) - \Delta E_{xz})/h = |\langle H_{SO}^{(z)}\rangle|^2 \Delta E^{-2} h^{-1} (2\beta_s - 2\beta_t) \cos ka \tag{60}$$

Letting

$$f = \frac{\Delta_{st}}{2\beta_t} = \frac{|\langle H_{SO}^{(z)}\rangle|^2 (2\beta_s - 2\beta_t)\Delta E^{-2}}{2\beta_t} \tag{61}$$

the band dispersion, $2\beta_t \cos ka$, of the lowest triplet state can be directly related to the microwave frequencey spectrum of the band:

$$(\Delta E_{xz}(k) - \Delta E_{xz}) f^{-1} = 2\beta_t \cos ka \tag{62}$$

Equation (62) indicates that the microwave frequency dispersion in the first Brilloun zone is linear in coska, a relation which is very important in discussing the magnetic anisotropy in dimers. This equation is identical to the one derived by Francis and Harris[15] for one-dimensional excitons. Moreover, the microwave band-to-band transition, derived from the above equations, will take a shape which is related to the density of states function (cf. Figure 4).

One should notice that although the anisotropy in the microwave band-to-band transitions is explained by incorporating H_{SO} in the total Hamiltonian, there is a very simple fact behind this idea; namely that the matrix elements between the k band states of the upper excited level and the k states of the lowest energy band are very selective. Thus if the two bands have different bandwidths (as is usually the case), the anisotropy is transmitted to the lowest sublevels of the band. We feel that these observations could be quite general, even in molecular crystals where the molecular spin-orbit routes are not highly selective.

To prove the band-to-band spin-orbit selectivity, one can write the Bloch functions for both the singlet and triplet bands, and take the matrix elements of H_{SO}. It follows that

$$\langle\phi^t(k)|H_{SO}|\phi^s(k')\rangle = \langle H_{SO}\rangle_{st}\,\delta(k - k') \qquad (63)$$

if the exciting photon length is much larger than molecular spacing. Intermolecular spin-orbital coupling is not included in these computations, and $\langle H_{SO}\rangle_{st}$ is again the molecular spin-orbital coupling matrix element. Extension of the above theory to any band dispersion is straightforward.

(B) Microwave Absorption in Coherent Dimer States

The treatment of the dimer case will be essentially like that developed for excitons, except the complication induced by the many k states of the band is now resolved since there are only two states in the dimer. Moreover, the anisotropy induced in the dimer

by H_{SO} should be related to the full band anisotropy (by extrapolation). The relationship is simple if the band dispersion is one-dimensional, and thus the observation of dimer microwave absorption could be very important in determining the band dimensionality.

To form such dimers, we need to shorten the chains somehow, e.g. by introducing barriers[76,50] at certain sites in the crystal However in most experiments performed one does not have a control over the randomization[77] in these chains. Thus the treatment of N-mers is necessary. The energies of an N-mer in a given chain is given by

$$\epsilon_K = \epsilon_0 + 2\beta \cos[K\pi/(N + 1)] \tag{64}$$

where $K = 1,\ldots.N$ and should not be confused with k since the translational symmetry is removed.

The energies of these N-mers in the band are given in Figure 5. Ideally the monomer, $K = 1$, is at the center of the band ($k = \pm\pi/2a$) and the infinite chain is at the band edge. It follows from equation (62) that the two dimer states, which are located at $\pm\beta$ relative to the monomer energy, should have a microwave transition frequency at

$$(\omega_{xz}(\pm) - \omega_{xz}) = \pm\beta_t f/\hbar \tag{65}$$

Therefore the frequency spread across the band (frequency difference of the transition at $k = 0$ and $k = \pi/a$; Δ_k) is related to the dimer spread (frequency difference of the transition at $K = 1$ and $K = 2$;

Δ_K) by

$$\Delta_k = 2\Delta_K \tag{66}$$

This relationship is demonstrated in Figure 5 for a one-dimensional system. Similar equations can be derived for higher members of the chain (trimer, tetramer,...etc.). Figure 6 shows the microwave frequencies calculated for the N-mers of translationally equivalent molecules and compared with the calculated exciton resonances.

It is clear from equation (65) that the Larmor frequency will be different for the two different states of the dimer. Such differences can be explicitly incorporated in the magnetic Bloch[78] equations, allowing for different states of the dimer to be probed by either conventional EPR spectroscopy or by optical detection of magnetic resonance as we shall demonstrate in the following section.

VI. THE INFLUENCE OF EXCITON-PHONON SCATTERING ON THE ZERO FIELD EPR TRANSITION PROBABILITIES IN THE TWO DIMER STATES

It is well-known that the shape and the cross section for the absorption of magnetic oscillators by a two spin level system can be deduced from the phenomenological Bloch equations.[78] In the dimer case, where each state has its own Larmor frequency, one additional parameter, namely the transfer probabilities

between the two subsystems, must be invoked in order to fully understand the relationship between the absorption of microwaves or radiofrequency (rf) fields and the scattering probabilities. The studies of these scattering rates by zero field EPR spectroscopy is particularly suitable since the coherence time is expected to be on the time scale of the correlation time associated with the oscillating magnetic field. Naturally, if the coherence time is much shorter than the experimental correlation time, the coherence information cannot be extracted. On the other hand, the rate of scattering between the two states and the difference in their Larmor frequencies determines the limit of exchange for the spin. Hence, three cases are known: fast, intermediate and slow exchange.

Mathematically, the three limits for the dimer can be obtained by using the Bloch equations in the rotating frame with the inclusion of scattering time constants, τ_{+-} and τ_{-+}. In the presence of a weak oscillating rf field of the form

$$H(t) = -\gamma H_1 \cos\omega t \tag{67}$$

The Bloch equations without the exchange part take the form,[78]

$$(du/dt) + (u/T_2) - \Delta\omega v = 0 \tag{68a}$$

$$(dv/dt) + (v/T_2) + \Delta\omega u - \gamma H_1 M_z = 0 \tag{68b}$$

$$(dM_z/dt) + (M_z - M_0)\, T_1^{-1} + \gamma H_1 v = 0 \tag{68c}$$

where $\Delta\omega = \omega_0 - \omega$; ω_0 is the resonance frequency, and u and v are the inphase and out-of-phase components of a complex moment defined by

$$G = u + iv \tag{69}$$

Since the macroscopic pseudomagnetization of the triplet state spin ensemble is not strongly disturbed, the equilibrium magnetization is approximately equal to $M_z(\overset{0}{r}_3)$; therefore equation (68) can be written as

$$(dG/dt) + i(\Delta\hat{\omega})G - i\gamma H_1 M_0 = 0 \tag{70}$$

where $\Delta\hat{\omega} = (\hat{\omega}_0 - \omega)$. The complex frequency $\hat{\omega}_0$ includes the spin-spin relaxation time: $\hat{\omega}_0 = \omega_0 - iT_2^{-1}$. The Bloch equations in the rotating frame, for both $\psi(+)$ and $\psi(-)$ states of the dimer can readily be written in the following form in the absence of scattering:

$$(dG_+/dt) + i(\Delta\hat{\omega}_+)G_+ - i\gamma H_1 M_0 = 0 \tag{71a}$$

$$(dG_-/dt) + i(\Delta\hat{\omega}_-)G_- - i\gamma H_1 M_0 = 0 \tag{71b}$$

For dimers isolated in molecular crystals, the resonance frequencies, ω_0^+ and ω_0^-, in the two stationary states, $\psi(+)$ and $\psi(-)$, could be different and at low temperatures (≤ 1.5K) the spin-lattice relaxation time [60] is expected to be longer than, say, the lifetime

of the excited state. However, exciton-phonon† coupling may connect the two states (T_1 process). Moreover, it may also contribute to the linewidth of the EPR resonances in the plus and minus states (T_2 process). Thus the magnitude of the scattering time can be obtained from the EPR spectra of dimers by two means; linewidth measurements and the difference in Larmor frequencies, as we shall demonstrate later. Following the formalism of Kubo,[23] Anderson,[24] and McConnell[79] for chemical exchange, and defining τ_{+-} and τ_{-+} as the scatteirng times between the two states, the modified Bloch equations are given by

$$(dG_+/dt) = i[N_+\omega_1 M_0 - \Delta\hat{\omega}_+ G_+] + (G_-/\tau_{-+}) - (G_+/\tau_{+-}) \tag{72a}$$

and

$$(dG_-/dt) = i[N_-\omega_1 M_0 - \Delta\hat{\omega}_- G_-] + (G_+/\tau_{+-}) - (G_-/\tau_{-+}) \tag{72b}$$

The power factor, γH_1, is abbreviated by ω_1, and $N_\pm$ is the fraction of spin in the plus and minus states.

In the steady state, where $dG_\pm/dt = 0$, the solution is simple since we are only dealing with two exciton states (plus and minus). The lineshape function $g(\omega)$ of the microwave transition in the dimer is simply given by

$$g_D(\omega) = \mathrm{Im}G_D = \mathrm{Im}(G_+ + G_-) \tag{73}$$

whereas in the case of one-dimensional excitons[12]

$$g_E(\omega) = \mathrm{Im}G_E = \mathrm{Im}\sum_k G_k \tag{74}$$

†By exciton-phonon coupling in the dimer case we mean to imply a two-molecule exciton chain coupled to the lattice.

Moreover, the solution of Bloch magnetic equations for the dimer is straightforward whereas in the case of exciton states, where the scattering probabilities between any two k states, k and k', are finite, the equations become more difficult to solve since a sum of all k' states must be included:

$$(dG_k/dt) + i\Delta\hat{\omega}_k G_k + i\omega_1 M_0^k - \sum_{k'} [(G_{k'}/\tau_{k'k}) - (G_k/\tau_{kk'})] = 0 \tag{75}$$

Recently the (2k + 1) equations, obtained from equation (75) under the steady state approximation, were discussed[12] for the slow, intermediate and fast exchange limits using the experimentally[63] determined values for ω_0^k and the population distribution among the k states of the one-dimensional exciton band of tetrachlorobenzene crystal. It is clear that both the energy dispersion of the band and the population distribution between the different k-states determine the magnitude of M_0^k. Thus, the analysis of the lineshape of the exciton resonance must give the band dispersion, density of states and the coherence time. However, the physics[63] of scattering must be assumed since the lineshape is a manifestation of many (number of molecules in the chain) states, each with a characteristic Lorentzian lineshape. For example, one has to assume that the actual scattering time from k to k' is much shorter than the time in a particular k state, and that there is no spin memory between the different k states.

In the case of dimers, the above assumptions can be verified if the resonances of the two states can be observed. The relative

absorption intensities and energies in the plus and minus states, can directly give the physics of scattering and the influence of the scattering amplitudes on the population of the two states. If there are no large host influences on the dimer states, the scattering probabilities, $1/\tau_{+-}$ and $1/\tau_{-+}$, should determine the explicit form of the exciton-phonon interaction.

On the other hand, if the two states of the dimer scatter utilizing different channels of the host, the resonance lineshape will depend on $1/\tau'_{\substack{+-\\-+}}$:

$$1/\tau'_{\substack{+-\\-+}} = 1/\tau_{\substack{+-\\-+}} + \sum_{k_h} 1/\tau_{k_h} \tag{76}$$

and the sum over k_h could be different for the plus and minus states. Therefore the absorption intensities and the transition lineshape are crucial in determining the nature of scattering in the pair.

Two cases are considered here: a Boltzmann distribution between the + and - states and a non-Boltzmann distribution with $N_+ = N_- = 1/2$, although the solution for any other limit is straightforward. The contribution to the linewidth due to processes other than exchange will be neglected in this calculation for the sake of simplicity.

(A) Non-Boltzmann Distribution; $N_+ = N_- = 1/2$ and $\tau_{+-} = \tau_{-+} = \tau$

$$\mathrm{Im}G_D = (\omega_1/2)M_0 \frac{R(\omega_+ - \omega_-)^3}{(\omega - \omega_+)^2(\omega - \omega_-)^2 + 4R^2(\omega_+ - \omega_-)^2(\omega - \bar{\omega})^2} \tag{77}$$

where $\bar{\omega}$ is the average frequency and R is the ratio of the scattering rate to the difference in Larmor frequencies of the plus and minus states, i.e.

$$(\omega_+ - \omega_-) = 1/\tau \times 1/R \tag{78}$$

It is evident from equation (78) that if R is small, both transitions of the dimer will be sharp and well separated. This means that if the exciton-phonon scattering rate is much slower than the rate corresponding to the difference in Larmor frequencies, the spin in each state can absorb the microwaves as if the two states are not connected. On the other hand, if the two dimer states are strongly coupled via the relaxation Hamiltonian, the spin can no longer distinguish between the two subsystems and averaging will take place. Increasing the value of R will result in overlap between the two transitions since the spin is no longer effectively quantized in one state. Figure 7 shows the dimer resonance spectra for different values of R, which cover the fast, intermediate and slow exchange limits. We notice also that for small R and when $\omega \to \omega_+$, a single Lorentz line will be obtained with a width given by

$$1/T_{2e} = 1/\tau \tag{79}$$

This exchange time, T_{2e}, gives the time the spin spends in the plus state during the exchange. This, of course, means that the linewidth of the plus and minus state is zero in the absence of exchange. If there is a residual linewidth (T_{2+}^{-1} and T_{2-}^{-1}) due to *e.g.* crystal and/or hyperfine fields, the total width will be given by

$$1/T_2 = 1/T_{2e} + 1/T_{2\pm} \tag{80}$$

(B) Boltzmann Distribution

In this case the exchange is between states of unequal population and the whole thermalization mechanism depends on the magnitude of the resonance interaction, β, and the temperature of the bath. Utilizing the partition function, z, of the system, the imaginary part of the magnetization is given by

$$\mathrm{Im}G_D = \omega_1 M_0(\epsilon/z)\frac{R(\omega_+ - \omega_-)^3}{(\omega - \omega_+)^2(\omega - \omega_-)^2 + R^2(\omega_+ - \omega_-)^2[\epsilon(\omega - \omega_-) + (\omega - \omega_+)]^2} \tag{81}$$

Again if R is small the characteristic resonances in the plus and minus states will be resolved. However the relative intensities will be different. Figure 8 shows the dependence of resonance spectra on the magnitude of R for a fixed temperature and constant value of β, while Figure 9 gives the spectra as a function of β for a fixed value of R. The sensitivity of the intensity ratio to both the temperature and β makes zero field EPR techniques very versatile in extracting

β and hence the bandwidth for Frenkel excitons. Within this thermalization mechanism, the relative ratios of the resonance transition intensities as a function of β are given in Figure 10. The knowledge of such ratios from experiments will directly provide β and establish the band dimensionality as well.

In addition, for both the Boltzmann and non-Boltzmann regimes, τ can be determined. The above considerations bear a direct relationship to the exciton case. Both the band dimensionality and the bandwidth were obtained from the exciton band-to-band transitions, observed by Francis and Harris.[63] Based on these experimental results and on their theoretical development, a detailed investigation of the effect of exciton-phonon scattering on the coherent properties of exciton states was recently given by Harris and Fayer.[12] It was also shown that in the fast exchange limit the coherent properties of individual k states average out resulting in a single homogeneous line centered around $k = \pm\pi/2a$, in agreement with the above findings for the dimer case.

Finally, we should mention here that the intensity of the microwave resonances is given by the imaginary part of G as in the case of conventional EPR spectroscopy.[80] However, in the case of optical detection of magnetic resonance from triplet states, the intensity is proportional to r_3.[81] It was shown[81] recently that the frequency spectrum is almost the same and therefore no attempt was made in this paper to express the resonance intensities in terms of r_3.

VII. SUMMARY

(1) The magnetic properties of translationally equivalent and translationally inequivalent pairs of molecules in crystals were explained and related to the magnitude of the resonance interaction between the two molecules. The effect of local symmetry of the excited dimer on the induced anisotropy in the Larmor frequencies of $\psi(+)$ and $\psi(-)$ states was discussed in detail.

(2) The dispersion of microwave absorption in chains of N-mer molecules was directly related to the microwave band-to-band dispersions of the infinite chain (exciton). This offers a new method for studying exciton dimensionality.

(3) Factors which determine coherence in excited states were explained and related to the magnitude of both intermolecular interactions between molecules and the exciton-phonon coupling matrix elements. The influence of the latter on the resonance absorption in the dimer states was shown in three limits of spin exchange; slow, intermediate and fast. In the limit where the scattering probabilities are small, the spin can absorb the rf fields in each state of the dimer and hence the two Larmor frequencies can be measured. On the other hand, fast scattering was shown to lead into a collapse of the resonance absorptions of

$\psi(+)$ and $\psi(-)$ into one line centered around $[\omega(+) + \omega(-)]/2$. Moreover, the linewidth of these transitions in the slow exchange limit can give a lower limit for the coherence time associated with the excited state.

(4) Finally, we have related the coherent properties of dimers to those of the exciton, hoping that the details of the physics behind scattering and their influence on energy migration in solids can be elucidated by studying the simplest member, the dimer. The different models of excitation scattering were discussed in terms of the population distribution in the pair. Both Boltzmann and non-Boltzmann thermalization regimes were considered and used as a tool in extracting both the magnitude and the sign of the resonance transfer matrix elements.

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FIGURE CAPTIONS

Figure 1: The magnetic axes of 1,2,4,5-tetrachlorobenzene monomer (D_{2h}) and dimer (translationally inequivalent). x_A, y_A, z_A and x_B, y_B, z_B are the molecular axes of molecules A and B respectively, while X, Y, Z are the crystal principal axes. The figure demonstrates that in the large limit of intermolecular interaction, the in-plane spin energies will average while the out-of-plane is approximately unchanged for this particular geometry.

Figure 2: Coherent properties of electronically excited dimers. (a) represents the two dimer (decoupled) functions while (b) represents the stationary (coupled) states, $\psi(+)$ and $\psi(-)$, of the dimer that are separated by 2β. (c) Coherence times associated with the plus and minus states of the dimer. (d) The effect of population distribution, N_+, N_-, on the expected intensities of $\psi(+)$ and $\psi(-)$ resonance transitions. β generates a rate of energy transfer between molecules and the coherence lifetimes, $\tau(+)$ and $\tau(-)$, generate a width to the state and are a measure of the coupling of the dimer to its environment (see text).

Figure 3: Coherent properties of one-dimensional excitons.

(a) The isolated molecule functions (one-site) and energy, E_0.

(b) The stationary states of one-dimensional band dispersion.

(c) Coherence time, $\tau(k)$, associated with the different k-states of the band.

Figure Captions continued

Figure 3 (continued):

(d) Energy dispersion, $E(k)$, for a one-dimensional exciton with a band width, 4β.

(e) Group velocity distribution, $V_g(k)$, in the band, which is maximum at $k = \pi/2a$.

(f) Theoretically calculated density of state function, $\rho(E)$, for a one-dimensional exciton.

(g) Population distribution function, $N(k)$, for the band states. β generates a rate of energy transfer, $V_g(k)$, between molecules and $\tau(k)$ generates a width to the state k and a mean-free path, $l(k)$, for coherent energy migration. $N(k)$ determines the partition of energy between states of different velocities.

Figure 4: Expected Larmor frequencies for one-dimensional systems. $\omega(M)$ is the Larmor frequencey of two spin sublevels, T_x, T_y, of the excited triplet state. $\omega(+)$ and $\omega(-)$ are the two different frequencies in $\psi(+)$ and $\psi(-)$ dimer states. $\omega(k=0)$, $\omega(k=\pi/a)$ and $\omega(k=\pi/2a)$ are the Larmor frequencies of $k = 0$, $k = \pi/a$ (band edges) and $k = \pi/2a$ (band center) states respectively. Extraction of the Larmor frequency for any other k-state from the schematic is straightforward. The right hand side of the figure demonstrates the effect of exchange on the microwave absorption in dimer and exciton states.

Figure Captions continued

Figure 4 (continued):

(a) The isolated molecule transition.

(b) Microwave absorption in dimers for a slow exchange limit; Δ_K is the difference in Larmor frequencies of $\psi(+)$ and $\psi(-)$ states.

(c) Microwave absorption in dimers for a fast exchange limit. Both $\omega(+)$ and $\omega(-)$ are centered around $\omega(M)$.

(d) Exciton band-to-band transition extrapolated from the dimer case "b" in the slow exchange limit. Δ_k is directly related to Δ_K (see text).

(e) Exciton resonance in the fast exchange limit. $\omega(k)$ is centered around $\omega(M)$.

Figure 5: The relationship between exciton and N-mer dispersions for one-dimensional systems. The figure on the left gives the k dispersion (cosine curve) for the exciton while the vertical lines give the energy position of the N-mers. The rest of the K states are not shown for the sake of clarity. The position of the monomer at the center of the band is only true if there is no host polarization or hyperfine effects. The schematic on the right-hand side of the figure gives both the energy and microwave dispersions for the different states of the different clusters. The position of the $k = 0$ level is arbitarily chosen. The figure clearly shows that there is

Figure Captions continued

Figure 5 (continued): a one-to-one correspondence between the optical and microwave dispersions.

Figure 6: Calculated Larmor frequencies for aggregates of one-dimensional systems. The continuous double-humped curve is the exciton band-to-band transition, calculated[15] for a Boltzmann distribution amongst the k states and $\omega(k = \pi/2a) = 5539$ MHz. The vertical lines represent the relative positions of the N-mer resonance transitions. The intensity distribution among the N-mer states is not calculated and only drawn this way to follow the exciton line shape.

Figure 7: Fast, intermediate and slow exchange of spin between the dimer states. The two states are equally populated and the transfer times for the two channels are equal.

(a) R = 0.1 (c) R = 0.5

(b) R = 0.2 (d) R = 1.0

Higher values of R will lead into a much sharper line which ultimately will have a width of zero (see text).

Figure 8: Fast, intermediate and slow exchange of spin between the dimer states. The two states are in thermal equilibrium with $|\beta| = 0.25\ cm^{-1}$.

Figure Captions continued

Figure 8 (continued):

(a) R = 0.2 (c) R = 1.0

(b) R = 0.5 (d) R = 2.0

R is defined for one-way transfer since the system is in Boltzmannian distribution. Notice the shift of the peak, in the fast exchange limit, from the $[\omega(+) + \omega(-)]/2$ value.

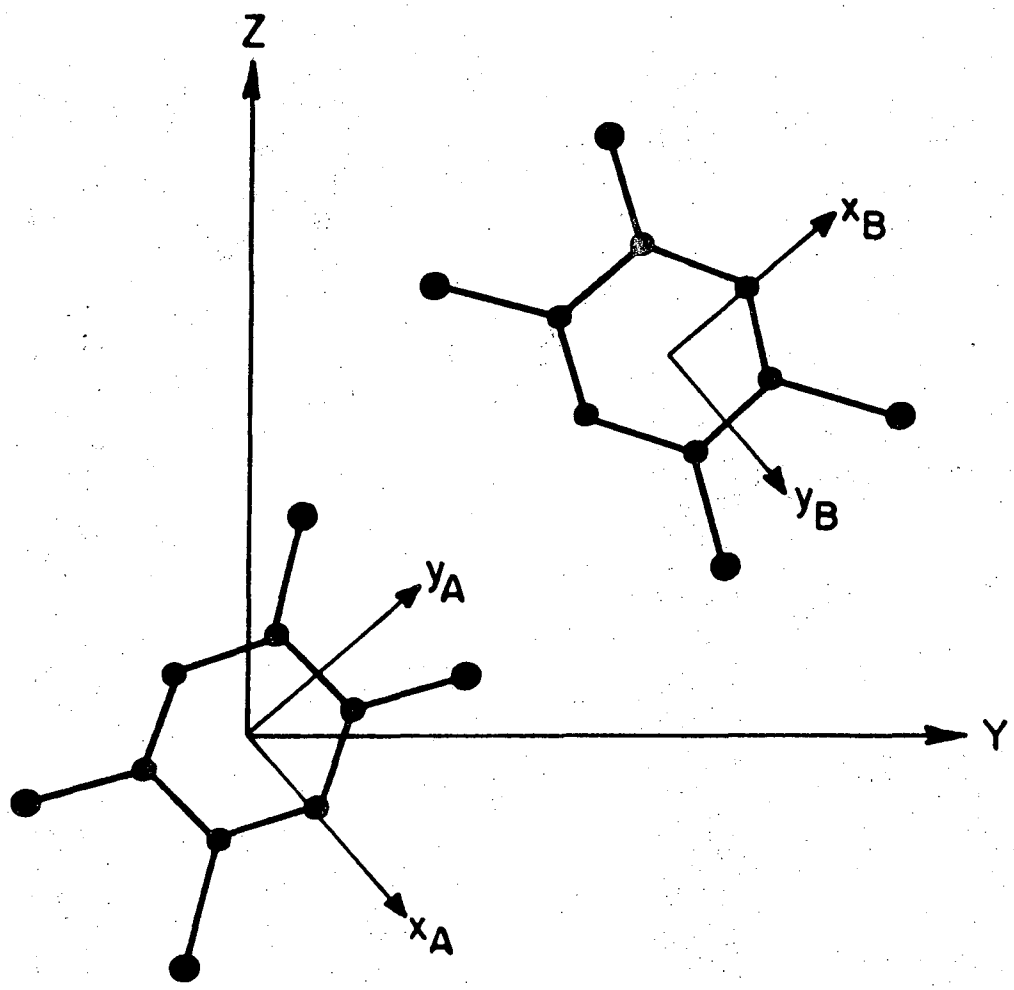
Figure 9: Effect of the resonance interaction, β, on the EPR line shape of a dimer. The calculated spectra is for the slow exchange limit; R = 0.1. The temperature is 1.75 K.

(a) $\beta = 0.5\ cm^{-1}$ (b) $\beta = 0.25\ cm^{-1}$ (c) $\beta = 0.05\ cm^{-1}$

Increasing the magnitude of β results in the disappearance of the line with low intensity (frequency units = 7).

Figure 10: Effect of resonance interaction, β, on the relative intensities of the EPR transitions in $\psi(+)$ and $\psi(-)$ states of the dimer. The temperature is 1.75 K. At this temperature it is clear from the figure that in order to see both transitions of the dimer, β must be small; for an intensity ratio of ≈ 5, β must be less than $0.5\ cm^{-1}$.

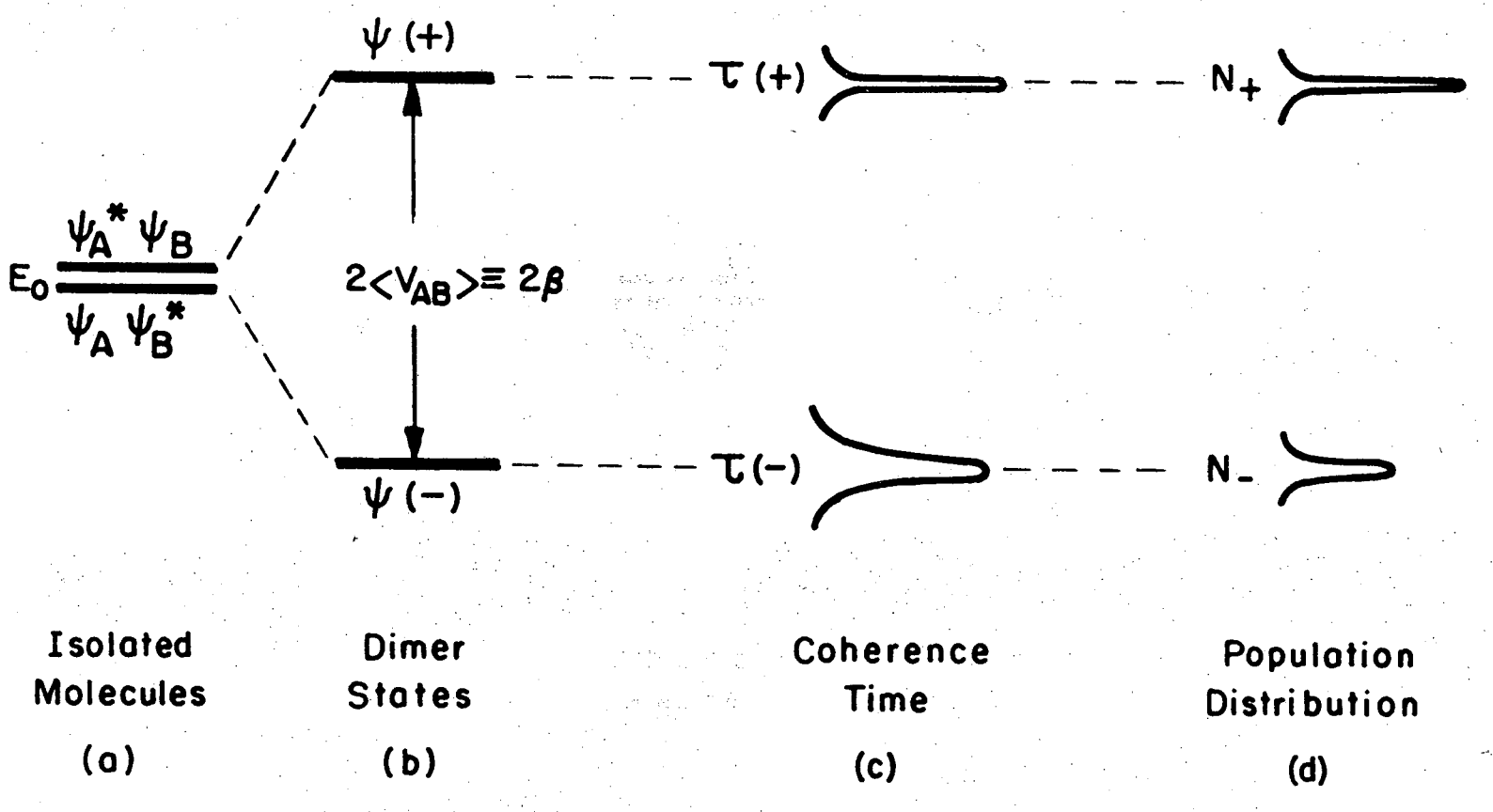
MAGNETIC AXES OF TETRACHLOROBENZENE MONOMER AND DIMER



XBL747-6800

Fig. 1

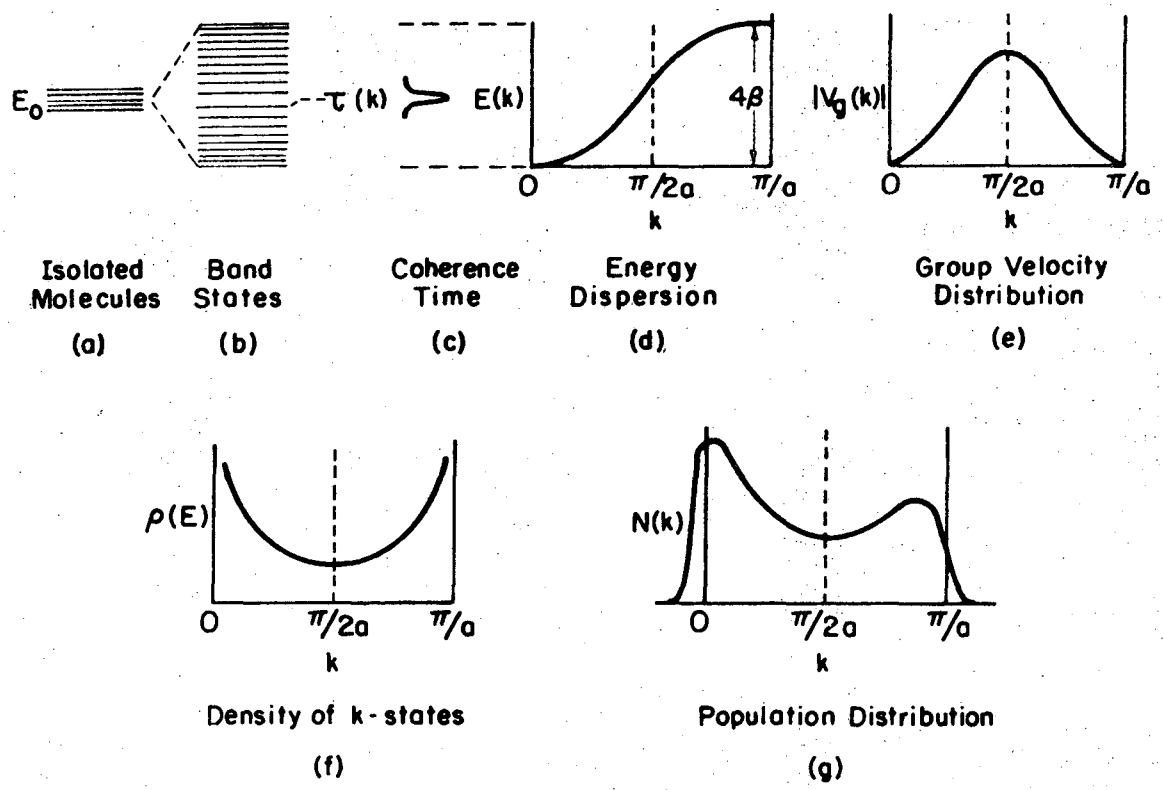
COHERENT PROPERTIES OF DIMERS



XBL 747-6801

Fig. 2

COHERENT PROPERTIES OF ONE-DIMENSIONAL EXCITONS



XBL 747-6802

Fig. 3

EXPECTED LARMOR FREQUENCIES FOR DIMERS AND EXCITONS OF ONE-DIMENSIONAL CRYSTALS IN THE SLOW AND FAST EXCHANGE LIMITS

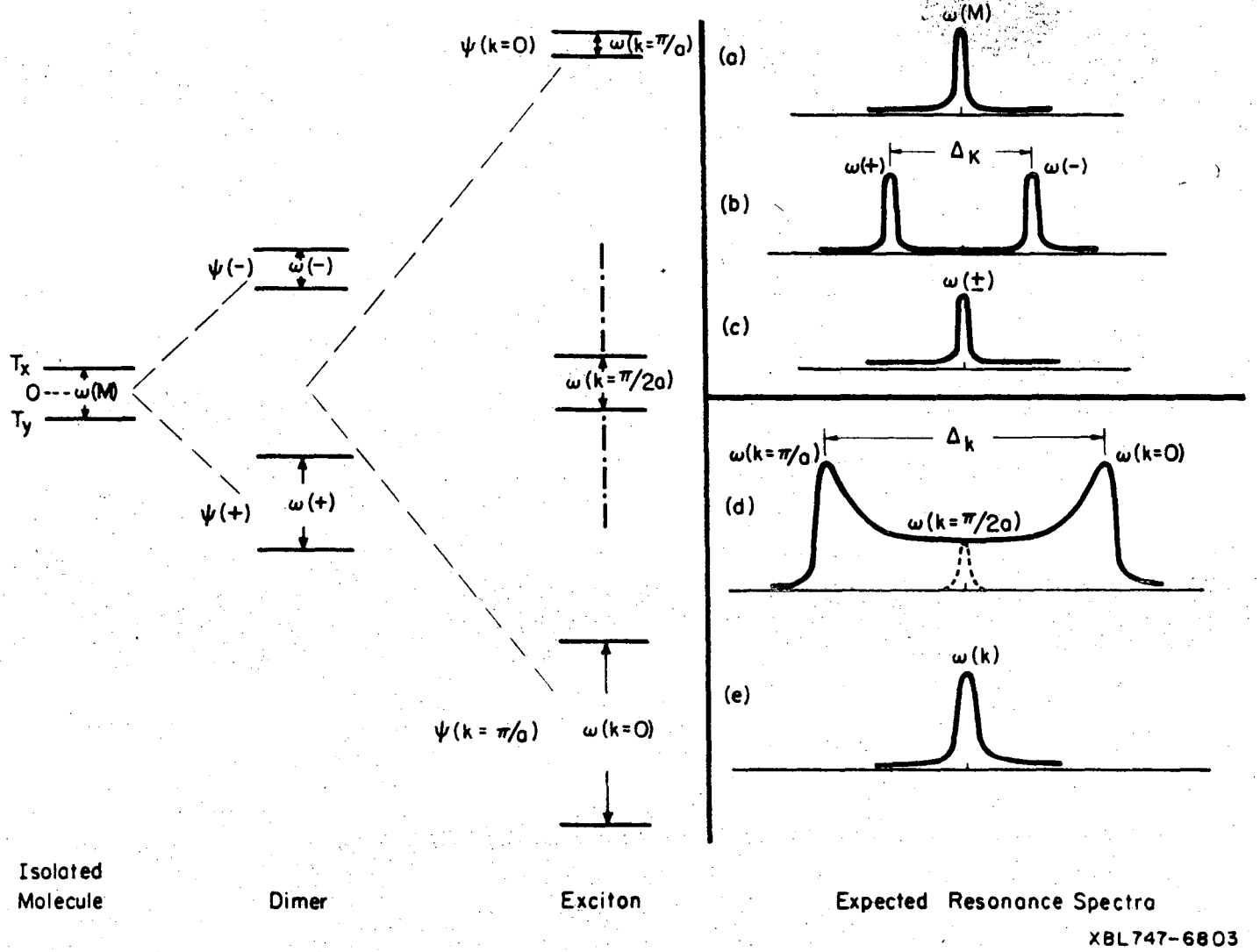
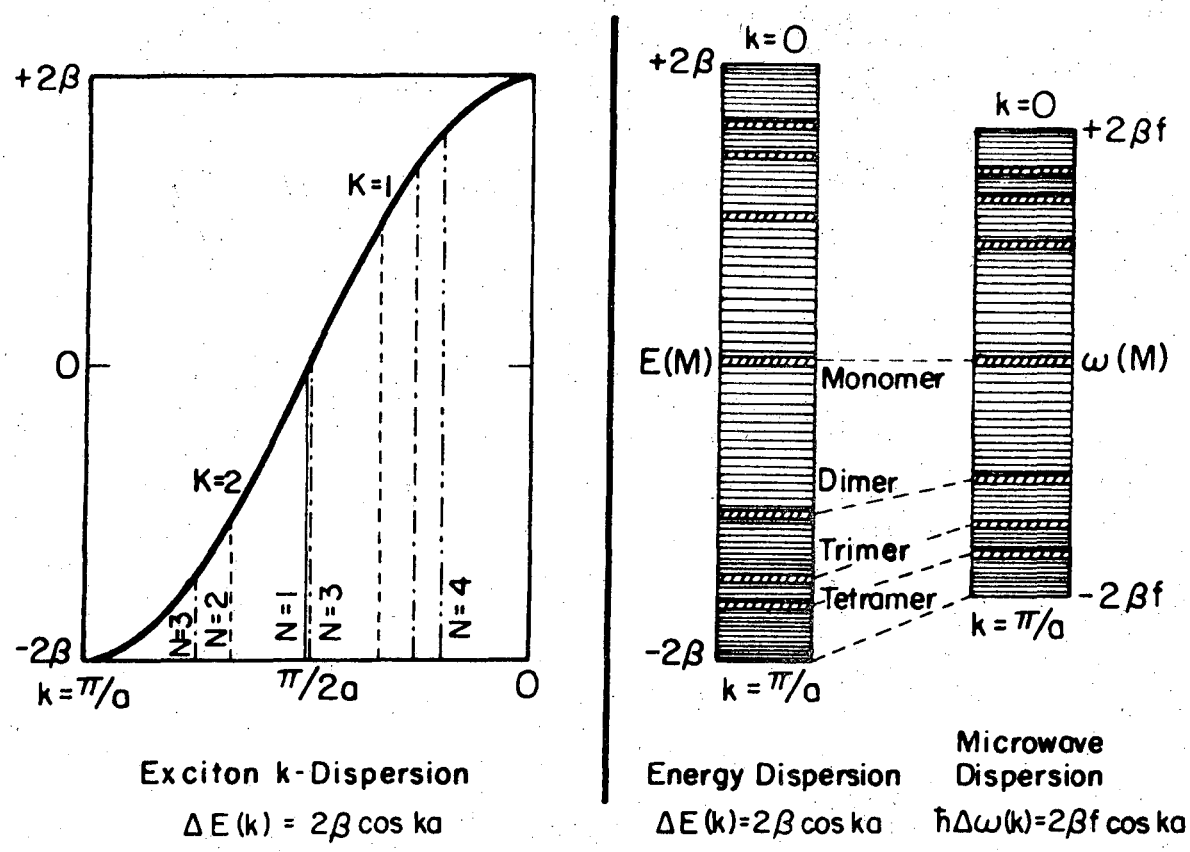


Fig. 4

THE RELATIONSHIP BETWEEN EXCITON AND N-MER DISPERSIONS IN ONE-DIMENSIONAL CRYSTAL



N-mer k-Dispersion

$$\Delta\epsilon(K) = 2\beta \cos(K\pi/N+1)$$

$$K = 1, \cdots N$$

XBL 747-6804

Fig. 5

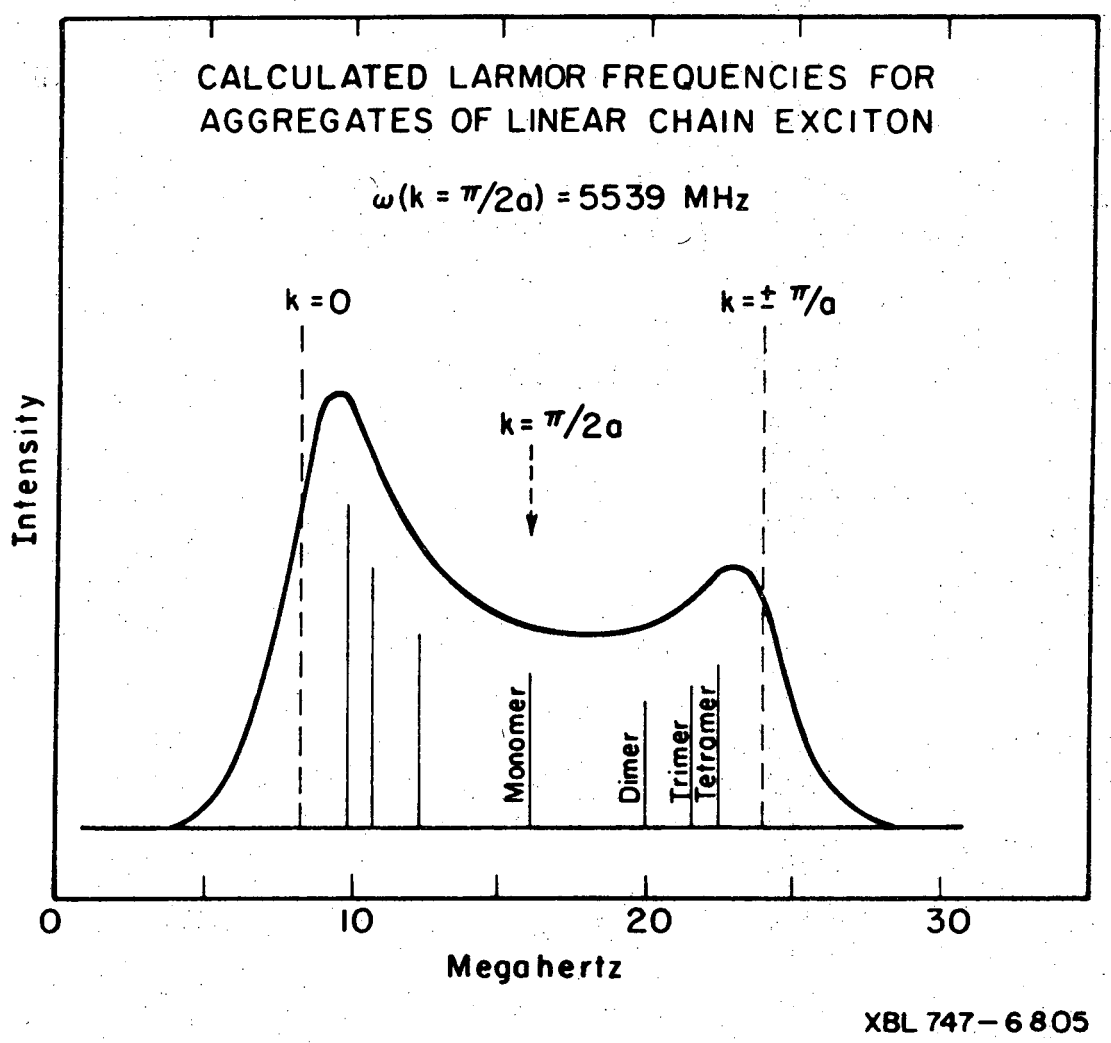

CALCULATED LARMOR FREQUENCIES FOR
AGGREGATES OF LINEAR CHAIN EXCITON
ω(k = π/2a) = 5539 MHz
k = 0
k = ± π/a
k = π/2a
Intensity
Monomer
Dimer
Trimer
Tetramer
0
10
20
30
Megahertz
XBL 747-6805

Fig. 6

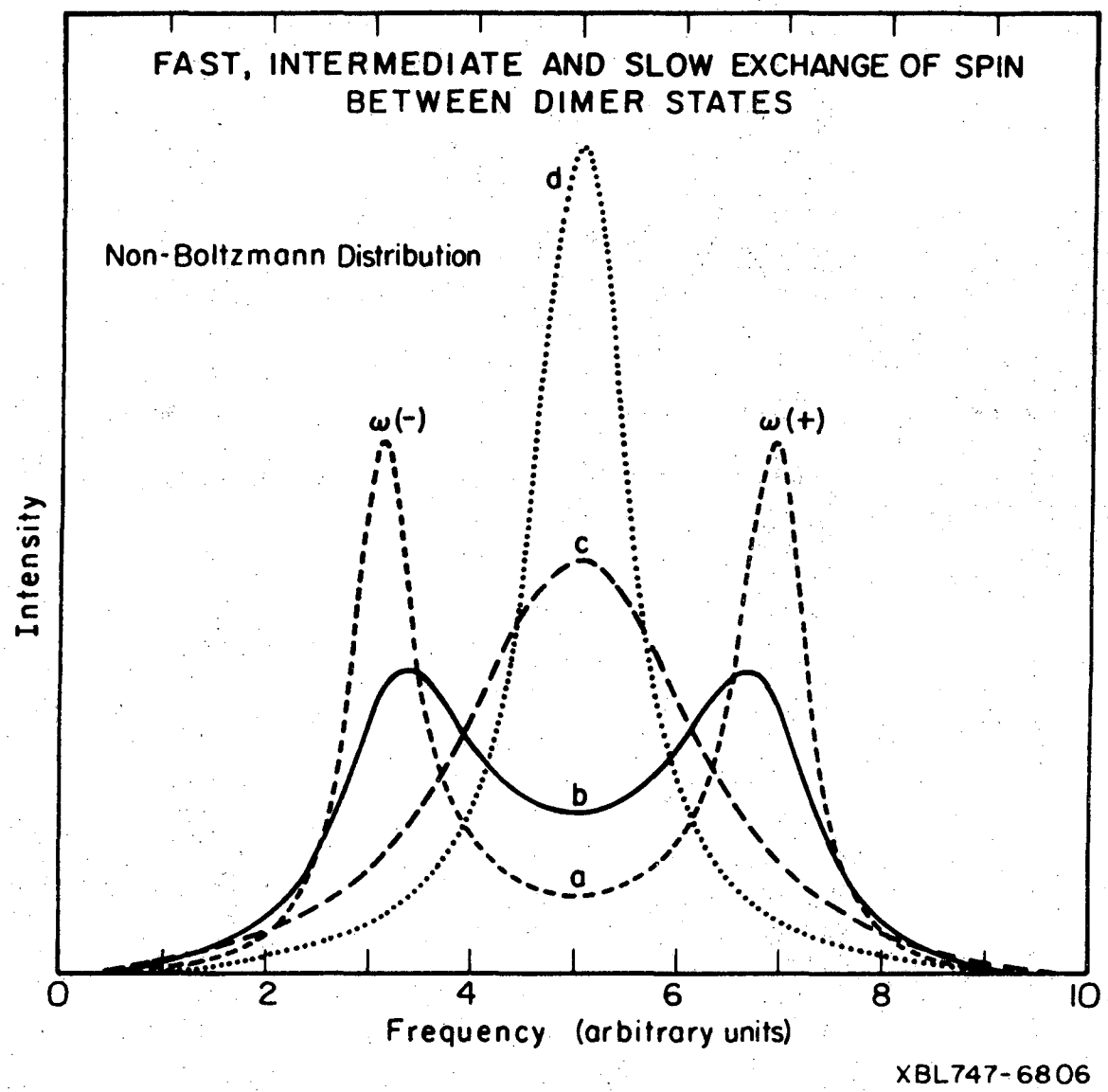
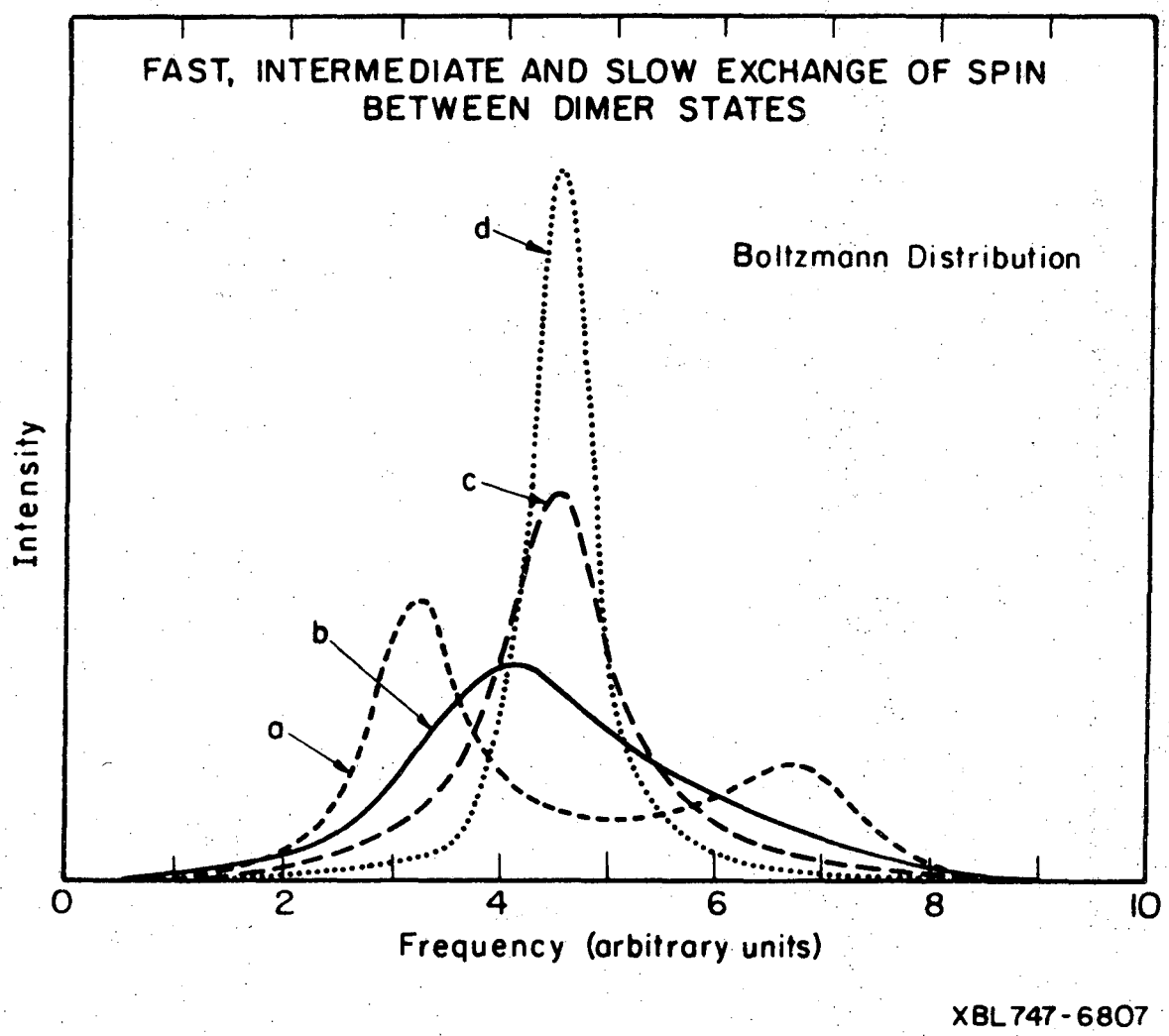

FAST, INTERMEDIATE AND SLOW EXCHANGE OF SPIN
BETWEEN DIMER STATES
Non-Boltzmann Distribution
d
ω(-)
ω(+)
c
b
a
Intensity
0
2
4
6
8
10
Frequency (arbitrary units)
XBL747-6806

Fig. 7



XBL747-6807

Fig. 8

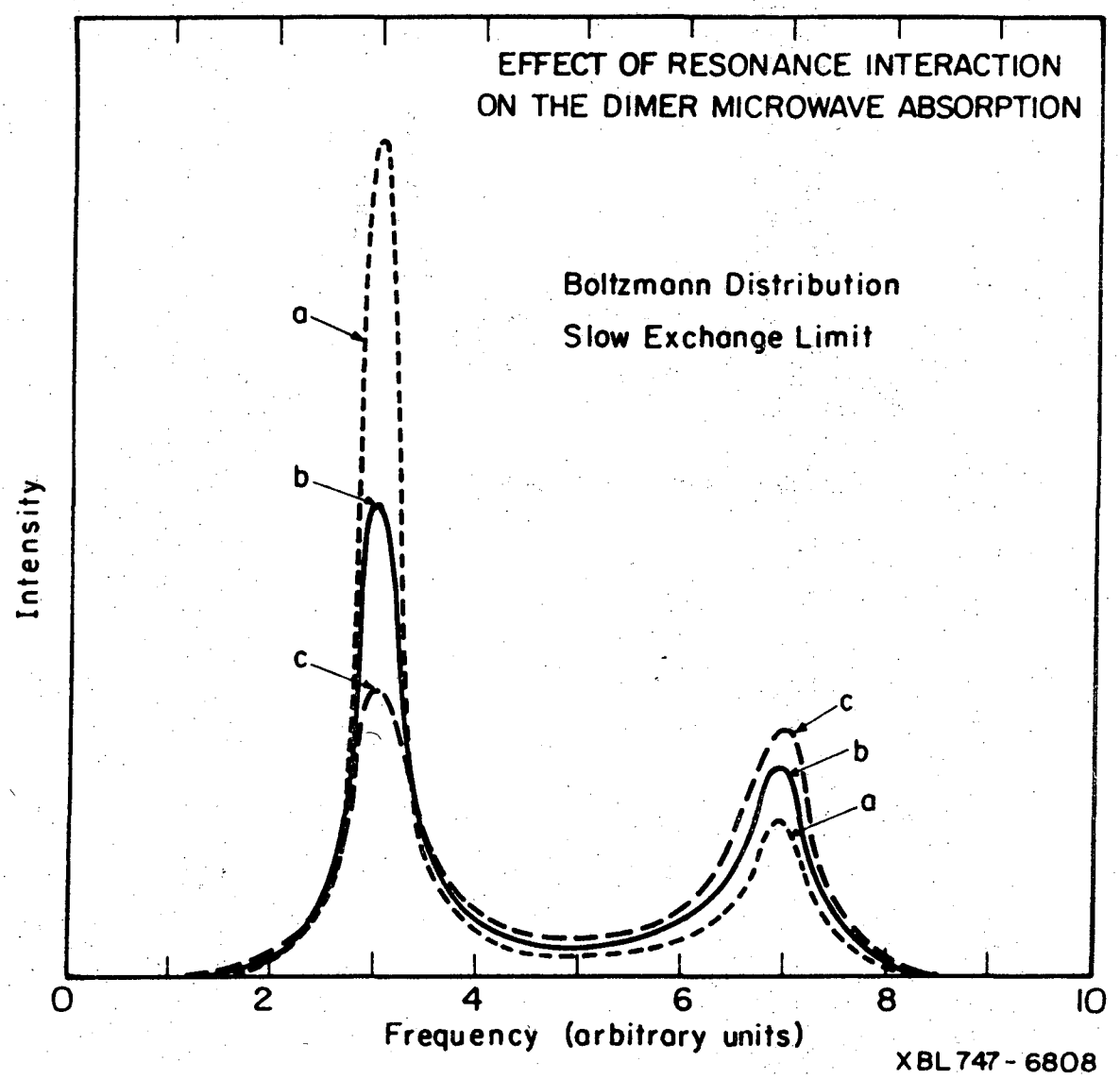
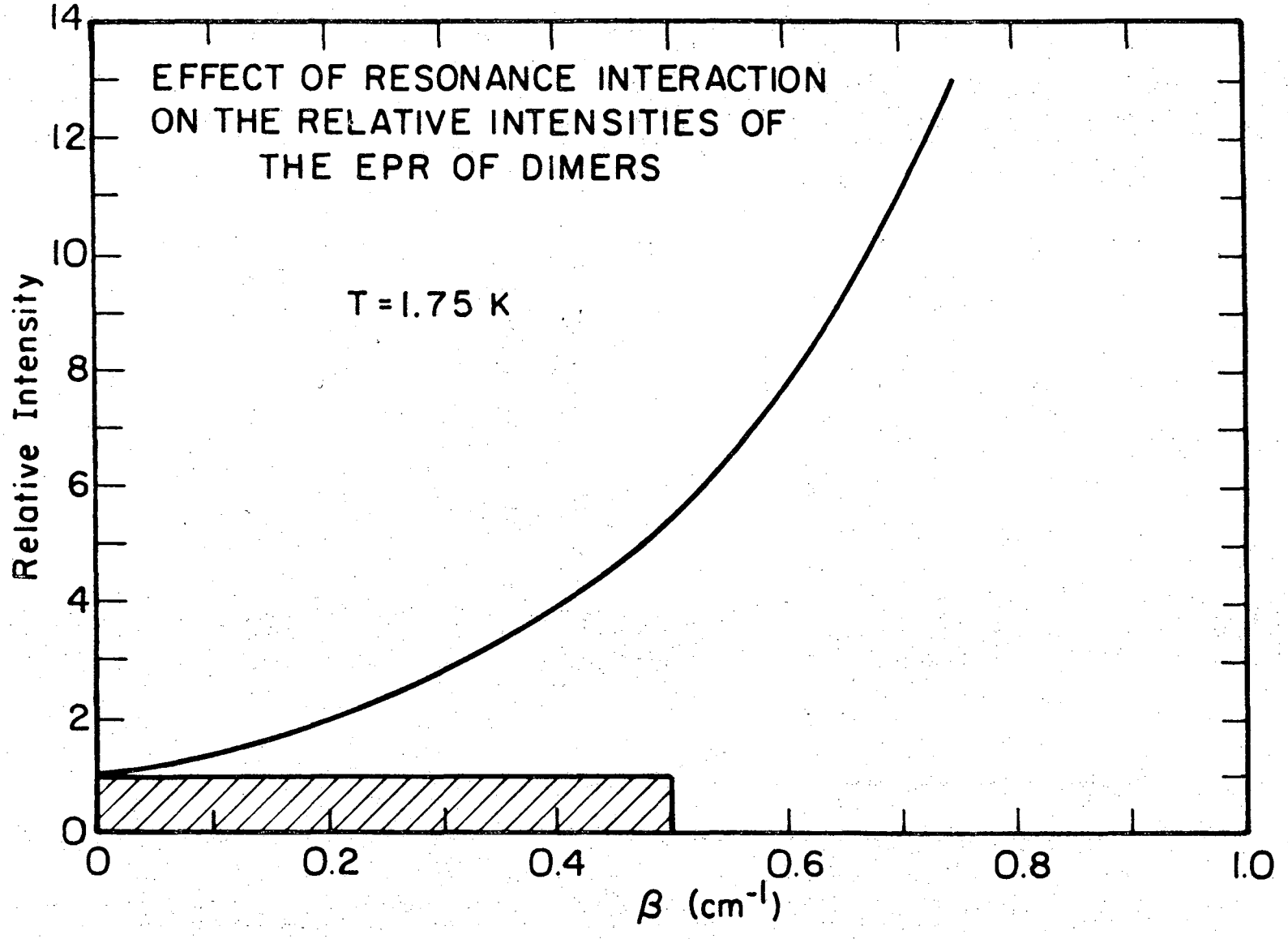

EFFECT OF RESONANCE INTERACTION
ON THE DIMER MICROWAVE ABSORPTION
Boltzmann Distribution
Slow Exchange Limit
a
b
c
c
b
a
Intensity
0
2
4
6
8
10
Frequency (arbitrary units)
XBL 747-6808

Fig. 9



XBL 747-6809

Fig. 10

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LAWRENCE BERKELEY LABORATORY
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BERKELEY, CALIFORNIA 94720