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Migration of Triplet Excitons in Benzophenone: A persistent coherence†

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Magnetic resonance profiles of triplet excitons in ultrapure orthorhombic benzophenone at liquid helium temperatures are presented. A band-structural theory which accounts for all the major features of these profiles is given in outline form. Phosphorescence decay data and excitonic spin-lattice relaxation data are brought into the analysis, and the behavior of the excitons is seen to be very nearly free of extrinsic influence. The magnetic resonance profiles are then recognized as characteristic of excitations which make their way coherently through a lattice with whose vibrations they strongly interact.

I. INTRODUCTION

A central question in the theory of exciton-mediated energy-transfer processes in molecular crystals concerns the excitonic migration mechanism. Is the exciton a randomly hopping, localized entity? Or is it a delocalized excitation which propagates as a wave? In principle, the answer to such questions is encoded in the shapes of intrinsic optical absorption and emission spectra. In practice, the decoding[1] of these shapes is complicated and perhaps not unambiguous. If the excitons are paramagnetic, purely optical information can be supplemented or supplanted by data taken in paramagnetic resonance. Because the profiles of the EPR signals are Fourier transforms of the autocorrelation function of the excitonic magnetic moment,[2] it should be possible to read the magnetic history of the exciton at a glance and to form an immediate and direct judgment of the coherence or incoherence of the excitonic motion.

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Studies of this sort were begun by Chesnut[3] and by McConnell,[4] who studied thermally excited biradical triplet excitons. Later, EPR studies on triplet excitons of optical energies were initiated by Wolf[5] and by Sharnoff.[6] To date the optical triplet excitons of anthracene,[5] benzophenone,[6] naphthalene,[7] tetracene,[8] 1,4-dibromonaphthalene,[9] and 1,2,4,5-tetrachlorobenzene[10] have proven susceptible to EPR investigation. In all but two of these cases the EPR signals were simple, quasi-Lorentzian lines, and authors' conclusions regarding coherence or incoherence of the excitons were by nature indirect, being drawn solely on the basis of the temperature-dependence of their EPR linewidth or relaxation time. In the remaining two cases, benzophenone and 1,2,4,5-tetrachlorobenzene, the lineshapes were distinctly non-Lorentzian functions of form sufficiently bizarre to invite suspicion[6] that they were underlain by a coherent propagation mechanism. It is our intention in this article to show that for the case of benzophenone, the suspicion is entirely justified: the complexities of the excitonic EPR provide direct and compelling evidence that the excitons are coherent.

II. EXCITONS, TRAPS, AND ENERGY TRANSFER IN BENZOPHENONE

Some ten years ago Hochstrasser and his collaborators undertook the study of the $T_1 \leftarrow S_0$ absorption spectrum of orthorhombic benzophenone. They established that the transition was electric dipole-allowed and determined the symmetry of the molecular triplet levels.[11] By applying magnetic and electric fields externally in combination, they succeeded in observing seven of the twelve subcomponents belonging to the crystalline transition ($Z = 4$). In unravelling the Zeeman–Stark patterns they obtained estimates of the intermolecular excitation-transfer matrix elements and estimates of the molecular spin-splitting parameters.[12] The latter proved to be in rough agreement with Sharnoff's direct measurements[13,14] of their values, and we may accept without hesitation their conclusion that the spectral splittings they observed in zero external field were, in essence, the factor-group splittings of the crystal.

For our present purposes, we find in their results a demonstration that the absorption of optical quanta by orthorhombic benzophenone involves the cooperative activity of many molecules: triplet excitons in benzophenone are born coherent. Whether the excitons observed subsequently in EPR experiments are coherent or not is determined by the excitonic lifetime and by the rate at which exciton-phonon or exciton-impurity or -defect scattering tends to destroy the coherence originally present. An exciton which quickly becomes trapped may *appear* to be coherent because it has had little opportunity to be scattered by a dynamic lattice. We shall be able to show that the coherent excitons which we observed in our optically detected EPR experiments on benzophenone were both long-lived and in strong interaction with lattice vibrations. Their coherence appears to be an intrinsic property.

Such traps as do remain—at very low concentration—in our ultrapure crystals are among those species which we were able to characterize in our earlier work as mis-shapen molecules of benzophenone.[14] While we made no detailed effort to study excitonic trapping in the ultrapure crystals, we were able to show in less pure crystals that trapping occurred irreversibly at helium temperatures. We were able to exploit that irreversibility to prove that the mechanism by which energy was transferred from excitons to traps was the spin-conservative, Heisenberg exchange mechanism.[15] These same experiments provided a graphic demonstration of the mobility of the triplet excitons by proving that the principal route of populating the trap levels was via the triplet exciton levels even though the excitation light was capable of populating the traps directly.[16]

Under steady state excitation at 3130 Å, approximately 75 % of the phosphorescence of our ultrapure samples was of excitonic origin.[17]

III. EXCITONS IN ULTRAPURE ORTHORHOMBIC BENZOPHENONE

a. Methods

We have reported elsewhere the methods which we generally employed for preparing and orienting our crystals,[14] observing triplet EPR,[14] and for positively identifying excitonic EPR.[15] For the present work we gave extra attention to growing our crystals slowly, over period of hours rather than minutes. By this strategem we produced crystals less elongated along the *c*-direction than previously and which proved to contain significantly lower concentrations of trapping sites. Insofar as our primary interests lay in careful and accurate recording of the excitonic EPR line-shape, we worked with relatively low microwave power so that power-broadening of the resonance profiles[6] might be avoided. We also were careful to limit the excitation flux (3130 Å) at our samples to 3×10^{11} photon/cm^{2}sec. This precaution eliminated the gradual build-up of photochemical reaction-products in our crystals that could be observed at fluxes of 10^{12} photons/cm^2 sec and higher.

In the early stages of our work we often used a $\frac{3}{4}$ meter scanning spectrometer to select individual vibrational bands of the excitonic phosphorescence. Because we could find no significant differences between excitonic EPR profiles detected this way and those detected without narrow-banding the phosphorescence, we carried out the preponderance of our measurements without using the scanning spectrometer.

b. Phosphorescence decay and excitonic lifetimes

The phosphorescence spectrum of our ultrapure crystals is given in Figure 2a of Ref. 17; the quantum yield under excitation at 3130 Å was approximately 15%. It is of interest to compare the decay of the excitonic phosphorescence with the decay of the phosphorescence emitted by deuterium-enriched benzophenone crystals. The protonated benzophenone molecules in these isotopically mixed crystals have the same configuration as in normal benzophenone[14] but behave as dilute triplet traps.[17] Their phosphorescence consists of three components whose decay rate constants are 768 sec^{-1}, 70 sec^{-1} and 60 sec^{-1}. By contrast, the excitonic phosphorescence (4133 Å or 4435 Å) of ultrapure benzophenone decays as a single exponential. Its lifetime ($1/e$) is 2.2 msec.

The decay of the excitonic phosphorescence is simple because the excitonic spin-lattice relaxation is fast enough to maintain the spin-sublevel populations in quasithermal equilibrium with one another throughout the decay. In the deuterobenzophenone crystals spin-lattice relaxation is sluggish below 2.5 K, and the three components of the phosphorescence represent the decays of spin-sublevel populations isolated from one another. Had spin-lattice relaxation been able to keep the sublevel populations in communication during the phosphorescence decay, a single exponential of rate constant $(768 + 70 + 60)/3$ sec^{-1} would have resulted. The reciprocal of this number, 3.3 msec, would have been the lifetime of the phosphorescence of excitations trapped on undistorted benzophenone molecules.

The lifetime of the excitonic phosphorescence amounts to $\frac{2}{3}$ of this value. Whatever are the new de-excitation pathways brought into play when the excitations become mobile, they are without strong effect on the excitation lifetimes. Intrinsic rather than extrinsic processes control exciton kinetics in ultrapure benzophenone.

c. Exciton-lattice interaction

A simple criterion of the strength of the interaction between excitons and phonons is the ratio of the excitonic phosphorescence lifetime to the excitonic spin-lattice relaxation time. Our earliest work showed[6] that the spin-lattice relaxation time was in the sub-microsecond range at 4.2 K. In ultrapure crystals, an exciton will suffer typically 10^4 spin flips between birth and annihilation. The processes which redistribute energy within the exciton manifold are therefore very much more rapid than those which affect its total population.

It is clear that phonons rather than defects, dislocations, and other static aperiodicities are the dominant source of such redistribution processes. The integrated intensities of our EPR signals are roughly proportional to $\beta H/kT$ and increase smoothly and monotonically by a factor of roughly 3 when the temperature of the helium bath is lowered from 4.2 K to 1.3 K. This is strong evidence that the exciton spins reach thermal equilibrium during the course of their lives. Their contact with the helium bath can be provided only by phonons, and the equilibration of exciton spin and bath temperatures implies that the phonons are, themselves, in equilibrium with the helium bath.

d. Excitonic EPR profiles

The excitonic EPR profiles depend in characteristic and striking fashion on the orientation of the external magnetic field. When the field lies exactly along any of the orthorhombic crystalline axes, the profiles are very nearly Lorentzian. Should the field be inclined by as little as $\frac{1}{2}°$ from an axis, the profile remains "simple" but fails to comply with any classical spectroscopic form. As the inclination of the field increases, subsidiary maxima (hereinafter dubbed "ears") and broad wings appear, their prominence growing smoothly with field inclination. The profiles presented in Figures 1 and 2 give an idea of what may be expected.

Not immediately obvious from the figures, but pervasive to our results, is the singular fact that the ears coincide quite closely in location with the resonances which would be observed from undistorted, individual triplet benzophenone *molecules* which behave as traps in deuterobenzophenone. This quasimolecular aspect, puzzling at first glance, is in the present spectra an entirely excitonic feature which appears equally prominently in optical detection via individual bands of the excitonic phosphorescence. And unlike molecular resonances, the ears have widths which are very sensitive to the direction of the magnetic field. The values range from less than 10 gauss, observed with **H** lying within a few degrees of the *c*-axis, to more than 40 gauss, observed with **H** steeply inclined to all crystalline axes. The widths of the molecular resonances in deuterobenzophenone are 20–30 gauss at all orientations of **H**.

We may accordingly judge the rather complicated profiles of Figures 1 and 2 to be essentially free of contributions from trapped triplet excitations. The ingredients of any attempt to explain their forms are but two: the exciton dispersion relation and the exciton-phonon interaction.

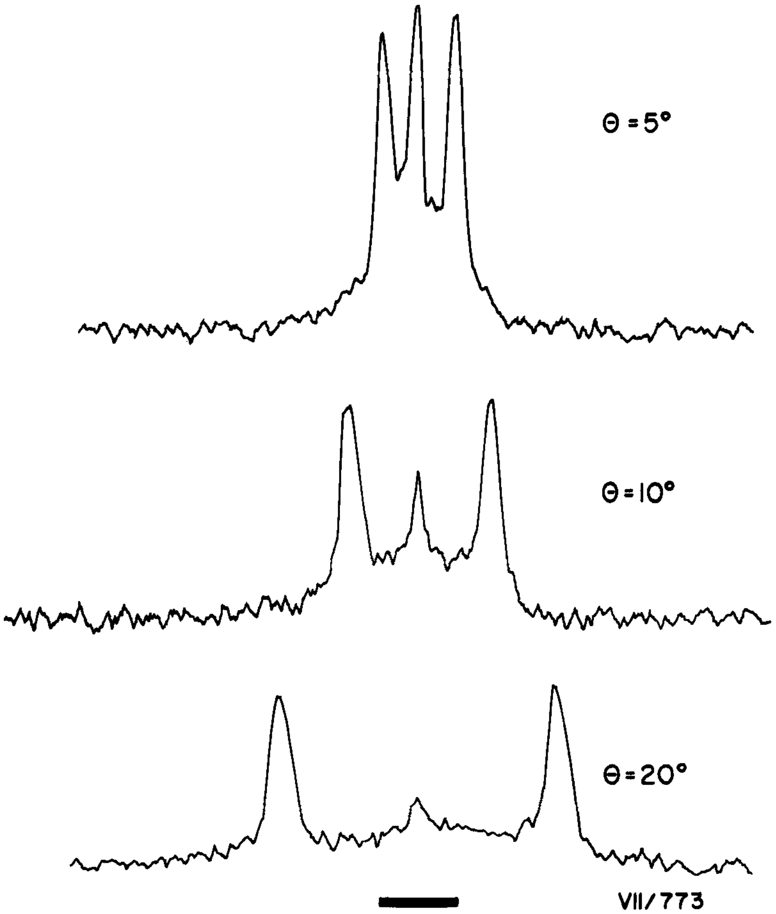

FIGURE 1 Magnetic resonance profiles of the low-field $\Delta m = \pm 1$ transition in the *ac*-plane at 4.2 K. Ordinates: optically detected magnetic resonance intensity in arbitrary units which are the same for all three traces; the microwave power level was the same throughout. Abscissae: magnetic field. The horizontal scales have been shifted so that the central maxima appear in register but are otherwise the same for all three traces. The horizontal bar represents 100 gauss. θ is the angle between **H** and **c**.

e. A sharpening of alternatives

Within this framework the question with which this article began must be recast as the question of whether the exciton-phonon coupling may, in first instance, be neglected in comparison with the effects of intermolecular electronic excitation-transfer interactions or whether, instead, it completely dominates them. The former is the case of complete coherence, and ordinary wave-mechanics is appropriate to its description. The excitons are well-

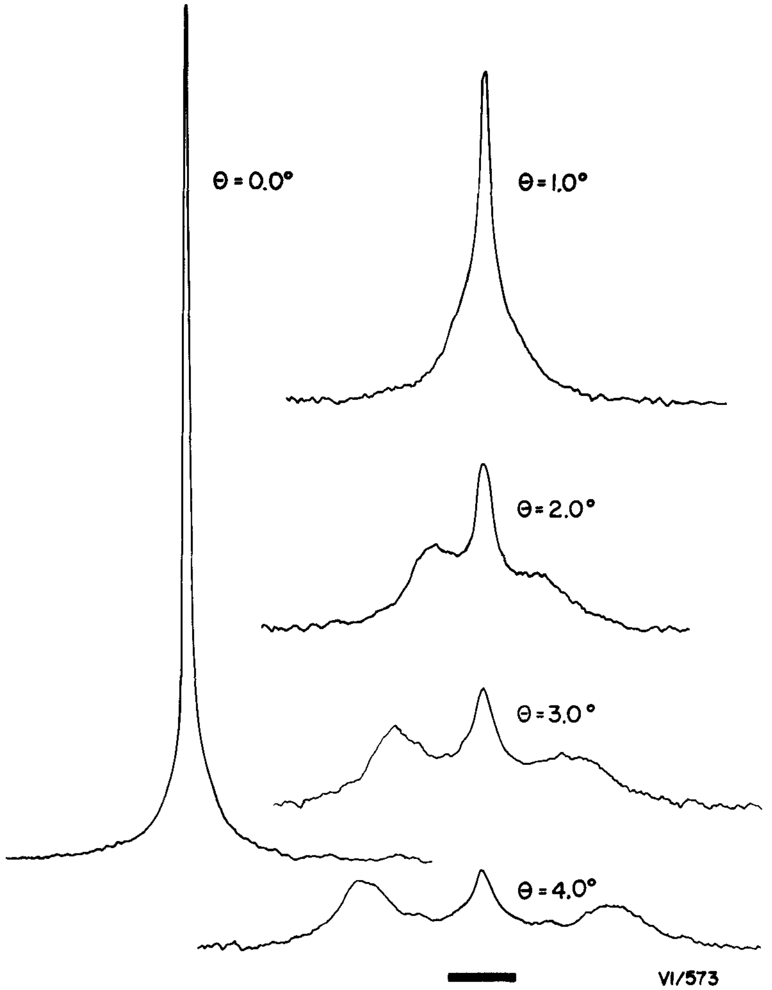

FIGURE 2 Magnetic resonance profiles of the low field $\Delta m = \pm 1$ transition in the *ac*-plane at 4.2 K, continued. Ordinates and abscissae as in Figure 1, except that the horizontal bar represents 20 gauss. The crystal used here is not the same as for Figure 1, and the microwave power level has been reduced five-fold in order to avoid distorting the profiles.

described as Bloch waves whose composition will depend sensitively upon the excitonic crystal-momentum, $\hbar\mathbf{k}$, as well as upon the magnetic field direction. The EPR line profiles would be very sensitive to the distribution of excitonic population among the various Bloch states.

The latter case cannot be handled wave-mechanically, but requires quantum statistical mechanics. **k** is no longer a good quantum number, and a proper description of the electronic excitations and their magnetic correlates would entail a density matrix formalism. If the lattice vibrations happen to be in quasithermodynamic equilibrium, there can be no question of coherence, and the basis states for the density matrix could be taken as the site-localized triplet electronic energy levels of the (distinguishable) individual molecules. Thermal fluctuations in the partitioning of energy between the electronic states of the individual molecules and the phonon bath would be well-described as a Gaussian–Markoff process, and triplet excitations localized on individual molecules would appear to execute random walks through the lattice. The characteristic time of the process—the interval between walks—would not depend upon the direction or strength of the external magnetic field, and such magnetic anisotropy as would remain observable in an EPR experiment would reflect only the anisotropies of individual molecules or the average of those anisotropies. Formally, the situation would be completely analogous to that widely encountered in magnetic resonance on chemically exchanging species.

More complicated situations may be imagined, of course. The phonon bath might not be in thermal equilibrium. Or the excitons might have to percolate through a lattice of shallow traps.[18] Or the excitons and phonons might be so strongly coupled as to propagate only conjointly. The first two of these possibilities are not consistent with what we have already adduced in our discussion of benzophenone. The third possibility cannot be dismissed so lightly, but it would in any event be encountered only at temperatures which lie within a very narrow range. Temperature is decisive in this case because the kinetics of exciton-phonon processes are controlled by the concentration of phonons available, and this is governed in turn by the cube of the temperature, the energy density carried by the phonons varying as T^4 when T is small compared to the Debye temperature. Our experiments on benzophenone spanned the range from 1.30 K to 4.26 K, corresponding to $2.86 \leq T^4 \leq 329$; over the course of this range there was little qualitative change in the benzophenone EPR profiles. We believe that this finding warrants our disregard of possibility three. Our analysis of the lineshapes will accordingly focus sharply on the alternatives of extreme coherence and total chaos. In the interests of simplicity, the discussion will be restricted to profiles observed when the external field, **H**, is confined to one of the three principal planes, *ab*, *ac*, or *bc* of the crystal. For all such orientations of **H**, the four orientationally distinct molecular sites of orthorhombic benzophenone become magnetically equivalent by pairs.[14,19]

f. The case against chaos

As the paramagnetic excitation hops randomly from molecule to molecule in the crystal, its magnetic resonance modulates randomly between two possibilities, A and B. The applicable theory, that of motional narrowing via chemical exchange, makes clear predictions.[20,21] Let the reciprocal of the characteristic time of the modulation be denoted by ω_c, and let resonances of A and B, as observed with the hopping process shut off, occur at frequencies ω_A and ω_B. In our crystal ω_c is independent of field but ω_A and ω_B will vary with the direction of the external field, **H**. At orientations of **H** for which $|(\omega_A - \omega_B)| \gg \omega_c$, A and B will appear as well-resolved resonances whose positions and profiles are practically unaffected by the hopping process; they would be very much the same as those observed in undistorted isotopic molecular traps in perdeuterobenzophenone crystals. As **H** were made less inclined to the nearest crystalline axis, the difference between ω_A and ω_B would diminish, and the hopping process would cause A and B to be somewhat broader and somewhat closer together than they would in the static case. The resonances would begin to merge as the rotation of **H** continued, and when ω_A and ω_B are sufficiently close that $|\omega_A - \omega_B| \ll \omega_c$, only one single smooth resonance, lying exactly midway between ω_A and ω_B would be discernible. The phenomenon would be observed separately, but equivalently, in the low field portion and in the high field portion of the multiplets A and B. Thus the low field portion of the magnetic resonance pattern would consist either of a doublet or of a singlet, depending upon magnetic field orientation. The behavior of the high-field portion of the pattern would mirror that of the low field portion. The theory of random hopping makes no provision that allows either portion to become a triplet. It is in flagrant conflict with our profiles.

g. The case for coherence

At the most basic level, the argument of coherence must explain the qualitative features of our resonance profiles: the triplet structure, the broad wings, and the angular dependence of the distribution of intensity among the central maximum, the wings, and the ears. As the argument is refined, one might hope also to synthesize the subtler details of the patterns: the difference between the slopes of the facing sides and the remote sides of the ears, the eccentricity of the location of the central maximum and, finally, the presence of substantial intensity between the central maximum and the ears. Much of this may be accomplished fairly economically with a band-structure formalism.

IV. WAVE MECHANICAL TREATMENT OF THE EXCITON STATES

a. The unit cell problem

Our problem is to find the K-band magnetic resonance absorption spectrum of the electronic triplet state of a perfect crystal whose unit cell contains four crystallographically distinct sites which are magnetically equivalent by pairs.

Our treatment begins by considering the quasistationary wavefunctions and energies of a unit cell occupied by a single triplet excitation. In the absence of external fields, inter-electron magnetic dipole interactions, and intermolecular transfer, the manifold of states would be 12-fold degenerate. When the spatial coordinates of the electrons are integrated out by the Slater determinant technique,[21] there results the unit cell spin-Hamiltonian

$$\begin{aligned}\mathscr{H} &= -\beta\mathbf{H}\cdot\mathbf{g}\cdot\sum_{i=1}^{4}\mathbf{S}_i - h\sum_{i=1}^{4}\mathbf{S}_i\cdot\mathbf{T}_i\cdot\mathbf{S}_i + h\sum_{i=1}^{4}\sum_{j=1}^{i}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \\ &= \sum_{i=1}^{4}\mathscr{H}(i) + \sum_{i=1}^{4}\sum_{j=1}^{i}hJ_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \qquad (1)\end{aligned}$$

in which appear the Zeeman terms $-\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}_i$, the intramolecular fine structure terms $-h\mathbf{S}_i\cdot\mathbf{T}_i\cdot\mathbf{S}_i$, and where the effects of intermolecular energy transfer have been represented by Heisenberg exchange constants J_{ij}, in accordance with the experiments cited in Section II. The operator $\mathbf{S}_i$ of this expression is a unit spin ($S = 1$) attached to the ith molecule. The symmetry operations of the unit cell permit only three of the six J_{ij} to be distinct. The finestructure tensors $\mathbf{T}_i$ must be expressed in a common system of coordinate axes. When the axes are taken as the orthorhombic axes **a**, **b**, and **c**, of the crystal, their elements will be called $T_{ab;i}$, $T_{bb;i}$, $T_{ca;i}, \ldots$. These elements have been given explicitly in Eqs. (14) and (16) of Ref. 14. The small anisotropy in the molecular g-tensors can be neglected.

The regime we shall have to consider corresponds[6,12] to $h^{-1}|g\beta\mathbf{H}| \gtrsim 3|J_{ij}| \sim |T_{uv;i}|\cdot$. It will accordingly be helpful to use Zeeman quantization in solving the secular determinant which arises from Eq. (1). The direction of **H** will define the z-axis which, for present purposes, we confine to the ac-plane. We shall take the y-axis $\parallel$ **b**, and define the x axis by $\hat{x} = \hat{y} \times \hat{z}$. We let θ be the angle of inclination of z or **H** with respect to $\hat{c}$, so that $\hat{z} = \sin\theta\,\hat{a} + \cos\theta\,\hat{c}$. In order to work with spins $\mathbf{S}_i$ quantized along **H**, we must transform all of the fine structure tensors to the xyz-system. The algebra involves similarity transformation by a simple rotation matrix and leads to lengthy forms which eventually are needed in full detail. The monomolecular terms of Eq. (1) are typified by that for molecule 1:

$$\begin{aligned}\mathscr{H}(1) = {} & -g\beta HS_z - h[\tfrac{1}{2}(T_{aa} + T_{cc}) + \tfrac{1}{2}(T_{aa} - T_{cc})\cos 2\theta + T_{ac}\sin 2\theta]S_x^2 \\ & - h[T_{ab}\cos\theta + T_{bc}\sin\theta](S_xS_y + S_yS_x) - hT_{bb}S_y^2 \\ & - h[T_{bc}\cos\theta - T_{ab}\sin\theta](S_yS_z + S_zS_y) \\ & - h[T_{ac}\cos 2\theta - \tfrac{1}{2}(T_{aa} - T_{cc})\sin 2\theta](S_xS_z + S_zS_x) \\ & - h[\tfrac{1}{2}(T_{aa} + T_{cc}) - \tfrac{1}{2}(T_{aa} - T_{cc})\cos\theta - T_{ac}\sin 2\theta]S_x^2 \qquad (2)\end{aligned}$$

The term for molecule 2 is similar except that $T_{ab} \rightarrow -T_{ab}$, $T_{ac} \rightarrow -T_{ac}$. Analogous alterations must be made for molecules 3 and 4.

The secular determinant which arises from Eqs. (1) and (2) is of rank 12, but it possesses sufficient symmetry to admit of a partial factorization. In effect it proves possible, irrespective of the value of θ, to express the eigenvalues and eigenstates in closed form. The computational details will be presented elsewhere, and we shall be concerned here only with the magnetic resonance spectrum which the solutions imply. This is given in universal form in Figure 3. The ordinates are proportional to the squares of the magnitudes of the matrix elements of the co-rotating component of the spin. The abscissae are measured with respect to the position which the resonance would assume in the limit in which the Heisenberg exchange is so strong as to suppress any magnetic individuality among the sites. In this limit the low-field $\Delta m = \pm 1$ resonance profile collapses into a single, structureless line, the high-field $\Delta m = \pm 1$ resonance behaving likewise.

Let us pursue now the behaviour of the resonance profiles for **H** lying in the vicinity of one of the crystalline axes. When **H** is precisely parallel to the axis, all four sites are magnetically equivalent and both $\Delta m = \pm 1$ transitions

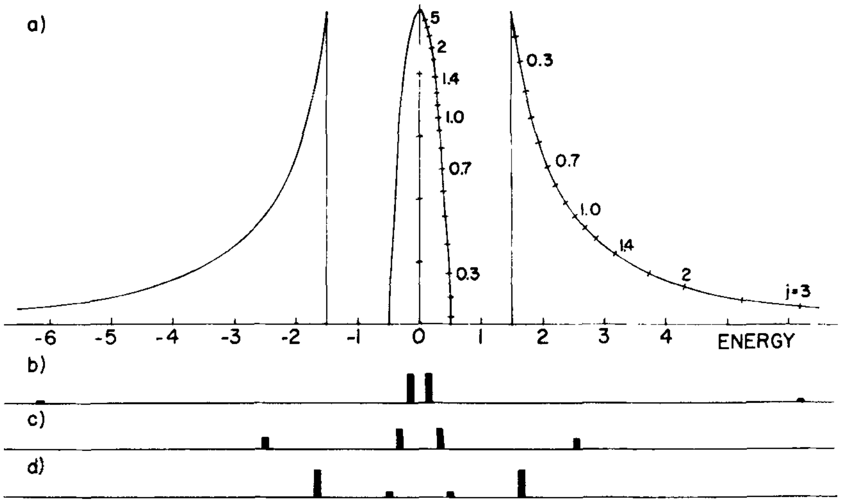

FIGURE 3 Spectral intensity diagram for either $\Delta m = \pm 1$ transition of the unit cell with magnetic field **H** directed in the ac-plane at an angle θ with respect to the c-axis. The abscissae represent energy plotted in units of $hT_{ac} \sin 2\theta$, which is a measure of the degree to which the molecules 1 and 3 are not magnetically equivalent with 2 and 4. The quasimolecular transitions lie at ± 1.5 units. The scale of abscissae can be converted into magnetic field units by dividing by $g\beta$. (a): Spectral distribution versus energy, with dimensionless exchange strength $j = |J/T_{ac} \sin 2\theta|$ as a parameter. The strength of exchange between magnetically inequivalent sites is $J = J_{12} + J_{14}$. (b) stick diagram of the spectrum when $j = 3$; (c) stick diagram of the spectrum when $j = 1$; (d) stick diagram of the spectrum when $j = 0.3$.

are simple. As **H** begins to move away from this direction, each of the transitions becomes composite, as indicated in Figures 3*b*, *c*, and *d*. The degree to which such complications set in is determined by the effective strength of the off-diagonal (site-distinguishable) parts of the intramolecular finestructure tensor *versus* the effective strength of intermolecular spin-exchange. In principle, their onset allows a determination of this ratio. The complications become more pronounced as **H** becomes increasingly inclined to the axis in question, only to recede when **H** reaches the neighborhood of the next crystalline axis. Analogous effects occur in the substantially weaker and less orientationally sensitive "$\Delta m = \pm 2$" transition.

b. The exciton spectrum of the static crystal

The states which diagonalize the unit-cell spin-Hamiltonian are degenerate, one-for-one, with those attached to any other unit cell in the crystal. Heisenberg spin-exchange between translationally equivalent molecules causes a removal of this degeneracy and leads to a band-structure of energy levels in the usual way.[22] In benzophenone it appears that exchange between adjacent translationally equivalent molecules is somewhat stronger than that between orientationally distinct nearest neighbors.[23] Insofar as exchange between orientationally distinct distant neighbours is expected to be weak in comparison to exchange between nearest neighbors or between translationally adjacent molecules, the magnetic resonance spectrum of an exciton of well-defined wavevector **k** will look exactly like the unit-cell spectrum just presented, the only changes required in the analysis being the following substitutions:

$$\begin{aligned} J_{12} &\rightarrow 2J_{12}\cos\left\{\mathbf{k}\cdot\frac{(\mathbf{a}+\mathbf{b})}{2}\right\} \\ J_{13} &\rightarrow 2J_{13}\cos\left\{\mathbf{k}\cdot\frac{(\mathbf{b}+\mathbf{c})}{2}\right\} \\ J_{14} &\rightarrow 2J_{14}\cos\left\{\mathbf{k}\cdot\frac{(\mathbf{a}+\mathbf{c})}{2}\right\} \end{aligned} \tag{3}$$

and

$$J \equiv 2J_{12}\cos\left\{\mathbf{k}\cdot\frac{(\mathbf{a}+\mathbf{b})}{2}\right\} + 2J_{14}\cos\left\{\mathbf{k}\cdot\frac{(\mathbf{a}+\mathbf{c})}{2}\right\} \tag{4}$$

The **k**-dependence in these expressions is dictated by the structure of the unit cell in accordance with the space-group of the lattice, which for benzophenone[19] is $P_{2_1 2_1 2_1}$. The excitonic magnetic resonance spectrum thus contains no direct information about spin-exchange between translationally equivalent molecules but is, in the case of moderate exchange between magnetically inequivalent sites, very strongly **k**-dependent.

The magnetic resonance spectrum of the crystal is the envelope of excitonic resonances belonging to all possible wave-vectors. Excitons having small **k** would have relatively large J and would give contributions tending to resemble Figure 3*b*; excitons of high crystal momentum or large **k** would have relatively small J and would tend to contribute spectra more like the kind presented in Figures 3*c* or *d*. The superposition of many spectra of these sorts would give an envelope which, in the case of moderate exchange, is qualitatively similar to Figure 3*a*.

The quantitative details of any such envelope will reflect the distribution of excitonic populations among the various **k**-states. We showed in Section III.C above that the excitonic spin sublevel populations are nearly in thermal equilibrium with the helium bath and, therefore, with the phonons. It would be reasonable to posit that the populations of the **k**-states are also distributed thermally. The width of the exciton band cannot be much larger than kT at 4.2°K,[23] and the **k**-populations in thermal equilibrium would thus be roughly uniform through the exciton band. Under these circumstances the diagram of Figure 3*a* comprises a nearly literal prediction of the resonance profiles that the crystal would exhibit at orientations for which $|J_{12}/T_{ac} \sin 2\theta| \sim 3$. One anticipates resonance profiles which appear like well-resolved triplets whose components are comparable in intensity. As **H** is made more nearly parallel to one of the crystalline axes, $|T_{ac} \sin 2\theta|$ diminishes, $|J_{12}/T_{ac} \sin 2\theta|$ rises, and there would be a shift of intensity from the side-peaks towards the wings and central maximum, all features sharpening and eventually collapsing into a very narrow, bell-shaped profile. Schematically speaking, this behavior is exactly what we have observed experimentally.

c. The effects of exciton-phonon scattering

The observed resonance profiles differ in two important respects from profiles expected from a static lattice. Firstly, the central maximum and the broad wings of the observed patterns are homogeneously broadened,[6,24] in contrast to the completely inhomogeneous profile expected of a truly static lattice. Secondly, the observed profiles contain considerable intensity in the regions $-\frac{3}{2} < |E/hT_{ac} \sin 2\theta| < -\frac{1}{2}$ and $\frac{1}{2} < |E/hT_{ac} \sin 2\theta| < \frac{3}{2}$, regions for which the static lattice predicts rigorously zero resonance intensity.

These discrepancies disappear when allowance is made for the interaction between excitons and phonons. We have already cited the unusually fast exciton spin-lattice relaxation as evidence that this interaction is strong. If it is strong enough to produce significant motional narrowing of the resonance profiles, the effects of the motional narrowing will be most apparent in the region between the ears and the central maximum. Resonance intensity would then be found in the region where the rigid-lattice approximation would exclude it. Furthermore, motional narrowing would tend to make the observed resonance profile homogeneously broadened.

There can be no doubt that dynamic processes in the benzophenone crystal are strong enough to produce such motional narrowing effects. Their rapidity can be estimated from the residual widths of exciton resonances observed with **H** directed along one or another principal axis, and a mean lifetime of 15 psec can thereby be established[6] for the mean longevity of any particular excitonic **k**-state at 4.2 K. The crystal momentum of a typical exciton therefore fluctuates rapidly enough to create spectral intensity between otherwise isolated features as much as 200–300 gauss apart.

The picture which emerges from our magnetic resonance profiles is thus one in which excitons in benzophenone at liquid helium temperatures propagate coherently throughout their lifetimes despite an intense barrage by phonons. The exchange coupling constants extracted from our lineshapes are in rough agreement with those which Hochstrasser and Lin[12] found in their optical absorption work; our values are $|J_{12}| \approx 0.1\ \text{cm}^{-1} \gg |J_{13}|, |J_{14}|$.

One nagging question remains which was posed to the authors by Prof. V. L. Broude: "How can the excitons move coherently when their own bandwidth is so narrow in comparison to the kT of the phonons with which they interact so strongly?" Our reply was based on the conservation rule for crystal momentum and the observation that the phonon temperature must be very small in comparison to the Debye temperature. An immediate consequence is that the phonons have relatively long wavelengths, mainly greater than θ_D/T times the lattice-constant: "Because the phonon wavelengths are so long, exciton-phonon scattering events cannot change the excitonic wave-vector very drastically in any one collision. Nor will diffraction of excitons by phonons strongly alter the large-**k** portion of the excitonic wave-packets. As a result, one anticipates a mean excitonic coherence length which is comparable with the mean wavelength of the thermal phonons. If we take the Debye temperature as 200 K, the excitonic coherence length would be about 50 lattice-constants; it's probably not too much longer than that." "This", we added, "is probably the reason why we seem to have been able to witness the entire band-structure of the magnetic resonance even though we detected the resonances optically. If the coherence lengths of the exciton wave-packets had been thousands of lattice-constants, we would have been able to see only what magnetic resonance signals could be conveyed on the $\mathbf{k} = 0$ portion of the phosphorescence."

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