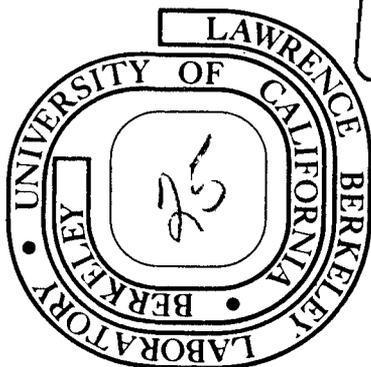RECEIVED
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COHERENCE IN ELECTRONICALLY EXCITED DIMERS.
I. THE OBSERVATION OF COHERENT DIMERS AND ITS RELATIONSHIP TO COHERENT EXCITONS.

A. H. Zewail and C. B. Harris

May 1974

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COHERENCE IN ELECTRONICALLY EXCITED DIMERS.

I. THE OBSERVATION OF COHERENT DIMERS AND ITS RELATIONSHIP

TO COHERENT EXCITONS.

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ABSTRACT

The coherent nature of molecular excited dimers in their triplet states is unequivocally established by a series of low temperature optically detected magnetic resonance experiments in zerofield. The results clearly establish that a minimum coherence time for the dimer $\psi(+)$ state in 1,2,4,5-tetrachlorobenzene $(\sim 1.7°K)$ is longer than 5×10^{-7} sec. while the exchange time in these systems is approximately 16×10^{-12} sec. This implies that the coherence persists for time approximately 10^5 that associated with the Stochastic limit The coherence time could, however, be even much longer. Moreover, these new results clearly demonstrate that there is a direct and quantitative relationship between coherent properties of dimers and the coherent properties of triplet Frenkel excitons.

1. GENERAL BACKGROUND

The theory[1-7] of dimer states in coupled molecules has been and still

is an area of moderate activity. Being a model for a <u>two-level</u> system,

it has attracted a considerable amount of attention in the optical

spectroscopy of dimer states[8-10] isolated in molecular crystals. Although

the solution to the stationary Schrodinger wave equation yields the

symmetric and antisymmetric states separated by 2β where β is the

intermolecular interaction between the two isolated molecules, there has

been some confusion on what criteria are necessary to establish whether

or not a dimer state is coherent or incoherent. The fact which should

be self-evident is that <u>the dimer states $\psi(+)$ and $\psi(-)$ which contain the</u>

<u>well-defined phases are not necessarily coherent for infinite time because</u>

<u>of the interaction between the dimer states and the environments via the</u>

<u>relaxation Hamiltonian.</u> Coherence in dimer states is established by the

lifetime of a specific single state, $\psi(+)$ or $\psi(-)$, relative to the

resonance transfer whose frequency is $1/h$ times the separation between

the two levels, 2β. Specifically, one must construct a well-defined set

of criteria to establish whether the lifetime of the states, $\tau(+)$ and

$\tau(-)$ for the <u>plus</u> and <u>minus</u> states respectively, are longer or shorter

than $h/2\beta$.

If $\tau(\pm) < h/2\beta$, the states are clearly incoherent and possibly

indistinguishable. On the other hand, if $\tau(\pm) > h/2\beta$, say, approaching

the lifetime of the excited species in the state, the dimer is coherent

because there has not been an energy fluctuation during that time period,

and hence the phase of the wavefunction is well-defined from the initial

time, t = 0, the time at which the excited state is created, to some latter time t = τ. In other words, <u>coherence times are determined by fluctuations of the off-diagonal matrix elements of the time-dependent density matrix when the stationary states are solutions to the zero order Hamiltonian matrix responsible for dimer splitting</u>. The important point to remember is that, experimentally, coherence can only be established by determining the rate at which the time-dependent Hamiltonian modulates the energies of the states relative to 2β.[11,12,13]

Couched in this language there are three terms which are interrelated, two of which can be used to establish coherence in dimers, and all are directly extendable to coherence in exciton states[13-17] by simple analogy. They are, for dimers, 2β, $\tau(+)$ and $\tau(-)$ [hereafter called the coherence times of $\psi(+)$ and $\psi(-)$], and $\vec{a}$, the separation between the isolated molecules; the relationship to excitons is as follows: (1) For one-dimensional exciton states, where the band results from the same β as is in the dimer case, a band dispersion of 4β results.[18] The splitting, 4β, between the $k = \pm\pi/a$ and $k = 0$ states in the exciton, is directly related to the splitting between the two states, 2β, in the dimer case. (2) The exciton coherence time $\tau(k)$ for a specific k state in the exciton band can be conceptually related to $\tau(+)$ or $\tau(-)$ of the dimer. (3) Finally, $\ell(k)$ for the exciton state is the length of propagation of a coherent exciton at a group velocity $V_g(k)$. For bands, this velocity[14] depends on many features of the physics of energy migration in coherent exciton states not found in the more simple dimer problem. For the dimer, the distance the excitations travel <u>by analogy</u> to the exciton is simply the distance between the two isolated molecules, $\vec{a}$.

Naturally, the above discussion is oversimplified. To approach the problem more completely, one makes the assumption that the physics that limit $\tau(+)$ or $\tau(-)$ are governed by first-order Stochastic-Markoffian processes.[19] In addition,[20] one must include the full time correlation function into $\tau(+)$ and $\tau(-)$, since one has to measure $\tau(+)$ and $\tau(-)$ as a function of some experimentally imposed observation time, t. Hence, we will define $\tau(+) \equiv \tau_t(+)$ and $\tau(-) \equiv \tau_t(-)$ where t is a single point in the time correlation function which is always determined by the type of experiments one performs. For example, in optical absorption, if 2β is much less than the electromagnetic radiation energy used to measure the energies of the two states, the single point in the time correlation function of $\tau(+)$ is $h/2\beta$. Thus even if $\tau(+) \approx h/2\beta$, the problem can appear to a large extent coherent although the off-diagonal elements of the time-dependent density matrix can be fluctuating at rates comparable to 2β. In such an example, the coherence time is approximately the exchange time. By analogy to the exciton problem, this would mean when all k states of the band have $\tau(k) \leq h/4\beta$, it propagates in an incoherent random walk fashion and $\ell(k)$ would be reduced to a single site transfer distance $\vec{a}$.

To the best of our understanding and knowledge, there has never been a clear and definitive demonstration of coherence in dimers on a time scale longer than approximately 2β and these are confined to the spectroscopic measurements of the dimer splitting from optical spectroscopy.

High Field Electron Paramagnetic Resonance (EPR) spectroscopy, on the other hand, can be used to measure qualitatively and quantitatively the properties of dimers. Schwoerer and Wolf[21,22] have shown that the dimer EPR frequencies in naphthalene are different from those of the monomer and

identified the pair as translationally inequivalent. 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,[23] cannot be determined from these high field linewidth measure-

ments. This is because the resonance linewidth is limited by the magnetic

field broadening, hyperfine splittings[24] and relaxation effects. Moreover,

the contribution of the latter becomes more difficult to obtain if the inter-

molecular interactions are multidimensional, as in naphthalene.[25] Finally,

considerations based on understanding of the full correlation function for

coherence must be taken into account in extracting the coherent properties.

Zerofield EPR, at low temperatures, of dimers, as we will demonstrate,

can be extremely important in answering questions about coherent and

incoherent properties, particularly if the dimers are formed in crystals

where the band dispersion is very simple.

Recently the phosphorescence microwave double resonance (PMDR)[26]

spectroscopy of pairs of 1,4-dibromonaphthalene in zerofield was reported.[10]

The identification of the pairs as translationally equivalent was consistent

with the resonance frequencies, and the strong coupling between the two

molecules was evident from both the optical and EPR results.[10] However, the

dynamics of coherence could not be established from these experiments

because of the interpenetration between the $D + |E|$ and $D - |E|$ transitions

as well as the large hyperfine interactions.

We will show in a series of experiments a clear demonstration of

coherence in dimers and its relationship to coherence in exciton states.

In this first paper of a series we will (a) establish coherence in

translationally equivalent dimers of 1,2,4,5-tetrachlorobenzene; (b) demon-

strate that the experiments of Francis and Harris[27] on coherence in excitons unambiguously measured coherence, and finally (c) we will give an estimate of the coherence time in these dimers by a series of low temperature PMDR experiments in zero applied magnetic fields.

2. EXPERIMENTAL

Both 1,2,4,5-tetrachlorobenzene-h_4 and the perdeutero materials were extensively zone refined. The isotopically mixed single crystals were grown from the melt by conventional Bridgeman techniques and the composition of these crystals was determined from their NMR spectra. All these crystals show the characteristic emission of both tetrachlorobenzene-h_2 (H_2) and tetrachlorobenzene-hd (HD) traps.

The single crystal was cut to fit inside a helical slow-wave structure matched to a 50 Ω rigid coaxial line. The assembly was immersed in a liquid helium Dewar which could be pumped to temperatures between 1.4°K - 2.0°K, depending upon the specific experiment. Microwaves were obtained from a Hewlett-Packard Model 8690B sweep generator and modulated by two PIN diodes (HP Model 33124A) in series giving a total modulation depth greater than 60 db. The rf field was then transmitted through a narrow pass band filter and amplified by a 20 watt TWT, whose output was terminated in the coaxial line.

The crystal was excited through the open helical structure with a 100 watt Hg-Xe lamp and a broad band filter whose peak is centered at approximately 2800 Å. The phosphorescence was collected at right angles to the exciting light, using a 0.75 m Jarrell-Ash spectrometer and an EMI

6256-S (cooled to -20°C) photomultiplier, whose output was phase sensitive detected at the microwave modulation frequency. The temperature of the bath was measured using the vapor pressure of the helium above the immersed crystals. Further details on these experiments will be published elsewhere.[28]

3. RESULTS

3.1 The Phosphorescence Spectra

The emission spectra of the isotopically mixed crystal shows the emission of H_2, HD and D_2. A resolvable resonance multiplet emission (emission of the different clusters) was not seen, even in the high concentration limit. Given the halfwidth of the 0,0 emission of H_2 in the high concentrated crystals (approximately 2 cm^{-1}) and the resolving power of our instrument, we estimated β_a must be less than 1.0 cm^{-1}.

3.2 The Zerofield ODMR Spectrum of H_2 Traps

A) Monomers.

The zerofield transitions together with their quadrupole satellites were observed in the isotopically mixed crystals at temperatures between 1.4°K and 2.1°K. A typical spectrum is shown in Figure 1. The analysis of the spectrum reveals all the features of isolated molecule spectrum with the characteristic quadrupole coupling constants for ^{35}Cl and ^{37}Cl isotopes.[29,30] One additional feature appeared in the spectrum of H_2 traps, namely the shallow trap resonance transition at 3560.3 MHz. This implies that there is a communication between the traps below the exciton band,

as has been discussed at length in an earlier publication.[14,30] The

mechanism for such excitation transfer in these systems is under

investigation.

B) Dimers.

At relatively low concentration (0.06% H_2), both the D + |E| and

D - |E| transitions have reasonably sharp lines with a half band width

of ~3 MHz, at very low power (0.1 mw). Furthermore, no quadrupole

satellites were observed. With higher power levels (62 mw) the lines

become somewhat broader, and the forbidden satellites appeared, due to

nuclear ^{35}Cl and ^{37}Cl quadrupole transitions.[29] It is important to note

(although not illustrated) that at the low power levels (0.6 mw), at

which the experiments were performed on the low and high concentrated

crystals, no ODMR dimer signals were observed around the monomer line

(Cf. Figure 2) in the low concentrated crystals. Increasing the guest

concentration, however, resulted in the appearance of new satellites on

the monomer electron spin transition. Figure 2 shows the 5.05% H_2

spectrum compared with the 0.06% H_2 spectrum under identical power output

for the D + |E| and D - |E| transitions. A complete power dependence study[28]

was done on the D - |E| transition. The results clearly indicate that the

saturation behavior for the satellites is different from that of the central

resonance line. At higher concentration (>5% H_2), the lines which are very

close to the monomer line ($\leq$ 3 MHz) could be seen (cf. Figure 3); hence,

the frequency could be measured. The conclusions of these concentration

dependence studies are:

(a) The satellites are absent from the zerofield ODMR spectrum of

the low concentrated crystals, even at high power.

(b) The separation between the two dimer states on the D - |E|

transition is 5.7 ± 1 MHz and on the D +|E| transition·is 7.6 ± 1 MHz.

(c) The linewidth of the D - |E| transition in the $\psi(+)$ state is

approximately 2 MHz.

4. DISCUSSION

4.1 1,2,4,5-Tetrachlorobenzene Crystal Structure

There are two molecules in the unit cell of s-tetrachlorobenzene

which belongs to $P2_1/c$ space group.[31]   At 188°K a phase transition changes

the lattice into a triclinic,[32] closely related in molecular orientations

and unit cell dimensions to the room temperature monoclinic structure.

Translationally equivalent molecules stack very nearly along the

a-crystallographic axis in both phases (monoclinic and triclinic). The

out-of-plane molecular axis is almost parallel to axis a. This fact,

together with the small length of a compared to the b and c lattice

constants, led to the conclusion that this system could be essentially

a linear chain exciton[27,33,34] associated with the translationally equivalent

interaction along the axis a.

4.2 Zerofield Microwave Transitions in the Symmetric and Antisymmetric Dimer States and Their Relationship to the Exciton Transition in 1,2,4,5-tetrachlorobenzene

We will not present details at this point but will simply state

that when one diagonalizes the full Hamiltonian in the properly anti-

symmetrized basis for the exciton and dimer states, including spin-orbit

coupling, an expression for the k dependence of the exciton band-to-band microwave dispersion in the first Brillouin zone yields:[11]

$$\hbar(\omega_{xz}(k) - \omega_{xz}) = 2\beta_t f_{xz} \cos ka \qquad 4\text{-}1$$

$$\hbar(\omega_{yz}(k) - \omega_{yz}) = 2\beta_t f_{yz} \cos ka \qquad 4\text{-}2$$

where $\omega_{ij}(k)$ corresponds to the ijth exciton microwave band-to-band transition frequency and ω_{ij} correspond to the ijth microwave transition of the monomer. These equations are identical to those derived by Francis and Harris.[13]

The same treatment for the symmetric and antisymmetric states of the dimer clearly shows the direct relationship between the exciton spread in Larmor frequency and the dimer spread $[\omega(+) - \omega(-)]$. Specifically,

$$[\omega(+) - \omega(-)] = 1/2[\omega(k=0) - \omega(k=\pm\pi/a)]. \qquad 4\text{-}3$$

Physically, this is because the dimer splitting, 2β, is half the total band width, 4β, for a one-dimensional exciton. As a result, the k-dependent spin orbit perturbation in the exciton is reduced by a factor of two for a two-molecule chain. Furthermore, the monomer EPR frequency should be at $k = \pm\pi/2a$ (the center of the band) if there is no polarization induced by the D_2 band.

The observed[27] exciton band spread in Larmor frequency was explained by invoking two important conditions, namely (i) s-tetrachlorobenzene crystal is a one-dimensional exciton system; and (ii) the lifetime of the individual k states of triplet band, $\tau(k)$, is longer than the reciprocal of the microwave dispersion across the band. Hence there is a finite coherent time for the excitons in these systems on the time scale of 10^{-7}

seconds.

Figure 4 shows the direct relationship between the measurements of band-to-band microwave transitions of the exciton and those of the ± states of the dimer. The variation in the + to − splittings of $D + |E|$ and $D - |E|$ transitions is attributed to the different strengths of spin-orbital coupling routes, as would be expected for both excitons and dimers (equations 4.1 and 4.2). <u>The most significant feature of the spectra is the presence of two peaks of different intensity in each dimer transition located at the expected frequency (from the band measurements)</u>. We therefore conclude that (a) these new experiments on the dimers could be used as a versatile tool in obtaining the coherent properties of triplet excitons, as well as the magnitude of intermolecular interactions; (b) the coherent properties such as the coherent lifetime of dimers can be directly measured, a quantity which has not been reported yet for molecular excited dimers, and finally (c) the coherent properties and the band dimensionality for s-tetrachlorobenzene, obtained by Francis and Harris,[27] are unambiguously confirmed.

Utilizing exchange theory[35] for dimers, the minimum coherent time of an isolated dimer can be estimated from the following equality:

$$[\omega(+) - \omega(-)] \, \tau \sim 1 \qquad\qquad 4\text{-}4$$

Therefore, a lower limit on the coherent time, τ, can be established from our experiments: $\tau > 10^{-7}$ sec. while $h/2\beta$ is approximately 16×10^{-12} sec., indicating a persistent coherence at one point in the time correlation function, namely, $t = 10^{-7}$ sec.

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[*]Alfred P. Sloan Fellow

We should point out, however, that it is known that dimers have a nuclear-electron spin hyperfine interaction[10,24] of approximately half the monomer, in the strong coupling limit. This means that the ~2 MHz linewidth of the dimer could be significantly inhomogeneously broadened. It is quite possible therefore that the homogeneous linewidth could be significantly narrower, implying much longer coherence time, i.e., τ must be longer than 5×10^{-7} sec. This point is currently under investigation.

Acknowledgement

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FIGURE CAPTIONS

Figure 1

The ODMR spectra of 1,2,4,5-tetrachorobenzene-h_2 traps in the D_2 host at 1.7°K. The strongest line in the spectrum is the allowed electron spin transition of the $D - |E|$ manifold, while the satellites are due to ^{37}Cl and ^{35}Cl nuclear spin transitions.

Figure 2

The zerofield ODMR spectra of isotopically mixed 1,2,4,5-tetrachloro-benzene crystals, at different H_2 concentrations. The spectra on the left is the $D - |E|$ transition of the 0.06% and 5.05% H_2 crystals while the one on the right is the $D + |E|$ transitions. The spectrum of each transition at different concentrations was scanned at identical power levels.

Figure 3

The zerofield ODMR spectra of H_2 traps (high concentration > 5%) in D_2 host, for both the $D + |E|$ and $D - |E|$ transitions. The spectra clearly shows the dimer ± satellites, and they should be compared with the 0.06% H_2 spectra. It should be mentioned here that   the actual energy position of the allowed electron spin transition is not necessarily the peak of the EPR band (cf. reference 10,29). This is due to the fact that the hyperfine interaction makes the apparent peak maximum correspond to frequencies different from those expected from the D and E values of the zerofield spin Hamiltonian. Therefore, the shift between the peak position of both the $D + |E|$ and $D - |E|$ transitions and the center of the band is expected.

Figure 4

The right hand section of this figure demonstrates the relationship between exciton and dimer microwave dispersions in coherent states. The energy dispersion of the band is one-dimensional. The dashed lines represent the position of the monomer and dimer energies, $E(\pm)$ and $E(M)$, in the band and their relationship to the microwave resonance frequencies, $\omega(\pm)$ and

FIGURE CAPTIONS (continued)

$\omega(M)$, which depends on the magnitude of the reduction factor, f_{ij}. The spectra on the left are the band-to-band microwave transitions taken from reference 27. The dashed vertical bars in the figures represent the experimental frequencies of the dimer in the $D + |E|$ and $D - |E|$ transitions and the width of these bars is the estimated error on these frequencies. The intensity relationships of the ODMR transitions in the plus and minus states are related both to the transition dipole moments and the dynamics of the decay channels from each state. Details of these features will be reported later.
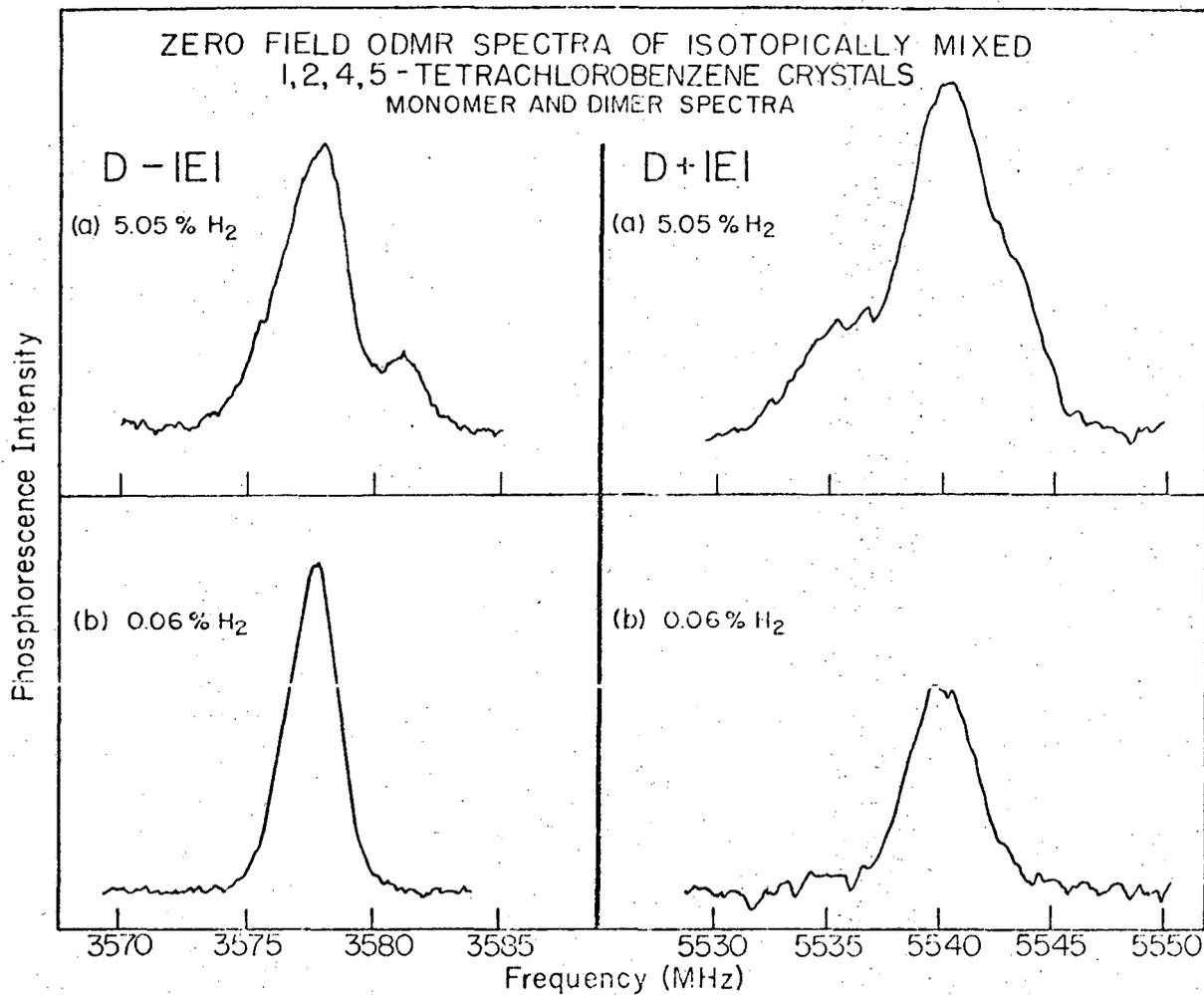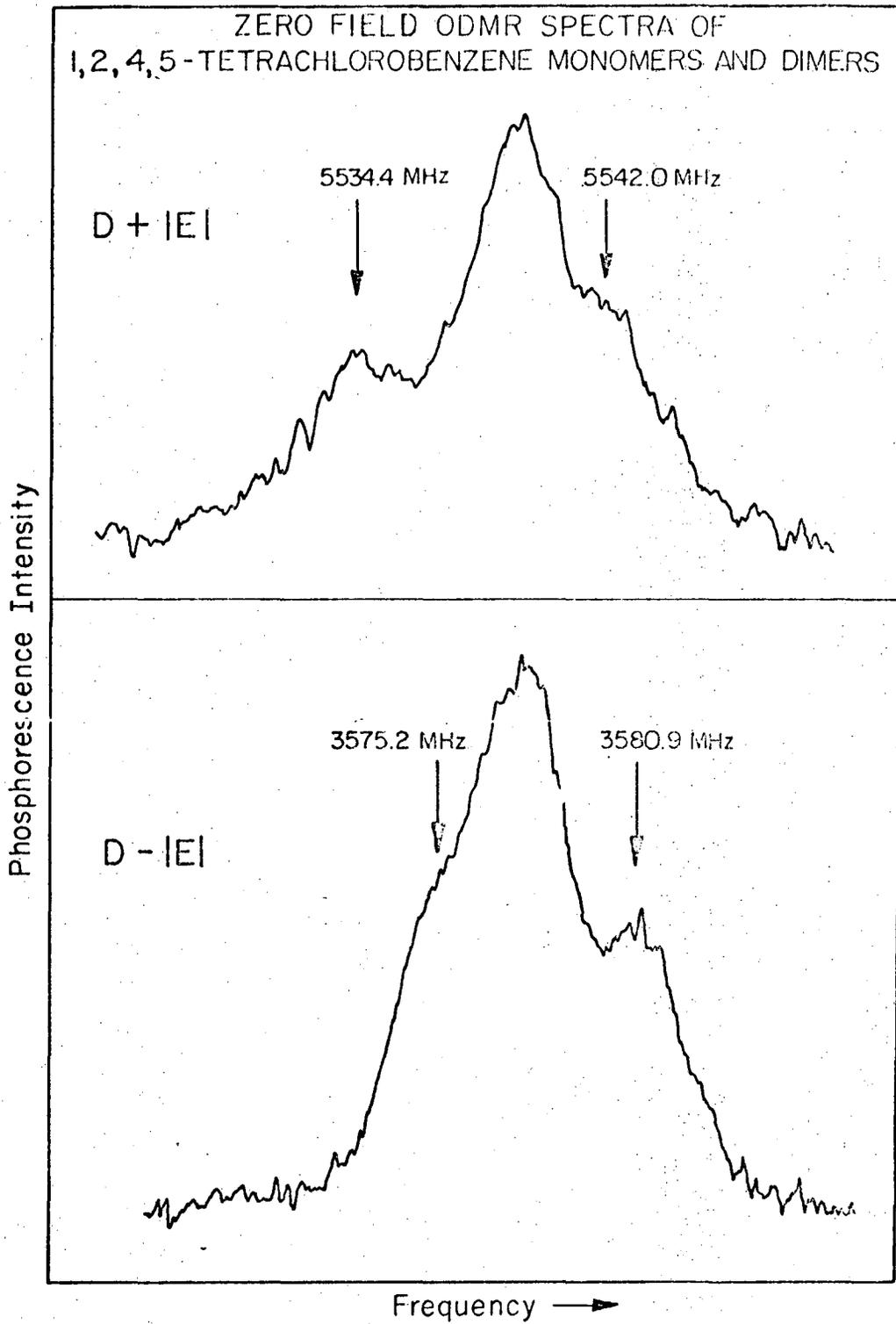
Fig. 1

ZERO FIELD ODMR SPECTRA OF ISOTOPICALLY MIXED
1,2,4,5-TETRACHLOROBENZENE CRYSTALS
MONOMER AND DIMER SPECTRA

D − |E|
(a) 5.05 % H_2
(b) 0.06 % H_2

D + |E|
(a) 5.05 % H_2
(b) 0.06 % H_2

Phosphorescence Intensity

Frequency (MHz)

XBL744−6122

Fig. 2

ZERO FIELD ODMR SPECTRA OF
1,2,4,5-TETRACHLOROBENZENE MONOMERS AND DIMERS

D + |E|

5534.4 MHz   5542.0 MHz

D - |E|

3575.2 MHz   3580.9 MHz

Phosphorescence Intensity

Frequency ⟶
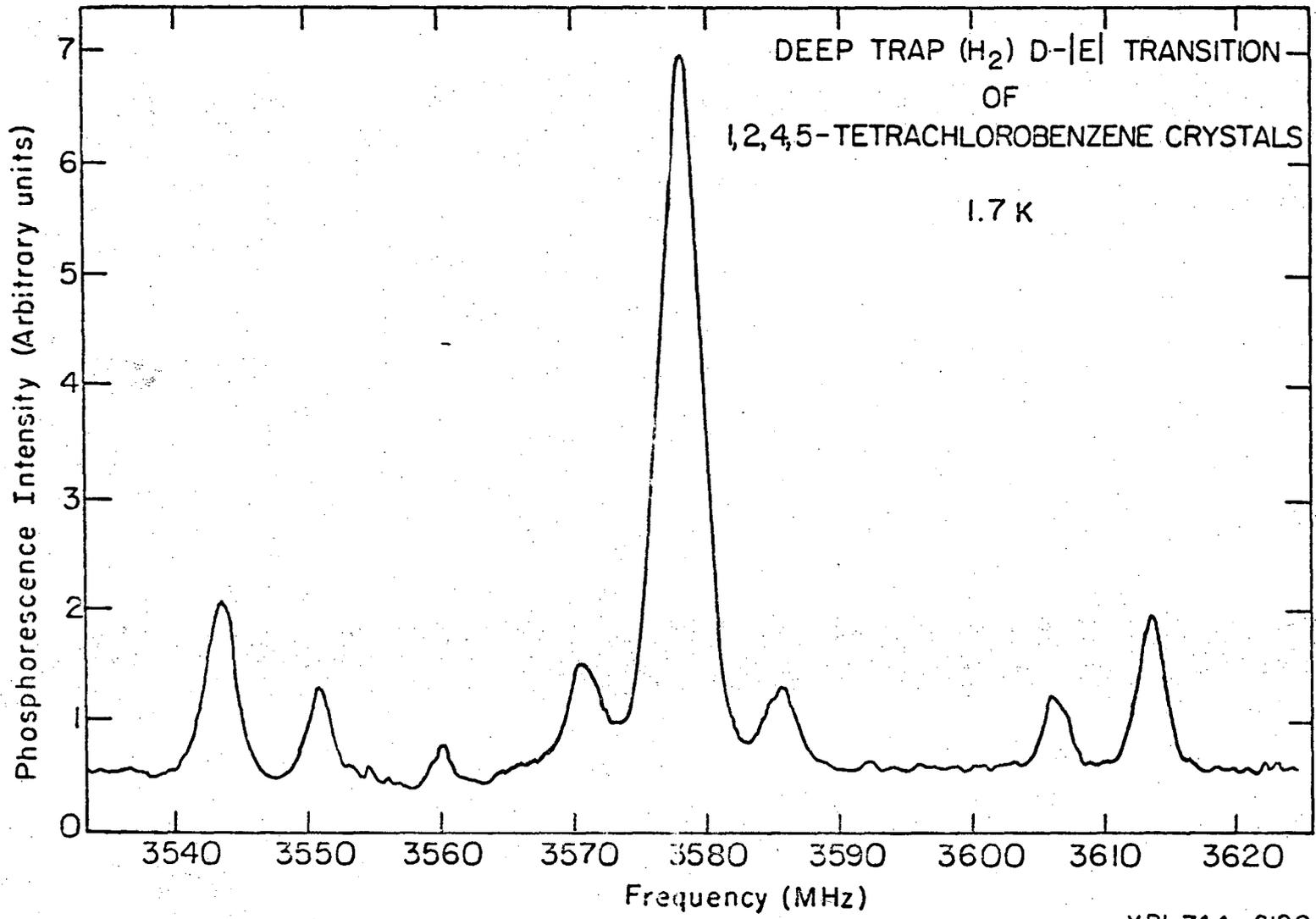
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Fig. 3

THE RELATIONSHIP BETWEEN EXCITON AND DIMER MICROWAVE DISPERSIONS IN COHERENT STATES AND THE EXPERIMENTAL RESULTS ON 1, 2, 4, 5- TETRACHLOROBENZENE

Fig. 4