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H. C. Brenner

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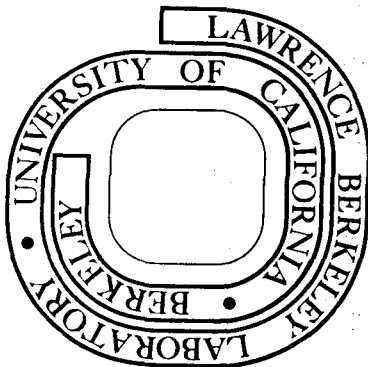
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ABSTRACT

Spin coherence experiments are used to determine the energy level structure, physical geometry, and exciton dynamics of a series of impurity-induced traps in 1,2,4,5-tetrachlorobenzene. The trap, a perturbed host molecule, is shown to be caused by an adjacent, translationally equivalent chemical impurity whose triplet energy may lie above or below the host exciton, but above the trap. The slow rates of thermal processes within the trap are interpreted as weak coupling between the lattice phonons and localized phonons induced at the trap by the impurity.

I.   INTRODUCTION

In recent years, the demonstration of coherent exciton migration
in one-dimensional molecular solids[1] has provoked great interest.
In these systems, the coherence length can be limited by either exciton-
defect scattering or by exciton-phonon scattering. For triplet states,
the relatively narrow bandwidth of the Frenkel excitons makes them
particularly sensitive to energy "traps" and "barriers" at temperatures
where coherent propagation is achieved.[2] Although triplet exciton
dynamics have been investigated in neat and isotopically-mixed systems,[3]
only a few studies have been made in chemically mixed systems because
the methods have been hindered by the unknown nature of the perturbations
in the crystal structure. These would include molecular site anisotropies
and interaction energy differences introduced by chemical substitution.
When the perturbation is sufficiently complex, the nature of the site
and the associated energy transfer dynamics are not accessible by
conventional spectroscopic techniques and more sophisticated probes
are necessary for a full understanding of both the static and dynamic
properties of the localized states.

In this letter, we present the results of a systematic study
of this problem using optically detected spin locking[4] in photo-
excited triplet states in combination with zero field optically detected
magnetic resonance. These techniques have been used to elucidate
the different structures and properties of a series of chemically-
induced triplet traps in 1,2,4,5-tetrachlorobenzene (TCB). Introduction
of certain chemical impurities gives rise to the appearance of a pre-
dominant trap in the phosphorescence spectrum below 4.2°K.[5] Similar

traps in other systems have been interpreted as host molecule states split from the bottom of the exciton band by an adjacent chemical impurity whose triplet energy lies above the band.[6] We should like to suggest that the TCB Y-traps are of a similar nature, where the physical geometry of trap and impurity in the host is largely independent of the identity of the impurity, but the energy level structure is very dependent on the impurity.

We will also demonstrate the use of optically-detected spin coherence experiments in measuring the coupling of local[7] and delocalized phonon modes of a disordered solid through the effect it has on energy exchange in which exciton propagation from the impurity is governed by processes such as thermal detrapping and thermally-activated tunneling,[2] which are in turn governed by the population of local phonon modes which provide the thermal energy. We have measured the rate of exciton promotion from the bottom of the trap to a phonon mode of the trap by the loss of spin coherence and we will show that the rate is slower when phonon modes are decoupled by an adjacent chemical impurity than when the phonon band is only slightly perturbed by isotopic substitution.

II. EXPERIMENTAL

Experiments were performed on five systems. 1,2,4,5-tetrachlorobenzene-h_2 (Aldrich Chemical, zone refined 200 passes) was doped with 5%, 1% and 0.05% 1,2,4,5-tetrabromobenzene, TBB (Eastman Organic, zone refined 50 passes), and crystals were grown by standard Bridgeman techniques. The final TBB concentrations in the crystals were confirmed by mass spectra. The TCB was also doped with 1% concentrations of 1,4-dichlorobenzene, DCB (Eastman), and

1,4-bromochlorobenzene, BCB (Aldrich), but mass spectra of the crystals showed that most of these dopants were removed during crystallization and dopant concentrations were less than 0.1 mol%.

The experimental arrangement for optically detected magnetic resonance and coherence experiments is identical to that described previously.[4,8-10] In the phosphorescence spectra, the Y-traps lie 44 cm^{-1} below the unperturbed TCB exciton band for DCB/TCB and TBB/TCB Y-traps and 48cm^{-1} below the band for the BCB/TCB Y trap. All three Y-traps show normal TCB vibrational structure.[5] Table I lists the zero-field ODMR parameters measured for the Y-traps with axes defined as in Ref. 5. In this table and throughout the paper, the results given for the TBB/TCB Y-trap are for the 0.05% crystal. Both optical and microwave transitions are broadened by dimer and higher multimer trap interactions in the more concentrated crystal. Phosphorescence-microwave double resonance (PMDR)[9] and microwave-induced delayed phosphorescence (MIDP)[10] experiments established the similarity of relative radiative rate constants, and triplet sublevel lifetimes and population among the three systems.

For the coherence experiments, all systems were spin-locked on resonance at the Y-trap D - | E | transition. The temperature-dependent components of the spin-locking decay time are plotted in Fig. 1.

III. DISCUSSION

A. Y-Trap Geometry and Energy Level Structure

Several experimental parameters of the Y-trap systems are largely independent of the identity of the chemical impurity. These parameters are related to the static or equilibrium properties of the trap and

impurity in the host. The trap depths measured in the phosphorescence spectra are very similar. The zero field splittings, listed in Table I, are within a percent of each other. The sublevel lifetimes, listed in Table II, were measured by microwave-induced delayed phosphorescence and only show significant variation in the τ_y lifetime. From the sublevel lifetimes and the phosphorescence-microwave double resonance spectra, unambiguous ordering of the sublevel populations N_n and the radiative rate constants k_n^R to the origin have been assigned to the DCB/TCB and BCB/TCB Y-traps.

$$N_x > N_y > N_z$$

$$k_y^R > k_z^R > k_x^R \quad .$$

The decrease in the τ_y sublevel lifetime for the TBB/TCB Y-trap revises the ordering of the populations,

$$N_x > N_z > N_y \quad ,$$

while the ordering of radiative rate constants does not change. This variation is relatively minor and on the basis of the otherwise similar values, we propose that the physical geometries of all Y-traps are qualitatively the same.

Spin coherence experiments, such as optically detected spin locking, give the dynamic behavior of the Y-trap system directly and this will be considered in detail in the next section. The decay of the spin-locking signal is sensitive only to processes that remove the molecule from the spin-locked ensembled and, as a consequence, is a useful probe for studying detrapping, tunneling, vibrational excitation,

or any transient exchange with a state having different zero field

splittings. One static parameter of immediate importance to the question

of energy level structure can, however, be extracted from the spin-

locking decay. When the temperature-independent contributions of

sublevel lifetime and relaxation against the microwave field are subtracted

out, the spin coherence decays in Fig. 1 show an activation energy

of 4 cm^{-1} for the TBB/TCB Y-trap and 25 cm^{-1} for the DCB/TCB and BCB/TCB

Y-traps.

We attribute the 4 cm^{-1} decay to detrapping from the TBB/TCB

Y-trap to an adjacent, translationally equivalent TBB molecule as

in Fig. 2. Below 188°K the unperturbed TCB crystal is monoclinic

with two molecules per unit cell.[11] The intermolecular spacing along

the c axis is 3.5Å and energy transfer is exclusively along this axis.

The optically-detected ESR spectra of the TBB/TCB Y-trap shows two

important effects. Bromine quadrupole satellites due to transferred

hyperfine interaction from the nearby TBB impurity appears symmetrically

at 291 and 245 MHz from the Y-trap transition frequencies. This

phenomenon was also observed with the ODMR of quinoxaline in TCB and

pyrazine in DCB host.[12] By itself, this evidence confirms proximity

(i.e., positions A or B in Fig. 2), not translational equivalence

(i.e., position A). The ODMR spectra at 20 W microwave power shows

the $D - | E |$ and $D + | E |$ transitions of the TBB molecule[13] in the

phosphorescent emission of the TBB/TCB Y-trap. In order to optically

detect spin polarization induced by a microwave field in resonance

with a TBB triplet transition, energy transfer between the TBB molecule

and Y-trap must be extremely rapid, which requires that TBB and Y-trap

lie adjacent along the c-axis. It has also been reported that the lowest triplet state origin in neat h_2-TBB triplet origin at 26,696 cm^{-1} (Ref. 14) is comparable to the h_2-TCB triplet origin at 26,676 cm^{-1}. It is plausible that the solvent shift of the TBB molecule in the TCB host could bring its energy close to that of the Y-trap.

We attribute the 25 cm^{-1} decay for DCB/TCB and BCB/TCB Y-traps to excitation to a vibronic level of the Y-trap molecule. The absorption spectrum of h_2 - TCB shows a 26 cm^{-1} lattice vibration in the triplet excited state.[15] No ODMR transitions of DCB or BCB appear in the spectra of their respective Y-traps. There is no evidence of detrapping to the DCB or BCB impurities, which probably lie much higher than the TCB host band. Unlike TBB, the lowest triplet origins of DBC and BCB lie 1214 cm^{-1} and 1184 cm^{-1} (Ref. 14) above the triplet origin of TCB. Figure 3 summarizes our models for the Y-traps.

B.   Excitation Exchange in Chemically-Mixed Systems

The decay of the spin-locking signal reflects the promotion of spin population to another state. The effectiveness of the cycle of promotion and subsequent relaxation in dephasing the spin coherence depends on τ, the lifetime in the upper state, and $\delta\omega$, the Larmor frequency difference of the two states.[16] In order to quantitatively correlate the spin dephasing rate with the promotion rate, W_+, it must be established whether the exchanging systems are in slow exchange, $\delta\omega\cdot\tau > 1$, where all spin memory is lost in promotion, or in fast exchange, $\delta\omega\cdot\tau < 1$, where significant spin memory is retained.[17] It has been shown that by observing both the linewidth of a transition, $T_{1\rho}^{-1}$, and its frequency shift, $\Delta\omega$, the type of exchange may be determined[18]

in the optical case. The same is true for the magnetic case. Specifically, the value of

$$T_{1\rho}^{-1}/\Delta\omega = \delta\omega\cdot\tau$$

determines the exchange region. The promotion rate to the upper system, W_+, can be extracted from $T_{1\rho}^{-1}$ and, assuming Boltzmann equilibrium between promotion and relaxation, the upper state lifetime, τ, can be determined by

$$W_+\tau = e^{-\Delta/kT}$$

where Δ is the measured activation energy.

On this basis, we propose that the population exchange between the trap origin and the 25 cm^{-1} local phonon state of the trap in the DCB/TCB and BCB/TCB systems is in slow or intermediate exchange, $\delta\omega\cdot\tau \approx 1$. The homogeneous linewidth, $(T_{1\rho})^{-1}$, can be extracted from a Fourier transform of the spin-locking decay and is about 30 Hz FWHM at 4.2°K. On the other hand, no frequency shift in the $D - |E|$ transitions could be observed between 1.4 and 4.2°K. Assuming, therefore, that $\Delta\omega \leq T_{1\rho}^{-1}$, we find that the system is in slow or intermediate exchange and we can estimate τ

$$3.6 \ \mu sec \leq \tau \leq 7.2 \ \mu sec$$

giving $\delta\omega \geq 0.28$ MHz. For the specific case of intermediate exchange, W_+ is plotted in Fig. 4.

The important observation here is that τ is extremely long for a vibrational level, $10^{-5} - 10^{-6}$ sec, as opposed to the vibrational relaxation times $10^{-12} - 10^{-13}$ sec measured by picosecond laser and Raman linewidth studies.[19] Similarly, the promotion rate W_+ is relatively low. In comparison, promotion to an excited vibrational level 21 cm^{-1} above a para-benzoquinone trap in an isotopically-mixed crystal is 10^4 times faster.[3] This behavior suggests that the rate limiting step for vibrational promotion or relaxation in the vicinity of a chemical impurity is the transfer of thermal energy between the lattice phonons and the localized phonon levels of the trap.

The TBB/TCB Y-trap system is somewhat unusual in spin coherence exchange studies in that both τ and $\delta\omega$ may be determined independently. τ is extracted from Eq. (3) giving $\tau \cong 30$ μsec. The D - $|E|$ transitions of both TBB and TBB/TCB Y-trap may be observed in the Y-trap phosphorescence, giving $\delta\omega \cong 2.5$ GHz. Therefore, $\delta\omega\tau \sim 7.5 \times 10^4 \gg 1$, and the system is in slow exchange. This is corroborated by the lack of a frequency shift in the ODMR temperature dependence. The interaction matrix element between the Y-trap and TBB molecule is quite small. The pre-exponential factor of W_+ is on the order of 10^4 sec^{-1} as opposed to 10^{11} sec^{-1} for equivalent TCB molecules[1] in the host band.

The major contribution to the slowing of the transfer process could be due to be the promotion of the trapped exciton to a trap-phonon state equienergetic with the impurity, and this step is hindered by the decoupling of lattice and local phonon modes. Alternatively, part of this difference may be due to a second dephasing mechanism

caused by a differing alignment of spin axes in the trap and TBB impurity, which Brenner, Brock, and Harris[20] have shown to cause spin dephasing on transfer. This mechanism would also explain the rapid spin-lattice relaxation which eliminates the ODMR signal above $2^{O}K$.

IV. SUMMARY

We have demonstrated the usefulness of spin coherence techniques in elucidating the complex structure of chemically-induced traps. BCB/TCB and DCB/TCB Y-traps contain impurity molecules whose triplet energies lies high above the host exciton band and do not take part directly in the trap dynamics. The TBB/TCB Y-trap, though spectroscopically similar, is induced by an impurity whose triplet energy lies below the band, although above the trap. Transfer of spin population between trap and impurity is observed in the Y-trap ESR spectrum for TBB/TCB, while spin dephasing occurs in a vibrationally excited level of the DCB and BCB/TCB traps. High energy impurity "barrier" states will attenuate long-range exciton migration in the latter systems relative to the TBB/TCB system.

The dynamics of the exciton-trap interaction have been classified within the slow and intermediate exchange region. The low promotion rate and long vibrationally-excited lifetime are interpreted as a decoupling of the lattice phonons from the localized phonon levels of the trap associated with the adjacent chemical impurity.

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Table I. Y-trap zero field splittings.

	DCB	BCB	TBB	
D - E	3608.3	3607.6	3593.0	MHz
D + E	5437.2	5436.2	5517.8	MHz
2 E	1829.4	1806.0	1925.3	MHz

Table II. Sublevel lifetimes.

	BCB	DCB	TBB	
z	21.5 ± 2	23 ± 1	21.6 ± 2	msec
y	21.5 ± 2	22.5 ± 1	14.3 ± 2	msec
x	835 ± 30	860 ± 15	815 ± 50	msec

FIGURE CAPTIONS

Fig. 1. Diagram of two translationally inequivalent chains in 1,2,4,5-
tetrachlorobenzene. Exciton transfer occurs along close-
packed axis running across page. Molecule in lower center
represents chemical impurity and sites A and B represent
nearest-neighbor translationally equivalent and second-nearest-
neighbor translationally inequivalent sites, respectively.

Fig. 2. Phase coherence lifetimes for Y-trap systems calculated from
temperature-dependent contribution to spin-locking decay
rate. Data was taken at D – E transistion of TCB Y-trap.

Fig. 3. Schematic diagram of proposed Y-trap triplet energy levels.

Fig. 4. Phonon absorption rate as a function of temperature for a
4 cm^{-1} activation energy exchange between Y-trap and impurity
in TBB/TCB and for a 25 cm^{-1} activation energy promotion
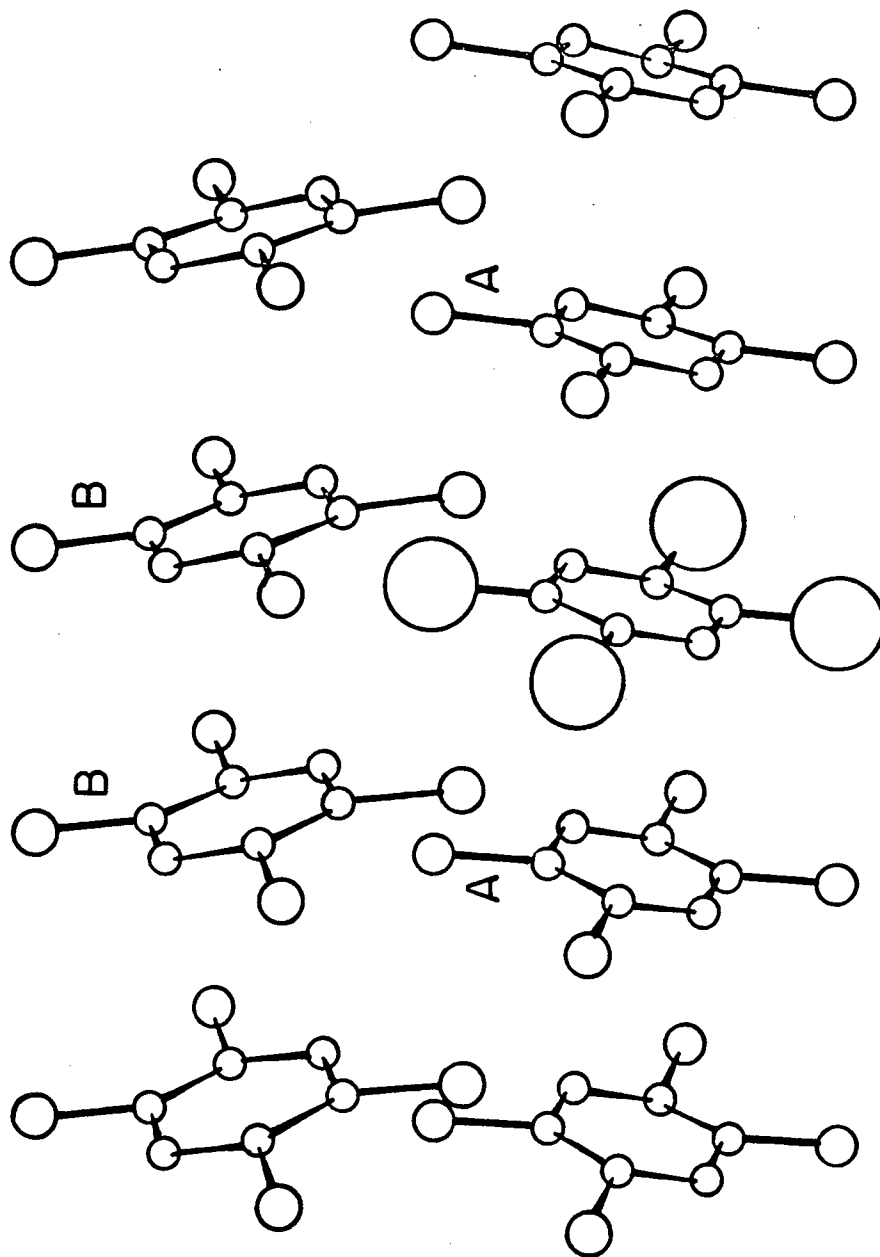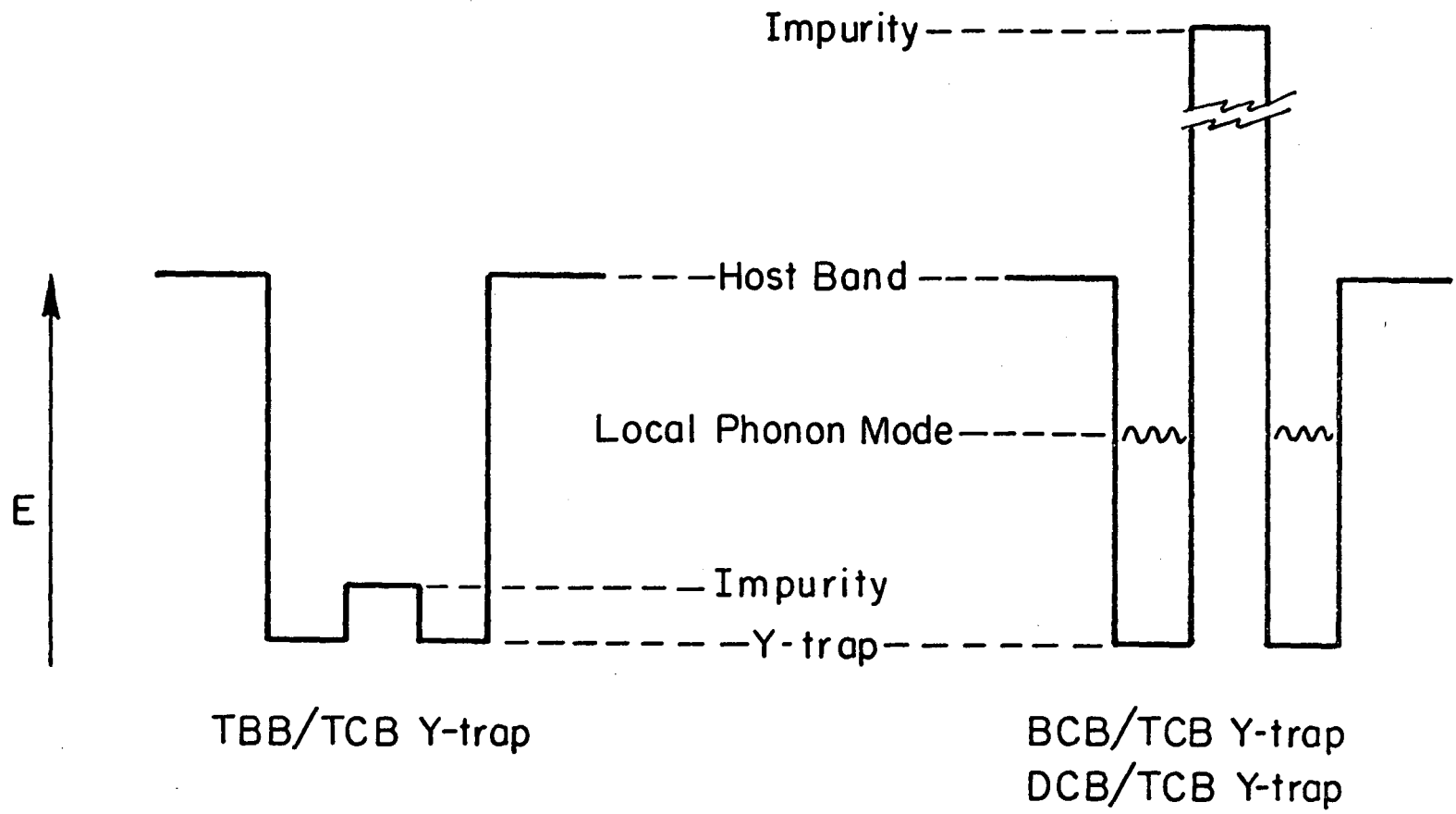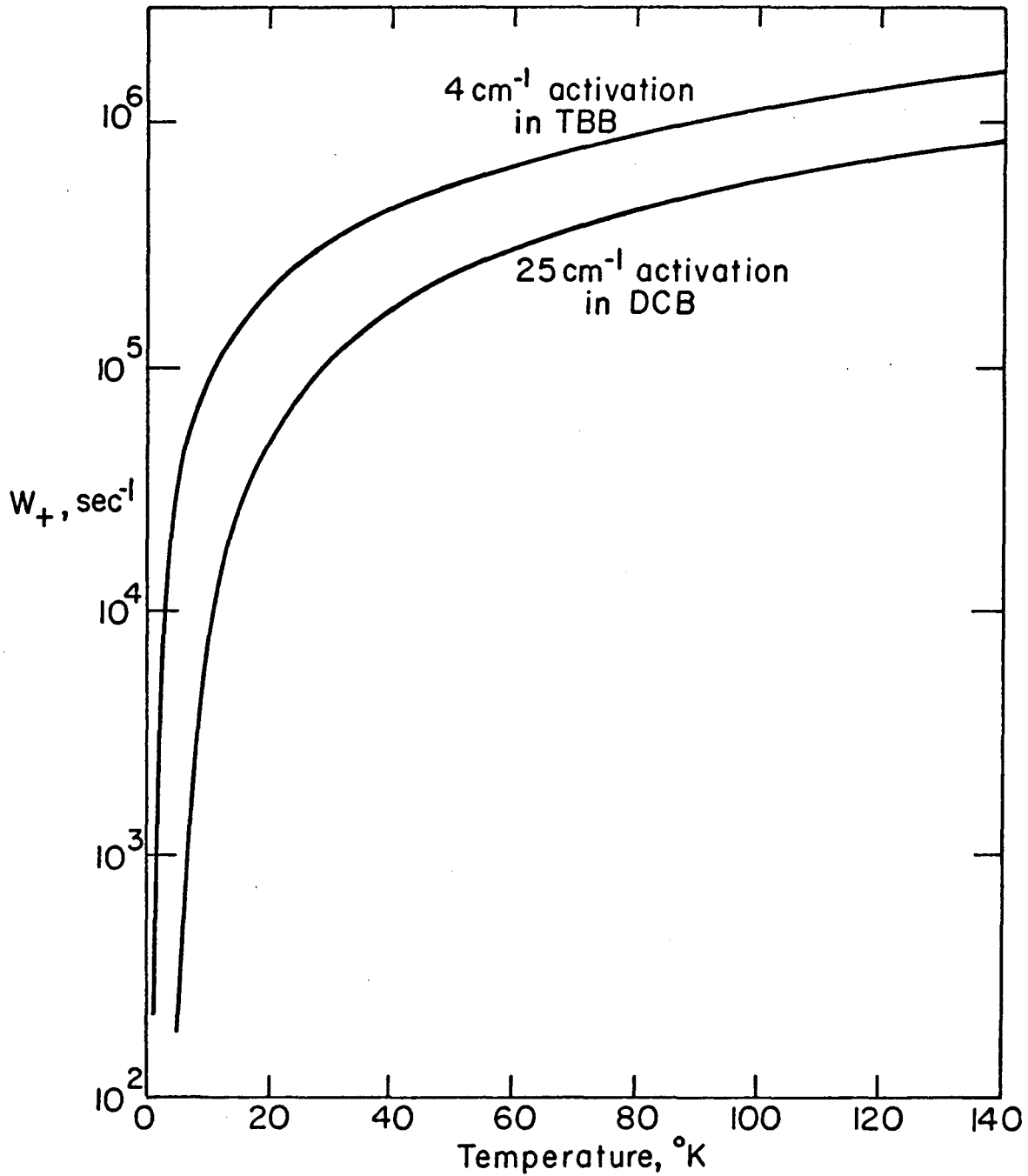to a local phonon mode in DCB and BCB/TCB.
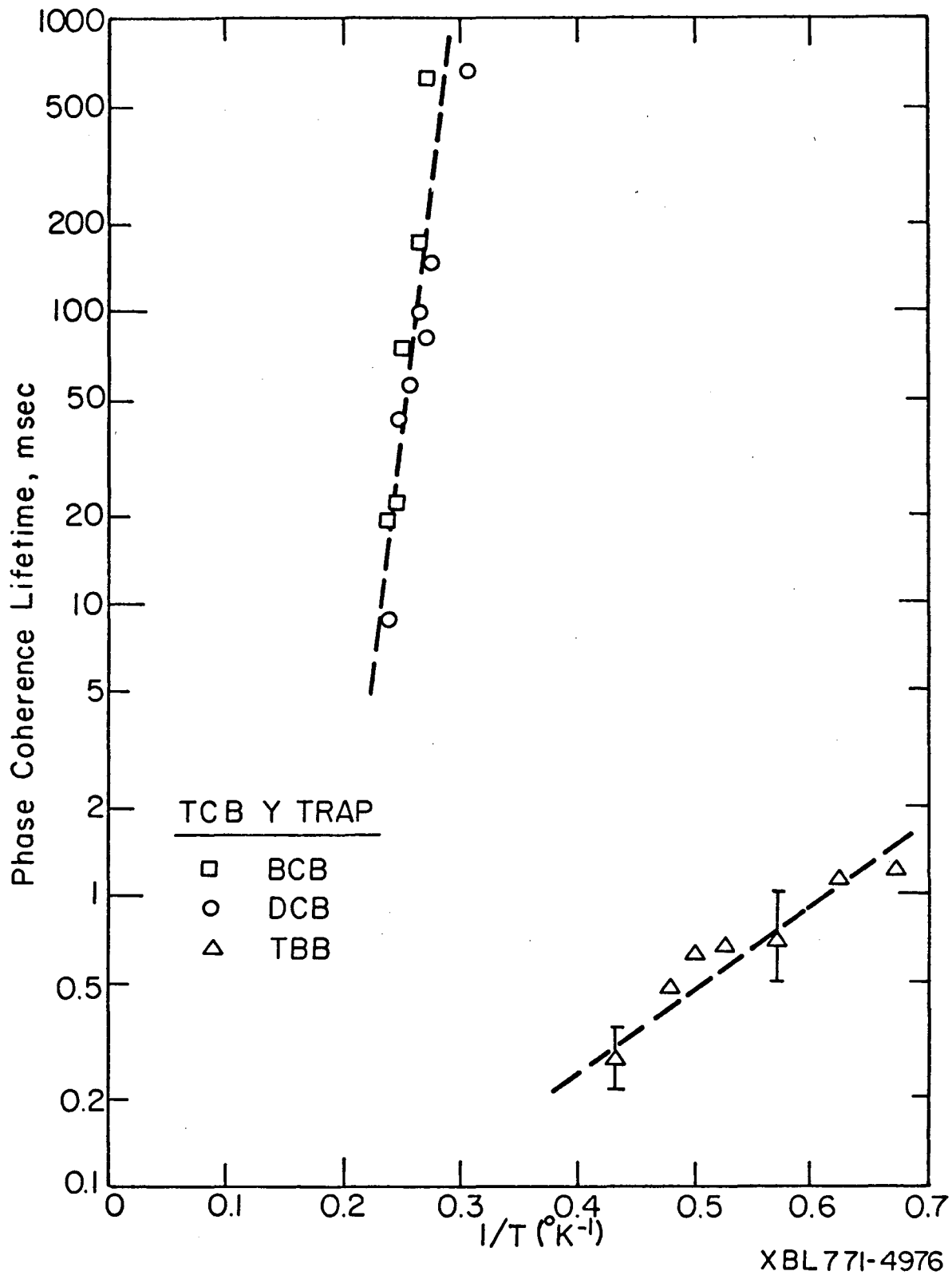
Figure 1

Figure 2

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Figure 3

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PHONON ABSORPTION RATE VS. TEMPERATURE FOR
LOSS OF EXCITON COHERENCE IN
1,4-TETRACHLOROBENZENE Y-TRAP

XBL776-5612

Figure 4

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