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ENERGY TRANSFER IN ONE-DIMENSIONAL MOLECULAR CRYSTALS: DIRECT AND INDIRECT ENERGY EXCHANGE AT NON-BOLTZMANN TEMPERATURES

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ABSTRACT

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Direct energy transfer between localized states via virtual coupling with the host states in one-dimensional molecular solids is demonstrated experimentally using optical and optically detected electron spin coherence techniques. The relative importance of direct transfer versus indirect transfer (which is characterized by the phonon-assisted promotion of the localized state to the band with the subsequent radiationless decay into a mobile exciton followed by retrapping) has been determined in isotopically mixed 1,2,4,5-tetrachlorobenzene crystals over a temperature range where the thermal energy of the lattice is insufficient to establish Boltzmann equilibria between the localized and delocalized states (non-Boltzmann regime). The results demonstrate that the transfer mechanisms between trap and host states are very sensitive to the trap concentration and the temperature of the lattice, and that direct exchange is dominant at high trap concentrations. Finally, the experimental results are compared to theoretical expectations in the various limits.

I. INTRODUCTION

A full understanding of the mechanisms and pathways for energy transport in real molecular crystals can only be obtained by considering the important effects of lattice imperfections such as dislocations, impurities, and other types of energy traps. Both optical and magnetic resonance studies have shown that excitations are transferred among different trap sites by at least two separate and distinct processes. The first involves the direct¹ exchange of energy between trap sites via a virtual coupling with the host states 2 while the second is an indirect 3 pathway involving the decay into the delocalized host states (exciton band), migration in the band and retrapping. By studying these processes, it is possible to obtain information not only on the resonance interactions between trap sites, but also on the nature of interactions between trap and host states. In addition, one can extract parameters detailing the exciton band structure of the host crystal. In earlier experiments, the relationship between trap depth (Δ , below the exciton band), trap concentration and the relative proportion of excited state population channelled into various types of traps was obtained by investigating. the phosphorescence spectra from various traps. Such measurements, however, were not capable of giving detailed information on the nature of the transfer process. This requires the use of additional techniques. 4,5 In this work we combine the results of the temperature dependence of phosphorescence with those of optically detected spin locking (ODSL)⁴ to examine the different routes for energy transfer.

Specifically, both direct and indirect transfer between traps and the host exciton band in excited triplet states of d_2 -1,2,4,5-tetrachlorobenzene (d_2 -TCB), a one-dimensional⁶⁻⁸ system containing two isotopic traps below the band, were elucidated (see Figure 1) and compared to theoretical expectations.

II. OPTICALLY DETECTED SPIN LOCKING AND THE KINETICS OF ENERGY PROMOTION

The essential features of the spin lock experiment can be viewed using a geometric representation⁹ for a two-level system. In this picture, the time evolution of the ensemble of excited triplet states is represented as a "pseudomagnetization" whose orientation in the geometric frame can be changed by applied rf pulses and fields in exactly the same manner as the real magnetization in a conventional NMR experiment.¹⁰ Initially the pseudomagnetization is aligned along the z axis in the interaction representation and corresponds to the population difference between the two zerofield spin sublevels involved. It should be noted that usually only changes in the population differences alter the phosphorescence intensity; hence the z component of the pseudomagnetization becomes the only observable in an optically detected experiment.¹¹

Spin locking^{12,13} is accomplished by applying a $\pi/2$ pulse to rotate the pseudomagnetization into the x-y plane of the frame, followed by the application of a strong "spin locking" H₁ field along the pseudomagnetization to prevent a loss of phase coherence. This results in a coherent triplet spin state that is destroyed whenever a

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fluctuation of the zero field transition frequency (Larmor frequency) occurs that is large relative to the applied field, γH_1 .⁵ The loss of spin coherence, in this case the decay of the spin-locked pseudomagnetization, is monitored optically by applying another $\pi/2$ "probe" pulse¹⁴ with appropriate phase to rotate the spin-locked component back to the z axis. This produces a change in the phosphorescence intensity proportional to the remaining coherence in the spin ensemble. A diagram of the phosphorescence response to the spin lock pulse sequence is presented in Figure 2.

Several features of the spin lock experiment make it particularly useful as a means for investigating energy migration. First of all, population intersystem crossing into the triplet ensemble during the course of the experiment enters the geometric frame along the z axis and for "on-resonance" experiments is driven in a plane perpendicular to the spin-locked component.³ In this manner, incoming population makes no contribution to the change in phosphorescence intensity when the probe pulse is applied. More importantly, the spin lock component is quite sensitive to energy transfer processes since most of them involve significant changes in the Larmor frequency. Energy promotion to different trap species or the host exciton band, for example, results in a loss of spin coherence because of a large frequency fluctuation the spin-locked ensemble encounters.

Three principal processes change the total lifetime of the spinlocked pseudomagnetization, $T_{1\rho}$. These are (i) the promotion of population from the spin-locked state to different trap states or the exciton band; (11) processes leading to radiative and non-radiative decay of the triplet state to the ground state; and (111) magnetic relaxation along the spin locking field. Consideration of these processes leads to the following kinetic equation for the time evolution of the spin-locked pseudomagnetization, M(t):

$$M(t) = M_0 \exp(-K^{T_{1\rho}} t) = M_0 \exp[-(K^{P} + K^{L} + K^{T_{1\rho}})t]$$
(1)

where K^{P} , K^{L} and $K^{T1\rho m}$ are the rate constants associated with the loss of the spin-locked signal due to processes (i), (ii) and (iii) respectively, and $K^{T1\rho}$ is the total decay rate constant.

The results of the spin locking experiment, when combined with T^{I} independent measurements of K^{L} and K^{I} independent trap states and K^{P} , the rate constant for promotion processes between different trap states and between trap states and the host exciton band. The temperature dependence of K^{P} , and hence of the promotion process, can then be used to detail the nature of the transfer mechanism (direct or indirect) as well as to amplify the qualitative results obtained from the temperature dependence of phosphorescence studies.

Isotopically mixed crystals are particularly suited for these types of experiments since it is expected that no significant geometrical deformations of the trap states are introduced by the isotopic substitution, and one can experimentally control the relative distance between the localized trap sites by concentration. Another helpful feature of isotopically mixed TCB crystals (see Figure 1) lies in the fact that trap depths of the shallow (hd) and deep (h_2) states are 11 cm⁻¹ and 22 cm⁻¹,

respectively, below the TCB-d₂ band; hence phonon-assisted promotion of population out of the deep trap should reveal the relative importance of detrapping processes between the deep trap and the band, and the deep trap and the shallow trap, and their dependence on deep trap concentration at low temperatures. This can lead to a detailed understanding of the transfer topology,¹⁵ percolation,¹⁶ and the effects of guest-host perturbations on the excitation distribution in the band that are indicative of Koster-Slater¹⁷ type interactions in the solid. Further, the correlation of the steady state phosphorescence results with the *ODSL* findings gives new direct information about the population of these traps upon singlet excitation.

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III. EXPERIMENTAL DETAILS

Two isotopically mixed TCB samples were prepared, each containing different proportions of TCB-h₂. The first was prepared from 97.5% deuterated zone-refined TCB which was synthesized in these laboratories. It contained 95.31% TCB-d₂, 4.63% TCB-hd, and 0.06% TCB-h₂. The second sample was prepared by adding a given amount of zone-refined TCB-h₂ (Eastman) to the 97.5% deuterated TCB such that the final sample contained approximately 5% TCB-h₂ on a weight-for-weight basis (more precisely, 90.5% TCB-d₂, 4.6% TCB-hd and 4.8% TCB-h₂). These samples (hereafter referred to as the 0.06% and 5% samples) were then analyzed by either mass spectral analysis or by proton NMR. Single crystals were grown from the melt by standard Bridgman techniques. Both crystals were annealed for one week at a temperature 2.4°C below the melting point. The quality of each crystal was checked by its ability to give exciton phosphorescence. The exciton emission was seen in neither the 0.06% nor the 5% crystal below the lambda point of helium, although strong emission from the exciton origin was observed at 4.2° K in the 0.06% sample.

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The experimental arrangement for optically detected magnetic resonance has been described elsewhere. 10,18 Microwave pulses of the appropriate phases for the ODSL experiment were obtained as follows. The microwave output of a Hewlett-Packard 8690B sweeper was divided into two separate channels by means of an Anaren Corp. 90° hybrid coupler. Phases were set by adjusting the relative path lengths in the two channels by means of two 10 cm General Radio sliding coaxial lines. Two Hewlett-Packard 33124A PIN diodes were inserted into each channel to switch the microwaves. Timing of the pulse sequences was controlled by TTL circuits constructed in this laboratory. The channels were recombined by means of a 180° hybrid coupler, the resultant signal being fed through a bandpass filter to a Varian 615M 20 watt traveling wavetube amplifier before delivery to a slow-wave helix surrounding the sample in a liquid helium cryostat. The temperature of the bath could be varied between 1.4° and 4.2°K by pumping on the helium and was measured by monitoring the pressure of gaseous helium with an NRC Equipment Corp. Model 530 Alphatron vacuum gauge. Temperature was stabilized by employing a pressure sensor capable of altering the pumping speed. For all measurements atany given temperature, the sample was allowed to equilibrate with the

bath for at least five minutes.

The experiments were performed as follows. The sample was illuminated by an Osram 100 watt mercury lamp filtered by a 3100 Å interference filter. Phosphorescence from h_2 -TCB trap origin was monitored, and the D - |E| transition at 3577.9 MHz was pumped. Pulse lengths were determined by rotary precession experiments;²⁰ $\pi/2$ pulses were typically 50-100 nanoseconds. Phases were set by maximizing the initial spin locking signal. The microwave experiments were repeated at a rate of 3-6 Hz, and the signals time-averaged with a Northern 575 signal averager.

IV. RESULTS AND DISCUSSION

(A) <u>Temperature Dependence of Phosphorescence</u>

Temperature dependence of phosphorescence studies on the 0.06% crystal revealed a marked dependence on temperature of the emission intensity for both the shallow (hd) and deep (h_2) traps. The emission spectra for these two traps in the 0.06% crystal are shown in Figures 3 and 4 for the temperature region between 1.4° and 2.1°K. As can be seen, the deep trap emission increases while the shallow trap emission decreases over this range. At the same time, however, the total phosphorescence intensity from the origin remains constant within ca. 10%. This result strongly suggests that excited state population is preferentially transferred from the shallow to the deep trap as the temperature is increased. It is clear that at these

temperatures the communication between the two types of traps is not governed by Boltzmann statistics.³ If one plots the natural log of the emission intensity ratio between the shallow and deep traps, I_c/I_p , versus the reciprocal of the absolute temperature, one obtains a straight line plot, the slope of which is reversed in sign to that expected if Boltzmann statistics were the controlling factor. What the temperature dependence of these results does show, however, is that there is an energy "gap" of $8 \pm 3 \text{ cm}^{-1}$ from the shallow trap to the band. This suggests that the transfer of excited state population from the shallow to the deep trap in the 0.06% crystal is occurring indirectly via the host crystal band states. A model³ for this transfer process in the triplet state has been proposed which entails three basic steps: (i) promotion of trap population by lattice phonons to the band states of the host crystal; and (ii) migration via a host crystal exciton; followed by (iii) retrapping in a different trap state.

For the 5% crystal only the emission of the deep (h_2) trap was observed from the phosphorescence origin over the temperature range from 1.4° to 2.1°K. Moreover, the emission intensity remained essentially constant over this range. This would imply that excited state population is partitioned effectively, due to the high concentration, into the deep trap over the entire temperature range.

The results of the temperature dependence of phosphorescence experiments for the 0.06% crystal were in good agreement with the previously published results³ for temperatures from 1.4° to 2.1° K.

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However, the present data for the 0.06% crystal for temperatures from 2.1° to 4.2°K is qualitatively similar to the earlier data, but quantitatively the agreement is inconsistent in two respects. First, at the lambda point of liquid helium (2.17°K) a sharp decrease of approximately 30% in the emission intensity of the deep trap is observed. This decrease is independent of exciting light intensity, h, trap concentration, the method by which the temperature was regulated, and whether or not the crystal sample was annealed or unannealed. Second, the loss of deep trap emission intensity between the lambda point and 4.2°K did not closely follow an exponential curve characteristic of Boltzmann equilibria, but instead appeared to fall off more linearly. The scattering of the data points, however, in this temperature range is greater than that of the data presented previously. ³ From our results we are unable to say with certainty whether or not trap-to-trap communication is governed by Boltzmann statistics above the lambda point of liquid helium in these samples. For this reason we confine our analyses to data collected in the "kinetic regime" between 1.4° and 2.1°K.

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(B) <u>Dynamics of Energy Promotion</u>: <u>Direct and Indirect Transfer</u>Processes in <u>TCB</u>

The results of the optically detected spin locking experiments were utilized to extract values of K^P , the promotion rate constant, for the deep (h_2) trap in both the 0.06% and 5% crystals as a function of temperature between 1.4° and 2.1°K. The total decay time, $T_{1\rho}$, was determined at ten different temperatures for the D - |E| transition of the 0.06% crystal and at 11: temperatures for the corresponding transition in the 5% crystal. A typical determination of $T_{1\rho}$ at a single temperature for the 0.06% crystal is shown in Figure 2. Values for K^L were calculated from experimental measurements of the lifetimes of the τ_x and τ_y zero field spin sublevels of the 0.06% crystal at 1.4°K.³

A value for K¹lom</sup> was obtained from spin-lock data of the 2[E] transition of a 1% m/m TCB-h₂ trap in a durene host.³ In this case the localized trap state lies about 1460 cm⁻¹ below the energy of the host band,²¹ and K^P is essentially zero.²² After subracting the contribution of K^L (again determined from individual sublevel lifetimes) to the total spin-lock decay rate, a value of K^Tlom = 13.8 sec⁻¹ was obtained.

These values for K^{L} and $K^{T_{1}\rho m}$ were then utilized to extract values for K^{P} at each temperature from values for the total decay rate, $K^{T_{1}\rho}$, by use of Equation 1. The effect of error in K^{P} due to the approximate values used for K^{L} and $K^{T_{1}\rho m}$ is not expected to be great, principally because of the large value of $K^{T_{1}\rho}$ in comparison.

The variation of K^P with temperature reflects the extent to which phonons couple to the excitation at a given temperature. In the dilute concentration limit, the promotion of excitation from the localized (shallow or deep) traps into the band could involve a state which is in "quasiresonance" with the dense manifold of stationary band states, |k>. The latter are primarily responsible for the decay to the band,

since the recurrence probability is relatively small because of the high density of band states. In such cases the probability per unit time for the interaction of a localized state $|L\rangle$ into $|k\rangle$ states is

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$$P_{k} = (2\pi/\hbar) \sum_{k} |V_{Lk}|^{2} \delta(E - E_{k})$$
 (2)

It is the nature of $|V_{Lk}|^2$ which determines the explicit form of the perturbation for the promotion process. If the detrapping probability is not k selective, the density of exciton states at energy Δ above the trap energy can be invoked into expression (2). For example, if the trap-exciton interaction is via an intermediate state |I> and a phonon $\chi(\varepsilon)$ of energy ε , Equation 2 takes the form:

$$P_{k}^{(\varepsilon)} = \frac{2\pi}{\hbar} \langle n(\varepsilon) \rangle_{T} |\langle L\chi(\varepsilon) | V_{LI} | I\chi(\varepsilon - \Delta) \rangle \langle I\chi(\varepsilon - \Delta) | V_{Ik} | k\chi(\varepsilon - \Delta) \rangle |^{2} \rho(\Delta)$$
(3)

The important thing to note is that the temperature dependence is explicitly given in the phonon distribution term (occupation number and phonon density of states), and that the problem is now somewhat simplified assuming that $\langle V_{Ik} \rangle$ which is a radiationless decay matrix element and $\langle V_{LI} \rangle$ are temperature independent. The energy of the phonon (or phonons for multiphonon processes) must either match the energy Δ (direct process) or exceed it (Raman process); hence, the total detrapping probability will depend on the sum over all phonons and also intermediate states which match the required energy.³

In the low-temperature limit, the Planck distribution function²³ takes a simple form:

$$n(T) = 1/(e^{\varepsilon/kT} - 1) \approx e^{-\varepsilon/kT}$$
(4)

Thus, in the limit where the bandwidth is small compared to Δ , as in the case of TCB⁶⁻⁸ crystals, or for selective detrapping with $\varepsilon = \Delta$, the detrapping rate constant is given by³

$$k^{(T)}(L \rightarrow k) = Ae^{-\Delta/kT} \rho(\Delta) \equiv K^{P}$$
 (5)

The above expression shows the

where A is a constant. This expression is valid in the limit where the density of phonon states is almost constant, e.g., in the linear range of the dispersion for acoustic phonons.²⁴

importance of at least two parameters in considering detrapping in crystals at low temperature: the density of states function and the phonon distribution.

The above result was shown for TCB system in different ways. In the kinetic regime, ³ where no thermal equilibrium exists between the localized and band states, the shallow trap excitations to the band are more frequent than those of deep traps. Consequently, at intermediate or low temperatures, the thermal steady state dynamics depend upon the temperature variation of the band group velocity and the detrapping rate constant from the shallow trap. ³ For a one-dimensional narrow band ⁶⁻⁸ TCB crystal, the change in group velocity with temperature is rather small. Hence, in the limit where K_S (total rate constant for relaxation to the ground state from the shallow trap) is small compared to the detrapping rate constant, the ratio of the steady state

populations of the shallow and deep traps is 3

$$(N_{S})/(N_{D}) = [(C_{S}/C_{D})K_{D}]/A\rho \times e^{+\Delta_{S}/kT}$$
 (6)

where C_S and C_D are the concentration of the shallow and deep traps respectively, K_D is the total rate constant for relaxation to the ground state from the deep trap, A is the constant associated with Equation 5 and ρ is the exciton density of states. Therefore the ratio of phosphorescence intensity of the shallow and deep trap as a function of temperature should give Δ_S , the energy separation between the shallow trap and the exciton band, as indeed shown experimentally (see Figure 3). Moreover, the "inverse-Boltzmann" behavior is explained.

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The second important feature is that Equation 5 indicates that if In K^P (obtained from the ODSL) is plotted versus 1/T, a straight line should be obtained, the slope of which reveals the energy separation, Δ , between the trap state and the final state connected by the promotion process. Plots of In K^P versus 1/T for the experimental ODSL results on the 0.06% and 5% crystals are given in Figure 2. It can be noted that the In K^P versus 1/T plots are essentially linear for both the 0.06% and 5% samples. More importantly, the differing slopes of these graphs indicate that promotion processes are occurring to different final states in the two crystals.

The slope of the data for the 0.06% crystal yields a value for Δ of 16 ± 4 cm⁻¹. This value is on the order of the optical separation between the deep trap and the host band. Thus, for the 0.06% crystal, where the density of host (d₂) band states is high, both the phosphorescence and ODSL results indicate that trap-to-trap communication is occurring

predominantly by an indirect process through the host band states.

The slope of the data for the 5% crystal, however, yields a value for \triangle of 11 ± 3 cm⁻¹ which is approximately the same as the separation between the deep and shallow traps. This result points toward the *predominance of direct processes in the 5% crystal*. Nonetheless, it must be noted from the phosphorescence results that any population promoted out of the deep and into the shallow trap is returned by a rapid process, either by a direct or indirect route, to the deep trap. This is essentially why the 5% cyrstal shows only h₂-TCB emission and no hd-TCB emission at steady state.

(C) Excitation Yields and Transfer Times in Isotopic Mixed Crystals

There has been much interest^{2,8} in mechanisms for long range transfer and transfer times in molecular systems. In clusters of isotopic impurities, located below a one-dimensional band, the transfer time can be extracted from a knowledge of the trap depth, the resonance interaction and the distance between traps through perturbation theory.^{8,25} Conventional optical^{2,8} and magnetic resonance experiments²⁶ have elucidated much about the detailed mechanisms important in energy transfer problems, but quantitative data about unequivocal pathways have been difficult to determine. The beauty of the optically detected spin locking experiments is that it can give these times directly and analytically. Moreover, if the triplet spins are adiabatically demagnetized in the rotating frame^{27,28} in zero field¹⁰ and the kinetics of the demagnetized state are compared to the kinetics of the spin-locked state, additional information such as the effective quantum yield for mobile band excitation can be determined.²⁹ Recently,²⁹ this was found to be ranging from 1 to 0.1

depending on the temperature which in turn determines the degree of scattering between the mobile excitons and phonons.

For a one-dimensional system, the trap-to-trap transfer time, t, in the isotopically mixed crystal can be related to the number of lattice sites, n, using perturbation theory:

$$n = [\log(t/t')][\log(\Delta/\alpha\beta)]^{-1}$$
(7)

where t' = $\hbar/\alpha\beta$, the effective nearest neighbor transfer time, and α is a measure of the fraction of localized states that are effective in transferring energy, and β is the resonance interaction energy. The difference in energy between the traps is provided by the phonon reservoir. Knowing t from spin locking kinetics, the dependence of n on $\alpha\beta$ can be determined (see Table 1). For example, if $\beta = 0.1$ cm⁻¹ and assuming unit transfer yield ($\alpha = 1$), then

$$t = (1/30)(10^{(2n-8)})$$
 (8)

The experimental value⁶⁻⁸ for β in TCB ranges from 0.15 cm⁻¹ to 0.4 cm⁻¹ depending on the method of the measurements. This predicts n to be on the order of 5 to 7. It should be noted that the composition of these crystals give.a statistical separation between traps of ten molecules on the average in reasonable agreement with theory considering the steep (logarithmic) dependence the transfer time, t, has on n with a fixed β . The above results were derived by considering only the in-chain interactions (linear chain system) since the interactions between chains is very small, being approximately 1 MHz.³⁰

V. SUMMARY

We have demonstrated the use of optically detected spin coherence to study the kinetics of energy transfer in solids at low temperature. Specifically, one can separate and distinguish direct transfer between localized states and indirect transfer, characterized by thermal promotion to the host exciton band. In isotopically mixed crystals of 1,2,4,5-tetrachlorobenzene at low temperatures and low trap concentration, the transfer was found to be predominantly via an indirect mechanism wherein lattice phonons promote excitations from a trap state to the host crystal exciton band after which migration in the band and retrapping occur. When the trap concentration is increased, however, direct transfer between trap sites becomes an important mechanism and is the dominant transfer process when the total trap concentration (deep and shallow) is on the order of 10%. Finally, we have demonstrated a technique capable of experimentally elucidating the transfer times which characterize long range interactions.

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reference 33 therein.)

TABLE I

The dependence of the trap-to-trap spatial separation on the effective resonance interactions in isotopically mixed 1,2,4,5-tetrachlorobenzene crystals at 1.54°K.

αβ(cm ⁻¹)	0.05	0.10	0.15	0.20	0.25	0.30 0.50	1.0 2.	0
n	3.6	4.2	4.8	5.2	5.6	5.9 7.1	9.5 14	.0

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FIGURE CAPTIONS

Figure 1: A schematic for the structure of the excited triplet state of isotopic TCB crystals: Δ is the trap depth, and H $_2$ or HD refer to the different isotopic species. The solid arrows represent emission to the ground state or trapping to trap sites; emission of the exciton to the ground state is not shown. The dotted arrows represent detrapping processes to the band and the wiggly double-arrowed line represents the communication between traps via a "direct" mechanism. Figure 2: (A) A schematic for the spin locking sequence and the hypothetical phosphorescence response: τ_{st} is the length of time the spin locking field is on, S denotes saturation, and i denotes inversion of population between spin sublevels. AI denotes the change in phosphorescence intensity associated with the population of the coherent state after the time τ_{SL} . (B) A typical decay of spin-locked spin ensemble of the 0.06% crystal at 1.84°K. (C) and (D) show plots of K^P vs. 1/T for the 0.06% and 5% crystals, respectively. Figure 3: Left: The phosphorescence intensities of H₂ and HD at different temperatures in the 0.06% crystal; the behavior for temperatures above 2.15°K is discussed in the text. Right Inset: the linear behavior for $\ln [I(HD)/I(H_2)]$ vs. 1/T.

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<u>Figure 4</u>: Moderate resolution phosphorescence spectrum of the pure electronic origin in isotopically mixed TCB (0.06%) crystals at 1.47°K; the exciton origin appears to high energy of HD emission for temperatures around 4.2°K and the H_2 emission is located at 26,668 cm⁻¹.



FIGURE 1



FIGURE 2



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