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THE OBSERVATION OF COHERENT TRIPLET EXCITONS
AND DENSITY OF STATES FUNCTIONS IN MOLECULAR CRYSTALS

by

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Abstract

The observation of coherent triplet Frenkel excitons is reported in a molecular crystal 1,2,4,5 tetrachlorobenzene. The results can be interpreted in terms of a one-dimensional model in which the largest intermolecular exchange interaction is associated with the translationally equivalent molecules along the a axis. Using the theory developed in the previous paper [A.H. Francis and C.B. Harris, Chem. Phys. Letters , XXX (1971)], the bandwidth, coherence length and density of states functions have been determined from a zero field optically detected microwave experiment for the lowest triplet band in tetrachlorobenzene at temperatures below 4.2° K.

[†] Alfred P. Sloan Fellow

1. Introduction

The wealth of experimental data on triplet Frenkel excitons in molecular crystals is truly impressive.⁽¹⁾ Despite this fact relatively little is experimentally known about the dynamics of exciton migration at low temperatures. A fundamental prediction of energy transport at sufficiently low temperatures is that the migration of triplet excitons should be described by the group velocity of the delocalized states of the molecular crystal.⁽²⁾ This description, known as coherent migration, has associated with it an implicit lifetime of an exciton of wave vector k known as the coherence lifetime, $\tau(k)$, and a coherence length, l , over which the exciton state is delocalized. In the simplest terms, the coherence length is related to the group velocity $v^G(k)$, as

$$l < v^G(k) \cdot \tau(k), \quad (1)$$

any may be thought of as the distance between scattering centers which destroys the coherence of the wave packet. Theories describing exciton migration must therefore concern themselves with, among other things, the nature of exciton-scattering site interactions.^(3,4,5,6) At low temperatures the density of localized molecular vibrations and lattice phonons is expected to become low; thus, the length between scattering centers would increase and, accordingly, the coherence lifetime would become long. Under these conditions coherence might be detected in triplet excitons via a microwave experiment.

In the previous paper⁽⁷⁾ we developed a theory for microwave transitions between the triplet exciton bands associated with the magnetic sublevels in the one-dimensional case where the coherence lifetime was longer than the intrinsic time scale associated with the microwave frequency, i.e.,

$$\tau(k) > \hbar/\Delta E(k), \quad (2)$$

where $\Delta E(k)$ is the energy separation between the magnetic sublevels of the triplet exciton band.

Specifically, when Eq. 2 is satisfied one expects to measure both the triplet bandwidth, $2\Delta_T$, and the density of states functions for the exciton band. In this communication we will show experimentally coherent migration of triplet excitons on a microwave time scale in a one-dimensional molecular crystal 1,2,4,5 tetrachlorobenzene at 4.2°K. In addition, an approximate bandwidth and density of states function for the lowest triplet state in this crystal have been determined.

The method employed is optically detected magnetic resonance in zero field⁽⁸⁾ where the intensity of exciton emission from 1,2,4,5 tetrachlorobenzene is monitored as a function of microwave frequency.

2. Experimental

Crystals of 1,2,4,5 tetrachlorobenzene which show exciton emission at 4.2°K were prepared by the Bridgeman technique using material purified by extensive zone refinement (120 passes at 1 inch/hr). The crystals were annealed for one week at ~10°C below their melting point. Crystals

prepared in such a manner show coincident $T_1 \rightarrow S_0$ phosphorescence and $T_1 \leftarrow S_0$ absorption at 3748.2 \AA .

A single crystal⁽⁹⁾ of 1,2,4,5 tetrachlorobenzene is cut to fit inside a helical slow-wave structure matched to a 50Ω rigid coaxial line. The entire structure is supported vertically inside a helium dewar. A microwave sweep generator drives a 1 watt broad band amplifier whose output terminates in the line. The sample is optically excited through the open helical structure with a 100 watt Hg arc, 3100 \AA radiation being isolated by means of an interference filter (Schott-UV-R-310). The phosphorescence is recorded at 90° angle from the exciting source using a $3/4$ -meter Jarrell-Ash spectrometer capable of 0.15 \AA resolution in first order at 3500 \AA . All experiments were recorded under c.w. optical excitation and 25 cps amplitude modulation of the microwave radiation. The photomultiplier output (EMI 6256 B) was phase detected at the microwave modulation frequency.

3. Results

3.1 $T_1 \rightarrow S_0$ Phosphorescence and $T_1 \leftarrow S_0$ Absorption Spectra

The phosphorescence spectra of 1,2,4,5 tetrachlorobenzene crystals consist of an exciton origin ($0,0: 3748.2 \text{ \AA}$) and two trap origins hereafter referred to as X ($0,0: 3751.2 \text{ \AA}$) and Y ($0,0: 3755.7 \text{ \AA}$). In addition to the electronic origin, the phosphorescence spectrum consists of a moderately intense vibronic origin involving a non-totally symmetric carbon-chlorine bend, and several totally symmetric progressions. The

exciton and Y-trap emission have been observed by other workers;⁽¹⁰⁾ however, the percentage of exciton and trap emission vary. In our samples, 95% of the total emission intensity is exciton in origin at 4.2°K, only 5% being distributed equally to the X- and Y-trap spectra. At 3.0°K the X-trap and exciton phosphorence are of about equal intensity, while Y-trap remains the same as at 4.2°K. Below 2°K the residual exciton phosphorescence is extremely weak while the X-trap phosphorescence intensity is greatly increased. Intense Y-trap emission is always obtained from impure samples. The emission continuum from a 75 watt Xe high pressure short arc was used to obtain the $T_1 \leftarrow S_0$ absorption spectrum. At both 1.6° and 4.2°K the (0,0) absorption is coincident with the 4.2°K emission with experimental error. Partial reabsorption of the exciton phosphorescence origin is clearly visible within the line width of the transition at 4.2°K

Although there are two molecules per unit cell in the tetrachlorobenzene space group,^(11,12) no Davydov splitting was resolved in the $T_1 \leftarrow S_0$ absorption. Given the line halfwidth of the (0,0) absorption ($\sim 3 \text{ cm}^{-1}$) and the resolving power of our spectrometer, we can say that the factor group splitting is less than 1.5 cm^{-1} .

3.2 The optically detected zero field microwave transitions of the X- and Y-traps.

The three electron spin transitions, those associated with the $\tau_z \rightarrow \tau_y$, $\tau_z \rightarrow \tau_x$, and $\tau_y \rightarrow \tau_x$, (defining the z axis as normal to the molecular plane of tetrachlorobenzene), of both the X- and Y-traps were

observed with satisfactory resolution monitoring the phosphorescence intensity of the respective electronic origins. The values for the spin Hamiltonian⁽¹³⁾ are given in Table 1. The $D + |E|$ and $D - |E|$ transitions correspond to increases in the phosphorescence intensity, while the $2|E|$ transition corresponds to a decrease. Figure 1 shows the $(D - |E|)$ transition of the Y-trap at 1.6°K.* The satellites associated with the electron spin transitions of the traps (cf. Figure 1), result from ^{35}Cl and ^{37}Cl nuclear quadrupole and hyperfine interactions as discussed in an earlier publication.⁽¹⁴⁾

3.3 Optically detected zerofield microwave transitions of the magnetic sublevels of the triplet exciton band.

All three optically detected microwave band-to-band transitions of the exciton states were observed with reasonable signal to noise. Two of these, $D - |E|$ and $D + |E|$ are illustrated in Figures 2 and 3 respectively. The important experimental features of these transitions are:

- (a) Their half widths at half height of the $D + |E|$, $D - |E|$, and $2|E|$ transitions are 18 MHz, 11 MHz and 7 MHz, respectively.
- (b) The $D + |E|$ and $D - |E|$ transitions have two maxima separated by 13.5 MHz and 8.5 MHz respectively. The two maxima were not clearly resolved within the narrower $2|E|$ transition.
- (c) The slope on the high frequency side of the transition is greater than that on the low frequency side.

* The apparent decrease in the base line at ~ 3580 MHz is real and reproducible. It occurs in the region of the exciton band-to-band transition and evidently results from spin selective exciton-trap interactions. The details of this observation will be reported subsequently.⁽¹⁸⁾

(d) There are no satellites separated at multiples of ~ 35 MHz from these transitions even at the highest microwave power (20 watts) available. (Not shown in the figure.)

(e) The intensity ratio of the double peak spectra for both the $D + |E|$ and $D - |E|$ transition show a Boltzmann behavior with temperature.

(f) The line shapes obtained are essentially independent of whether or not one detects the transition monitoring the exciton electronic origin or the vibronic origin phosphorescence.

4. Discussion

4.1 1,2,4,5 Tetrachlorobenzene Crystal Structure

1,2,4,5 tetrachlorobenzene crystallizes in a monoclinic space group (P_{21}/c) with two molecules per unit cell.⁽¹¹⁾ At 188°K a phase transition occurs to a triclinic modification,⁽¹²⁾ closely related in unit cell dimensions and molecular orientations to the high temperature monoclinic modification. In both structures, translationally equivalent molecules stack very nearly plane-to-plane along a, with the molecular out-of-plane axis almost parallel with a. The triclinic cell dimensions are $a = 3.76 \text{ \AA}$, $b = 10.59 \text{ \AA}$, and $c = 9.60 \text{ \AA}$. Since we observe no Davydov splittings and because the b and c dimensions are long we have essentially a model for a one-dimensional exciton associated with the translationally equivalent interaction along the short axis a. The same features have been found in other halogenated aromatic molecule crystals such as 1,4 dibromonaphthalene and the p-dihalobenzenes by Hochstrasser⁽¹⁵⁾ and coworkers.

4.2 Exciton Band-to-Band Microwave Transitions

All features of the experimental microwave band-to-band transitions so far investigated are consistent with a one-dimensional exciton whose k state lifetime, $\tau(k)$, is longer than the reciprocal of the microwave transition frequency. We shall assume initially that exciton phosphorescence obeys the selection rules, $\Delta k \approx 0$ and $k' \approx k'' \approx 0$. The first selection rule will apply generally to both electronic and vibronic transitions, while the second restricts the electronic origin to $k = 0$ only. Emission terminating on a ground state vibrational quantum may arise from all thermally populated k states of the triplet magnetic sublevel manifold. Assume additionally that the lifetime $\tau(k)$ is substantially shorter than the exciton lifetime. Under these circumstances, a microwave band-to-band transition associated with some non-zero k value transfers population from one sublevel to another at a specific k . However, because $\tau(k)$ is shorter than the exciton lifetime the population is scattered to other k states, including $k = 0$, within the emission lifetime; thus the line shape of optically detected microwave transitions does not depend on whether an electronic or vibronic origin is monitored. Only if $\tau(k)$ were longer than $\sim 10^{-4}$ second would it be possible to see differences ($0,0$ vs $0,v$) and then only at high microwave modulation frequencies ($\sim 1 - 10$ KHz).

The lack of ^{35}Cl and ^{37}Cl satellites in the exciton band-to-band transitions is an important characteristic which distinguishes excitons from traps. In either the hopping model^(16,17) or in coherent migration a feature of microwave transitions associated with triplet excitons is

that transitions associated with nuclear states must vanish when the intermolecular interaction gives rise to an exchange frequency greater than the microwave frequency associated with exciton electron spin transitions.

Utilizing the theory developed in the previous paper, specifically the relationship between the energy dispersion of the band and the microwave transitions, e.g.,

$$\Delta E_1^{yz}(k) = \Delta_{ST}^{\xi} \cos ka \quad (k = 0 \text{ to } \pi/a), \quad (3)$$

where

$$\Delta_{ST}^{\xi} = \xi^2 \left[\frac{\Delta_S - \Delta_T}{(E_{ST}^{\circ})^2} \right], \quad (4)$$

we can estimate the width of the microwave band-to-band transition.

ξ is a spin-orbit coupling constant for a specific magnetic sublevel in 1,2,4,5 tetrachlorobenzene, Δ_S and Δ_T are half the singlet and triplet bandwidths and E_{ST}° is the separation between the triplet and excited singlet state. Reasonable values are

$$\left. \begin{aligned} (\Delta_S - \Delta_T) &\sim 200 \text{ cm}^{-1} \\ E_{ST}^{\circ} &\sim 10000 \text{ cm}^{-1} \\ \xi &\sim 10 \text{ cm}^{-1} \end{aligned} \right\} \quad (5)$$

we get

$$\Delta_{ST}^{\xi} \sim 2 \times 10^{-4} \text{ cm}^{-1} \quad (6 \text{ MHz}), \quad (6)$$

Thus, the width of the microwave transitions would be ~ 12 MHz.

Naturally these parameters are subject to variations but none the less the half widths of the observed transitions are consistent with reasonable values of the parameters.

The variation in the observed band-to-band transition line widths is attributed to spin-orbit coupling to more than one magnetic sublevel. It is clear that within the framework of the model, the same relationship exists between the observed line widths as between the effective D and $|E|$ values at $k = 0$ and $k = \pm\pi/a$. In particular, given any two bandwidths, the third must be their sum or difference. This can be seen more clearly by referring to Figure 1b in the previous paper. It is precisely this feature that allows the determination of the relative amount of spin-orbit coupling to the individual sublevels. (18)

The most significant feature of the spectra in Figures 2 and 3 is the presence of two peaks of different intensity in each band-to-band transition. Both of these are expected for one-dimensional excitons where the lifetime of a k state is long compared to the microwave time scale. The maxima correspond to the maxima in the density of states function at $k \sim 0$ and $k \sim \pm\pi/a$ in the first Brillouin Zone and the difference in heights of the two maxima correspond to the Boltzmann factor across the band. The sharp onset at $k \sim 0$ (cf. Figure 2 or 3) results because the Gaussian⁽¹⁹⁾ scattered density of states function modified by the Boltzmann factor is steepest at $k = 0$. Using equations 22b and 23 developed in the previous paper for the intensity of the band-to-band transition, $I \left[\Delta E^{yz}(1) \right]$,

$$I \left[\Delta E^{YZ}(E) \right] = C D^B(E), \quad (7)$$

where C is an experimental constant, E is related to the energy dispersion of the band by,

$$E = \Delta_T \cos ka, \quad (8a)$$

or the microwave frequency by

$$E = f \Delta_T \cos ka. \quad (8b)$$

Refer to the previous paper⁽⁷⁾ for the definition of the reduction factor f . $D^B(E)$ is related to a Gaussian broadened-Boltzmannized Van Hove density⁽²⁰⁾ of states $D(E')$, by,

$$D^B(E) = \sqrt{\frac{\ln 2}{\pi \delta}} \int_0^{2\Delta_T} D'(E') \exp(-E'/kT) \exp\left[-(E - E')^2 \ln 2 / \delta^2\right] dE', \quad (9)$$

where kT is the Boltzmann factor, we note that the slope of $I \left[\Delta E^{YZ}(E) \right]$ is appreciably greater around $k = 0$.

Similar ratios of the peak heights, $k \sim 0$ vs. $k \sim \pm\pi/a$, for both microwave band-to-band transitions shown in Figures 2 and 3 are observed. Small differences are, however, apparent and may be due to a variety of reasons, one being that the lifetime of the k state, $\tau(k)$, may be approaching the slow exchange region in $D - |E|$ transition. This may account in part for the lack of resolution of the $2|E|$ transition. If that is so, it is best to use the $D + |E|$ data to obtain the triplet bandwidth since the experimental time scale is shorter. A theoretical fit can be obtained using the experimental values for the temperature (3.2°K)

and the interval between the maxima while varying the scattering parameter and bandwidth. Figures 2 and 3 illustrate the agreement between theory and experiment. The bandwidth and scattering parameter obtained from the best fit to the $D + |E|$ band-to-band transition (cf. Fig. 3) were used to predict the $D - |E|$ transition (cf. Fig. 2) and the $2|E|$ transition (not shown). The calculated spectra in Figures 2 and 3 were obtained using a scattering parameter, $\delta = 0.14 \text{ cm}^{-1}$ and a triplet exciton bandwidth, $2\Delta_T = 1.3 \text{ cm}^{-1}$. The minimum coherence time necessary for this fit is $\sim 10^{-9}$ sec. This corresponds to a minimum coherence length of $\sim 50\text{-}100 \text{ \AA}$. The actual coherence length, however, may be longer.

It is important to note that the same scattering parameter δ was used to fit both transitions. This is reasonable because δ should be a feature of the crystal states, not the inhomogeneity of the microwave transition. In all likelihood the scattering parameter has its largest contribution from the fact that we do not have a homogeneous sample. Specifically all the exciton chains are not of the same length and thus for any energy difference there corresponds different k values for chains of differing length.

5. Acknowledgements

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TABLE I

Trap and Exciton Electronic Origins and Microwave Transition Frequencies

	Origin	D + E (MHz)	D - E (MHz)	2 E (MHz)
Y-Trap	3755.7 Å	5439.8 ± 1	3612.8 ± 1	1829.1 ± 1
X-Trap	3751.2 Å	5525.9 ± 1	3600.0 ± 1	1928.2 ± 1
Exciton [‡]	3748.2 Å	5537.4 ± 0.5	3577.9 ± 0.5	1960.0 ± 0.5

[‡]Frequencies correspond to band centers ($k = \pm\pi/2a$).

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Figure Captions

Figure 1. The optically detected $D-|E|$ zero-field transition of the Y-trap in tetrachlorobenzene. Phosphorescence monitored is the Y-trap electronic origin.

Figure 2. The optically detected $D-|E|$ band-to-band transition associated with the triplet exciton. The phosphorescence intensity of the exciton electronic origin (0,0) is monitored as a function of frequency. The solid line is the theoretically predicted spectra.

Figure 3. The optically detected $D+|E|$ band-to-band transition associated with the triplet exciton. The phosphorescence intensity of the exciton electronic origin (0,0) is monitored as a function of frequency. The solid line is the theoretically "best" fit spectra using the theory developed in the previous paper.

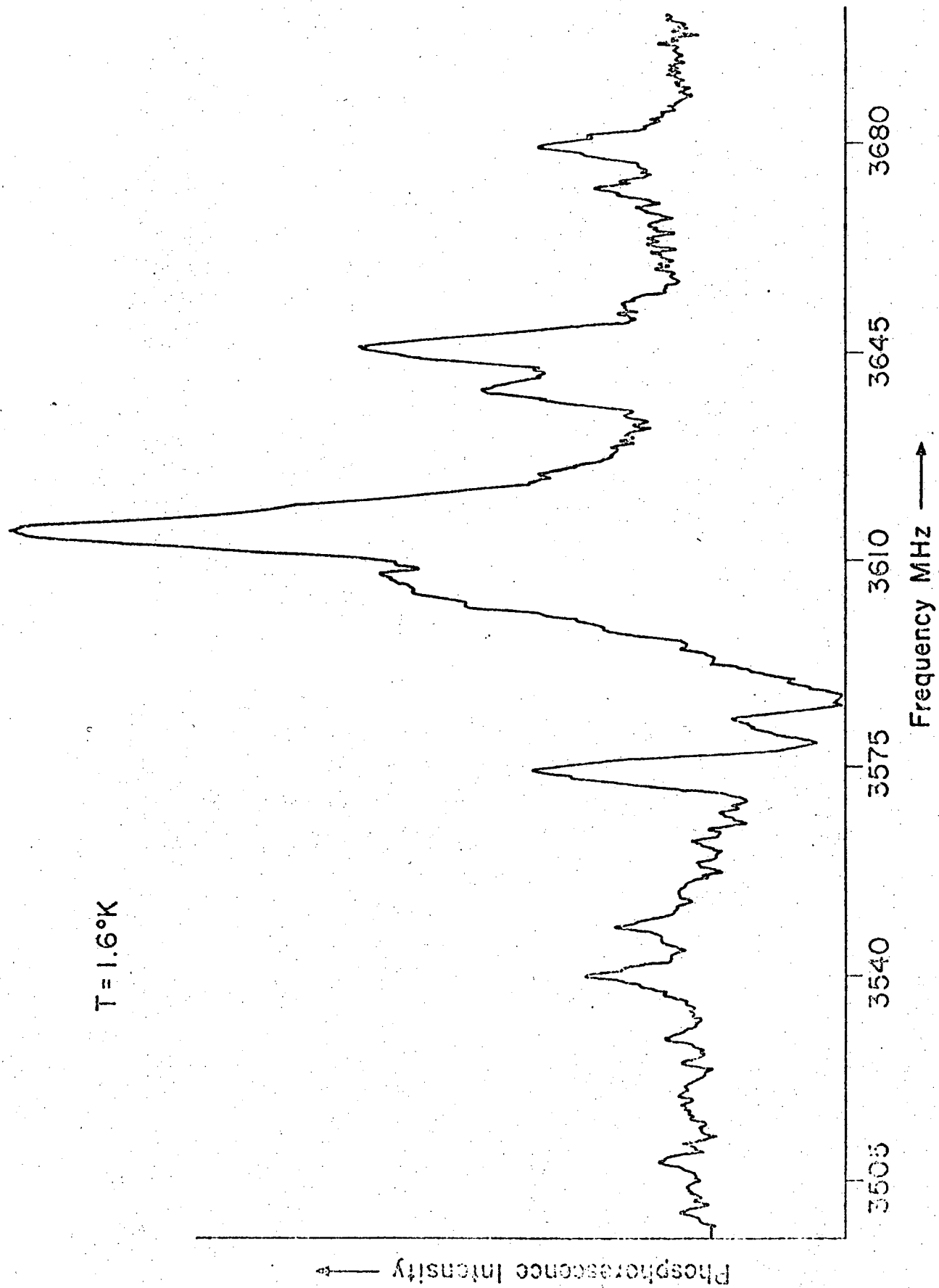


Fig. 1.

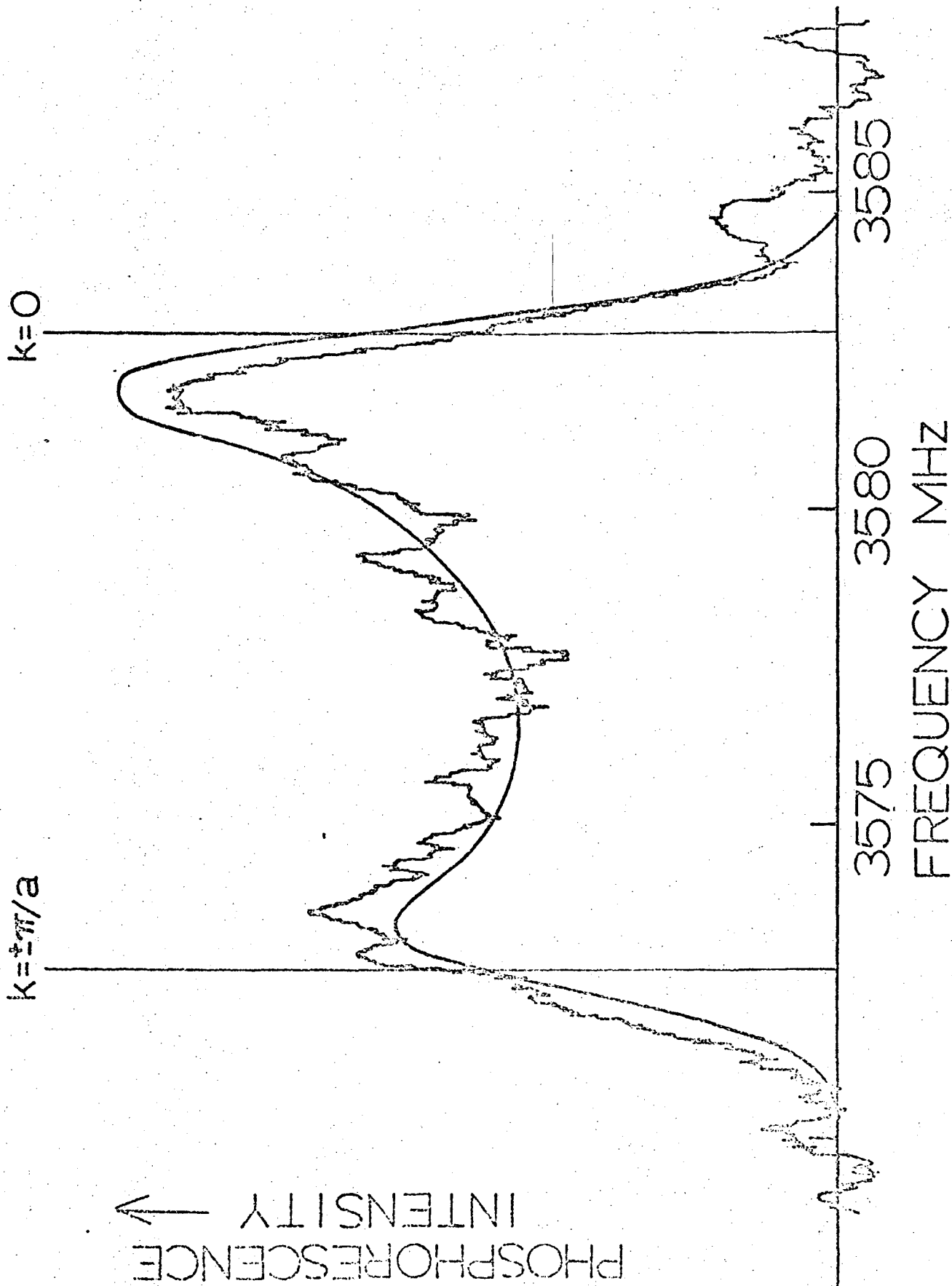


Fig. 2.

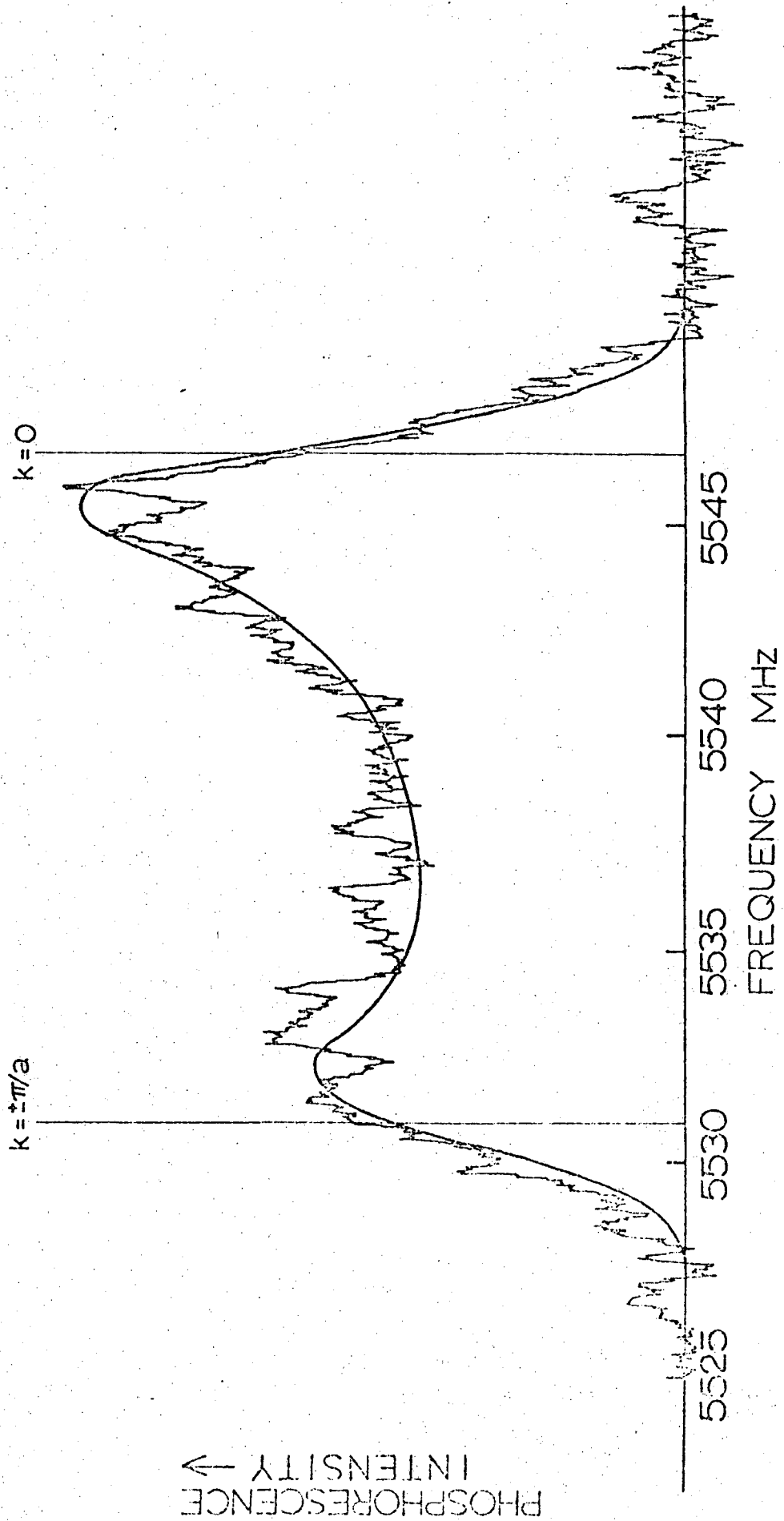


Fig. 3.

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